

The Coordination Chemistry of Dinuclear Molybdenum(III) and Tungsten(III): d^3 - d^3 Dimers[†]

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The coordination chemistry of a metal ion is largely determined by its size, charge/oxidation state, and valence configuration.¹ For main-group elements and to a large extent lanthanide and actinide elements, the size and charge associated with the ion are dominant. For example, they provide the basis for the very different biological roles of Na^I and K^I or Mg^{II} and Ca^{II} . For the transition elements, the effects arising from valence-shell configuration are of paramount importance and often far outweigh the effects of charge and size. A specific d^n configuration will lead to preferences in coordination number and geometry as a result of ligand field stabilization energies. Also, kinetic aspects of ligand substitution and electron-transfer reactions are greatly influenced by ligand field effects.² For example, the rates of H_2O exchange in $\text{M}(\text{H}_2\text{O})_6^{n+}$ ions span a range from 10^9 to 10^{-8} s^{-1} at room temperature. For a given d^n configuration, ligand field effects are dependent on both the ligands and the metal. For a given group within the transition series, these effects become more pronounced on descending from the first to the second and to the third row. Thus, while salts of Ni^{II} may be tetrahedral, octahedral, or square planar, those of Pt^{II} are almost invariably square planar and never tetrahedral.

There is, however, another phenomenon that is now recognized to be important in the field of transition-metal coordination chemistry: metal-metal bonding. M-M bonding may modify the effects of the ligand field or may be completely dominant.³ For example, the extreme rarity of mononuclear Pt^I or Pt^{III} complexes can be contrasted with their common occurrence in dinuclear complexes with M-M bonds. Additionally, the whole field of multiple bonds between metal atoms⁴ provides a distinct departure from classical coordination chemistry.

The strength of metal-metal bonds increases down a group within the transition series. The importance of metal-metal bonding is particularly well illustrated by the coordination chemistry of the group 6 elements in their +3 oxidation states. Whereas octahedral, six-coordinate complexes are the rule for Cr^{III} (a result of the ligand field stabilization energy associated with the t_{2g}^3 configuration), W^{III} complexes are dinuclear or polynuclear with M-M bonds. For Mo^{III} , both octahedral, mononuclear complexes and dinuclear complexes with M-M bonds are found. This Account focuses on the ground-state geometries and bonding in

d^3 - $d^3 \text{ M}_2^{6+}$ containing compounds of molybdenum and tungsten. A brief discussion of their modes of reactivity is also presented.

Preferred Coordination Geometries for d^3 - $d^3 \text{ M}_2$ Containing Dinuclear Complexes. Often complexes containing d^3 - $d^3 \text{ M}_2$ units are referred to as dimers. Strictly speaking this is incorrect when the monomer d^3 unit is unknown. In formulating their structure, however, it is convenient to view them as the sum of two d^3 fragments just as the electronic structure of ethylene can be derived from the combining of two methylene fragments.^{5,6}

It is appropriate to ask, what is the preferred coordination geometry about a d^3 - $d^3 \text{ M}_2$ center ($\text{M} = \text{Mo}$ or W), a question that takes on special significance when the coordination chemistry of the mononuclear M^{III} ion is virtually nonexistent. There are, in fact, several commonly observed coordination geometries, and it is not possible to specify one that is preferred. The observed structure depends upon the mutual influence of metal-ligand and metal-metal bonding.

$\text{L}_3\text{M}\equiv\text{ML}_3$ Compounds. These are common for bulky uninegative ligands, such as $\text{L} = \text{CH}_2\text{SiMe}_3$,^{7,8} NMe_2 ,^{9,10} OR ,^{11,12} SAr' ,¹³ SeAr' ¹⁴ ($\text{Ar}' = \text{mesityl}$), and combinations of ligands as in $\text{M}_2\text{Cl}_2(\text{NMe}_2)_4$ ¹⁵ or $\text{M}_2\text{R}_2(\text{OR}')_4$.^{16,17} In the ground state these adopt

[†] Dedicated to Professor Fred Basolo on entering his eighth decade.

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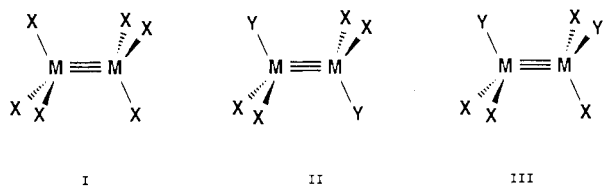
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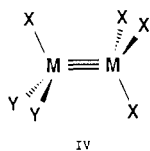
Malcolm H. Chisholm was born 1945 in Bombay, India, to Scottish parents and was educated in England, receiving his Ph.D. in 1969 at Queen Mary College. He spent three years as a postdoctoral fellow at the University of Western Ontario before joining the faculty at Princeton University in 1972. He is currently Distinguished Professor of Chemistry at Indiana University. His research interests are in dinuclear and polynuclear transition-metal chemistry, the reactivity of coordinated ligands, and metal-containing polymeric materials. He was elected a Fellow of the Royal Society, London, in 1990.

staggered structures, I, and are sometimes referred to as ethane-like d^3-d^3 dimers. There is no electronic barrier to rotation about the central M-M triple bond, which is composed of one σ component and two equivalent π components. However, steric factors may impede rotation about the M-M triple bond, leading to the isolation of anti and gauche rotamers, II and III, that interconvert only relatively slowly.



The energy of activation for anti-gauche isomerization for 1,2- $M_2X_2(NMe_2)_4$ compounds where X = alkyl or PR_2 , for example, falls into a 15–23 kcal mol⁻¹ range.^{16,18} For compounds of formulas $M_2R(OR')_5$ and 1,2- $M_2R_2(OR')_4$, the rotational barriers are much lower, with some being less than can be determined by dynamic NMR techniques.^{19,20} The difference between the alkoxide and dimethylamide supported $(M\equiv M)^{6+}$ units arises from the cogging of the NC_2 units in the latter. The single-faced π -donor NMe_2 ligands have π interactions with the metal atoms as will be described later.

For a compound of formula $M_2X_4Y_2$ with an ethane-like geometry, there is the possibility of obtaining 1,1- or 1,2-substituted products. The 1,2 isomer may exist in anti and gauche rotamers, but although rotation about the central bond may be slow because of steric congestion, there is only one 1,1 isomer, as shown in IV. There is a substantial barrier to isomerization between 1,1- and 1,2- $M_2X_4Y_2$ isomers, which was first observed for $Mo_2(CH_2SiMe_3)_4(NMe_2)_2$.²¹

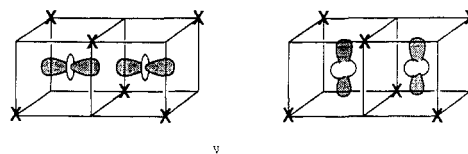


The typical M-M distances in these ethane-like d^3-d^3 dinuclear complexes (I-IV) span a very small range, 2.20–2.30 Å, with the W-W distances being 0.08 Å longer than the Mo-Mo distances in otherwise identical compounds. In compounds where the $X_3M\equiv MX_3$ skeleton is forced to adopt an eclipsed or near eclipsed conformation because the ligand atoms X are united by a C_2 bridge, e.g., as in $M_2(MeNCH_2CH_2NMe)_3$ ²² and $M_2(OCMe_2CMe_2O)_3$,²³ the M-M distances are ca. 0.02 Å shorter than in the related unbridged compounds,

$M_2(NMe_2)_6$ and $M_2(O-i-Pr)_6$. This very small change in distance is presumed to have a steric origin, although it was once suggested that there might be an electronic preference for an eclipsed geometry for $X_3M\equiv MX_3$ compounds.²⁴

The bonding in d^3-d^3 ethane-like dinuclear compounds can be envisaged as follows: Taking the M-M axis to be the Z axis, the M-M triple bond is formed from overlap of z^2 (σ) and degenerate xz , yz (π) orbitals to give the M-M $\sigma^2\pi^4$ valence configuration. The three M-L σ bonds may utilize metal s, p_x , and p_y atomic orbitals, leaving the d orbitals $x^2 - y^2$ and xy available for π bonding with ligands such as NMe_2 that have filled π orbitals. The important consequence of the vacant in-plane metal π -type orbitals is seen in the preferential orientation of the NC_2 planes along the M-M axis in all NMe_2 -containing compounds. This allows $Me_2N p_\pi$ to $M d_\pi$ bonding without disruption of the M-M $d_\pi-d_\pi$ bonding. The salient features of this simple bonding description are supported by detailed MO calculations²⁵⁻²⁷ and by data obtained from UV-visible and photoelectron spectroscopy.²⁸⁻³⁰

$L_2M(\mu-X)_2ML_2$ Compounds. The existence of unbridged $X_3M\equiv MX_3$ compounds emphasizes the importance of metal-metal bonding. The commonly preferred geometry for M_2X_6 dimers is based on the formation of ligand bridges. Two tetrahedrally coordinated metal ions share a common edge, as seen for Al_2Cl_6 . This bridged structure maximizes metal-ligand bonding, but for a d^3-d^3 dinuclear complex, it does not give rise to effective M-M bonding. This can be seen from the pictorial model of a hypothetical $X_2M(\mu-X_2)MX_2$ molecule shown in V.



In a tetrahedral field the d orbitals give rise to a t_2 (xz , yz , xy) and an e ($x^2 - y^2$, z^2) set, and with the axes shown in V, the former are used in metal-ligand σ bonding and the latter set is available for M-M bonding. As shown in V, the z^2 interactions will yield σ and σ^* molecular orbitals and the $x^2 - y^2$ interactions, the δ and δ^* molecular orbitals. For a d^3-d^3 dinuclear compound, a $\sigma^2\delta^2\delta^*2$ M-M configuration is expected. There would likely be some mixing of the δ and δ^* orbitals with ligand p_π orbitals of the bridging groups. This might invert the relative ordering of the δ and δ^* orbitals as has been seen in edge-shared octahedral compounds $L_4M(\mu-L)_2ML_4$.³¹ This matter is of little consequence, however, in connection with comparing the M-M bonding to a dinuclear compound of struc-

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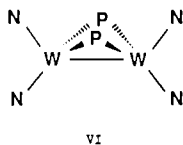
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tural type I with that of V. For the latter only the M-M σ bond is significant, and with a greater M-M distance because of the presence of μ -X groups, this too would be weaker than the σ component of the M-M triple bond in I. The bridged $X_2M(\mu-X)_2MX_2$ structure will be favored only when the formation of ligand bridges compensates adequately for the loss of M-M bonding that would otherwise be provided in the unbridged structure.

The isolation of isomers of bridged and unbridged d^3-d^3 dinuclear units has been realized.^{18,32} The molecular structures of the unbridged compounds of formula $1,2-Mo_2(PR_2)_2(NMe_2)_4$ reveal the π -donating order $NMe_2 > PR_2$ based on an analysis of the relative M-N/M-P distances. Furthermore, whereas the coordination at nitrogen is trigonal planar, that at phosphorus is pyramidal. For R = cyclohexyl, both bridged and unbridged isomers have been characterized. The unbridged isomer is the kinetic product in the reaction between $1,2-W_2Cl_2(NMe_2)_4$ and $LiP(c-C_6H_{11})_2$ (2 equiv) in toluene or tetrahydrofuran at or below 0 °C. At room temperature, isomerization occurs to give the thermodynamic product, the bridged isomer, which, rather interestingly, has a puckered $W_2(\mu-P)_2$ central core as shown in VI. For $W_2(PPh_2)_2(NMe_2)_4$, an equilibrium mixture between unbridged and bridged isomers is present in toluene solutions indicating the balancing of M-M and M-P bonding in these molecules.



VI

The puckering of the $W_2(\mu-P)_2$ core enhances M-M bonding in a bridged structure (relative to structure V) though the W-W distance in VI, 2.570 (1) Å, is considerably longer than in the unbridged gauche rotamer, III, 2.294 (2) Å.³² In solution, the puckered W_2P_2 moiety inverts, passing through a planar transition state. The energy of activation for this process is ca. 12 kcal mol⁻¹ as determined from the coalescence behavior of the P-cyclohexyl α -H atoms in variable-temperature NMR studies.¹⁸ This presumably reflects the difference in energy between the puckered and planar bridged structures, VI versus V.

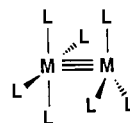
The four W-P distances in the bridged structure, VI, 2.36 (1) Å, are slightly shorter than the two in the terminal isomer, III, 2.40 (1) Å, providing clear evidence that W-P bonding is maximized in VI.

M_2L_7 and M_2L_8 Compounds. These are derivatives of the $X_3M\equiv MX_3$ compounds and have unbridged M-M triple bonds as indicated by the drawings VII and VIII. The conformational preference for the ligands is determined by intramolecular ligand-ligand interactions across the M-M bond, and the M-M bonding configuration remains $\sigma^2\pi^4$, though by symmetry, the π_x and π_y orbitals are no longer degenerate. The M-M distances are essentially the same as those for compounds of type I.

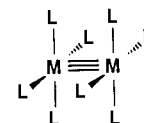
Structurally characterized examples of VII are currently limited to $Mo_2(O-i-Pr)_4(CH_2Ph)_2(PMe_3)^{33}$ and

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VII



VIII

$W_2(\text{tolyl})_2(O-i-Pr)_4(HNMe_2)^{20}$ Complexes of type VII must be involved in the commonly observed equilibria between the dinuclear alkoxides $M_2(OR)_6$ and Lewis bases L, eq 1, where L = an amine or phosphine.³⁴



The equilibrium 1 interconverts compounds of types I and VIII and is sensitive to the steric factors associated with R and L. The Lewis base adducts VIII may be used as a source of the unligated compounds I (M = W) in solution when the reactivity of the $W_2(OR)_6$ compounds does not allow their isolation because of cluster-forming reactions: $2W_2(OR)_6 \rightarrow W_4(OR)_{12}$.^{35,36} In studies of reaction 1, compounds of type VII, the monoligated adducts, are not detectable by NMR or UV-visible spectroscopy and therefore they must be kinetically labile intermediates. The equilibrium 1 is typically rapid at room temperature and gives rise to line broadening and coalescence behavior on the NMR time scale. Although both M_2X_6 and $M_2X_6L_2$ are unbridged, there is reason to believe that the monoligated compounds M_2X_6L can exist in a bridged form. For example, the addition of PMe_3 to $1,2-Mo_2(CH_2Ph)_2(O-i-Pr)_4$ yields an alkoxide/benzyl migration in the formation of $(PMe_3)(PhCH_2)_2(i-PrO)Mo\equiv Mo(O-i-Pr)_3$.³³

There are a number of compounds that involve four-coordinate metal atoms united by a M-M triple bond where two of the attendant ligands are bidentate and span the $M\equiv M$ moiety, e.g., $M_2(OR)_4(O_2CR')_2$ ³⁷ and $M_2(NMe_2)_4(PhNNNPh)_2$.³⁸⁻⁴⁰ The formation of the five-membered ring (carboxylate or triazine) involving the M-M bond forces a near eclipsed geometry of the two four-coordinate metal centers. A bidentate ligand can also behave as a chelate to one metal as in $M_2(OR)_4(acac)_2$ compounds, where acac = the anion derived from deprotonation of 2,4-pentanedione.^{41,42}

In compounds of types VII and VIII, one of the in-plane metal d orbitals ($x^2 - y^2$ or xy) is used to form the new metal-ligand σ bond. When ancillary π -donor ligands such as OR or NMe_2 are present, one ligand-metal π bond is sacrificed as the new M-L σ bond is formed. There is no change in the total electron count about the metal center. Lewis adduct formation results in a significant increase in M-N or M-O bond distance,

(34) For a listing of structural parameters in $M_2(OR)_6L_2$ compounds, see: Chisholm, M. H. *Polyhedron* **1983**, *2*, 681, Table IV.

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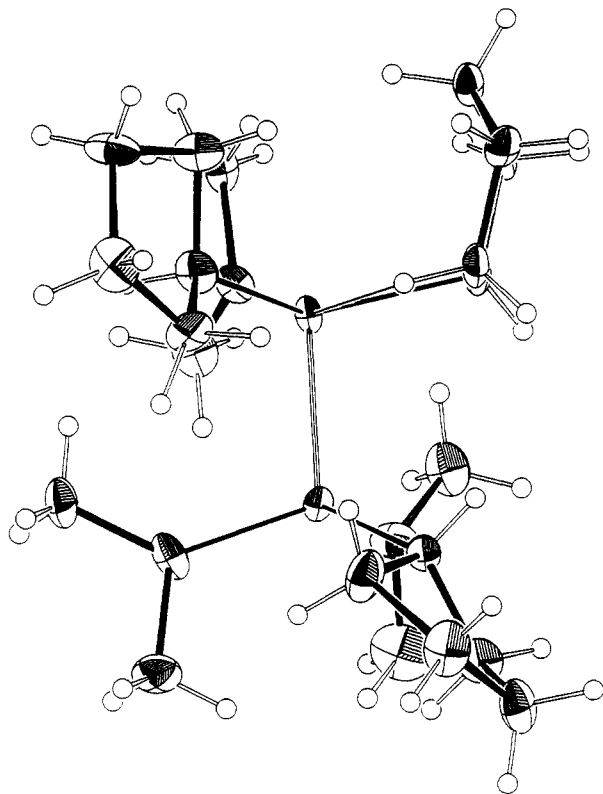
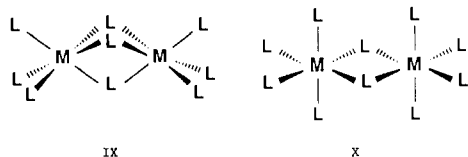


Figure 1. An ORTEP drawing of the $W_2(c-C_5H_9)_3(NMe_2)_3$ molecule showing the η^2 -cyclopentyl ligand. Pertinent distances (Å) are $W-W = 2.30$ (1), $W-N = 1.94$ (1) (av), $W-C = 2.17$ (1) (av), and $W-\eta^2$ -cyclopentyl = 2.13 (1) ($C\alpha$) and 2.56 (1) ($C\beta$).

reflecting, at least in part, the decrease in ligand-metal π bonding.³⁴ The importance of this in-plane bonding involving the metal xy and $x^2 - y^2$ orbitals is seen in the structure of $W_2(c-C_5H_9)_3(NMe_2)_3$.⁴³ See Figure 1. One tungsten is ligated to two cyclopentyl ligands and one NMe_2 ligand. One of the xy or $x^2 - y^2$ orbitals is involved in π bonding with the NMe_2 ligand while the other is used in what is now commonly referred to as an "agostic" $CH-M$ interaction.^{44,45} One cyclopentyl ligand behaves in a bidentate manner leading to a four-coordinate metal center. The $W_2(c-C_5H_9)_3(NMe_2)_3$ molecule can be viewed as a member of the M_2L_7 class of compounds where a $C-H$ to W bond is involved.

M_2L_9 and M_2L_{10} Compounds. The confacial bioctahedron IX and the edge-shared octahedron X are common geometries in the chemistry of dimeric and dinuclear compounds. The $M-M$ separation is very sensitive to the nature of the $M-M$ bonding.



The $M_2X_9^{3-}$ ions of structural type IX are known for $X = Cl$ and Br and $M = Cr, Mo,$ and W and reveal the relative importance of $M-M$ bonding within the series

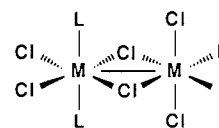
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of the group 6 elements.⁴⁶ For $M = Cr$, the $M-M$ distance is ca. 3.5 Å and the $t_{2g}^3 \dots t_{2g}^3$ electrons are only weakly antiferromagnetically coupled, whereas for $M = W$, the $M-M$ distances are very short, ca. 2.40 Å, and the ions are diamagnetic. For $M = Mo$, the $M-M$ separations, though much shorter than for $M = Cr$, span a range 2.50 – 2.80 Å, often being dependent on the nature of the cation, and they are usually paramagnetic.

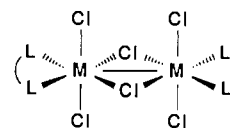
The edge-shared structure is also common for metal halides, e.g., $[NbCl_5]_2$ and $[ReCl_5]_2$, that have $M-M$ nonbonding distances in the range 3.5 – 3.7 Å.⁴⁷ For $W_2Cl_6(py)_4$ ⁴⁸ and $W_2Cl_6(PMe_3)_4$ ⁴⁹ that adopt the chloride-bridged structure shown in XI, the $M-M$ distances are ca. 2.70 – 2.75 Å, indicative of $M-M$ bonding.



XI

By symmetry, the fusing of two octahedra along a common edge allows a $t_{2g}^3-t_{2g}^3$ interaction to give a $\sigma^2\pi^2\delta^2$ $M-M$ MO configuration. It was first noted by Hoffman³¹ that the relative ordering of the δ and δ^* orbitals can be inverted in the presence of bridging ligands having filled p_π orbitals. At a $M-M$ distance of 2.7 Å, the $M-M$ bond strength must be significantly less than in $W_2Cl_9^{3-}$ with $M-M$ distance 2.40 Å.

Poli⁵⁰ has recently observed that for $M = Mo$, where $M-M$ bonding is not as strong as for $M = W$, complexes of the general type X with chloride bridges sometimes have $M-M$ bonds while in other instances they do not. For example, compare $Mo-Mo = 2.762$ (1) Å in $Mo_2Cl_6(dppe)_2$,⁵¹ where $dppe$ is $Ph_2PCH_2CH_2PPh_2$, with $Mo-Mo = 3.730$ (1) Å in $Mo_2Cl_6(PEt_3)_4$.⁵⁰ The structure of $Mo_2Cl_6(dppe)_2$ is depicted by XII and is variant of X. Subtle factors influence the $M-M$ interactions in these Mo_2 compounds in ways that are not presently understood.



XII

The confacial bioctahedron IX generates a $t_{2g}^3-t_{2g}^3$ interaction that affords a triple bond of configuration $\sigma^2\pi^4$, and we see in the chemistry of tungsten a subtle interplay between maximizing metal-metal bonding (structure IX) and maximizing metal-ligand bonding (structure X) in the relative preference for one or the other of IX and X. For example, $W_2Cl_6L_4$ and $W_2Cl_6L_3$ compounds may exist in equilibria as shown in eq 2.⁵²

(46) See ref 4, section 5.4.

(47) For an excellent review of the structure of edge-shared bioctahedra for d^n-d^n complexes where $n = 0-5$, see: Cotton, F. A. *Polyhedron* **1987**, *6*, 677.

(48) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

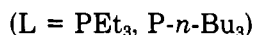
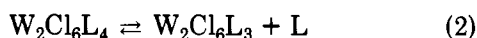
(49) Chacon, S. T.; Chisholm, M. H.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1989**, *28*, 5.

(50) Poli, R.; Mui, H. D. *Inorg. Chem.* **1989**, *28*, 3609.

(51) Agaska, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 4051.

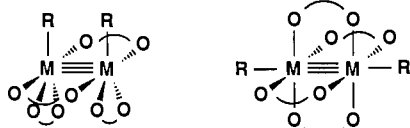
(52) Chacon, S. T.; Chisholm, M. H.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *28*, 5.

Also in tetrahydrofuran solutions the $W_2Cl_7(THF)_2^-$ anion is maintained with structural type IX, although addition of pyridine yields $W_2Cl_6(py)_4$, having structure type X (specifically XI where $L = py$).⁴⁸



It has long been known that the rates of $^*Cl^-$ substitution for bridging and terminal W-Cl bonds in the $W_2Cl_9^{3-}$ anion are "indistinguishable".⁵³ This observation is most easily explained by the facile opening and closing of halide bridges (eq 2) wherein confacial and edge-shared octahedra are in equilibrium upon ligand loss or uptake.

There are two other M_2L_{10} structural types for d^3-d^3 W_2 containing compounds. These are shown schematically in XIII and XIV. Compounds of structural



XIII

XIV

type XIII include $W_2Me_2(O_2CNET_2)_4$ ⁵⁴ and $W_2(CH_2-t-Bu)_2(O_2CMe)_2(S_2CNET_2)_2$ ⁵⁵ wherein two of the bidentate ligands span the M-M bond and two act as chelates (one to each metal atom). The X_5M moiety approximates a planar-pentagonal unit, and the presence of the bridging ligands causes the two ends of the molecule to be eclipsed. The bonding in the X_5M plane involves metal atomic orbitals s , p_x , p_y , $d_{x^2-y^2}$, and d_{xy} , and the M-M triple bond is still of the configuration $\sigma^2\pi^4$ being derived from $d_{z^2}(\sigma)$ and d_{xz} , d_{yz} (π_x , π_y) orbitals. Closely related to XIII are the structures seen for $W_2(O_2CNMe_2)_6$ ⁵⁴ and $W_2(O_2C-t-Bu)_6$ ⁵⁶ which are depicted in XV and XVI, respectively.



XV

XVI

As in XIII, five ligand atoms are contained in a pentagonal plane, but in XV and XVI there is an additional relatively weak O-W interaction (as judged by the W-O distances of ca. 2.50 Å) along the W-W axis. This brings into bonding the remaining metal atomic orbital, W $6p_z$. The metal atoms in complexes of structural types XV and XVI attain an 18-electron valence shell whereas for XIII they are formally unsaturated having 16 valence electrons. The relatively weak axial ligation in XV and XVI presumably arises from the mutual trans influence of M-M σ and axial M-L bonding. The W-W distances in $W_2Me_2(O_2CNET_2)_4$, $W_2(O_2CNMe_2)_6$, and $W_2(O_2C-t-Bu)_6$ are

(53) Hawkins, G. L.; Garner, C. S. *J. Am. Chem. Soc.* 1958, 80, 2946.

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

(55) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* 1987, 109, 6817.

(56) Chisholm, M. H.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* 1985, 24, 3214.

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

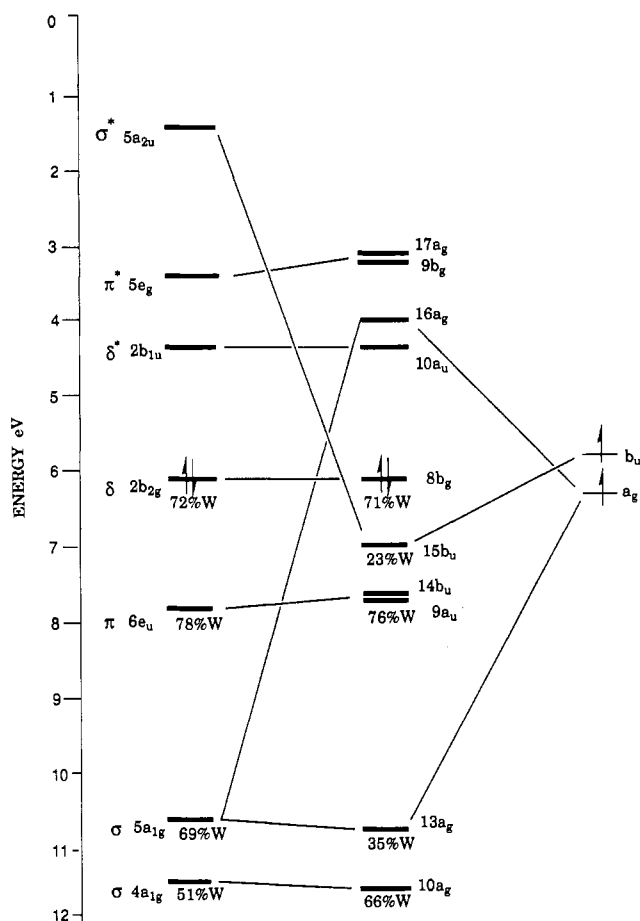


Figure 2. This diagram shows the correlation of the M-M bonding orbitals in $W_2(O_2CH)_4$ with two CH_2 fragments in the formation of $W_2(O_2CH)_4(CH_3)_2$. The HOMOs are denoted by spin-paired arrows. In $W_2(O_2CH)_4$ there are two σ -type bonding orbitals, $4a_{1g}$ and $5a_{1g}$, having W $6s$ and W d_{z^2} character, respectively. Both have some M-O bonding component. The $6e_u$ and $2b_{2g}$ orbitals are the M-M π and δ orbitals, respectively. In forming two new bonds to the CH_3 groups, the M-M π and δ orbitals are perturbed little. The two lower energy σ orbitals are stabilized slightly while the new σ orbital $15b_u$ is principally W-C bonding and only slightly W-W antibonding.

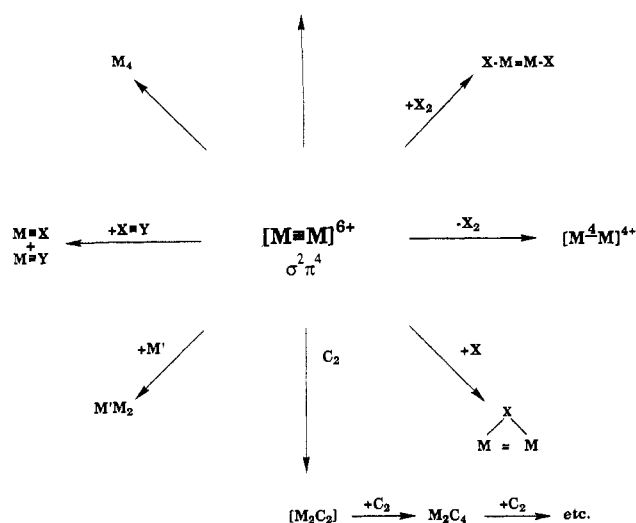
essentially identical with the W-W distances in compounds of types I-IV, VII, and VIII, consistent with their common M-M MO configuration $\sigma^2\pi^4$.

By contrast $M_2R_2(O_2CR')_4$ compounds adopt the structure shown in XIV.⁵⁷ The central $M_2(O_2C)_4$ core is typical of that seen in the d^4-d^4 M-M quadruply bonded tetracarboxylates of molybdenum and tungsten. The M-M distances are shorter by 0.1 Å compared to those of the ethane-like $X_3M\equiv MX_3$ compounds, I, and the related compounds of structural type XIII. The axial ligation by the alkyl ligands is strong, which contrasts with the weak axial coordination in XV and XVI. The benzyl compound $W_2(CH_2Ph)_2(O_2CET)_4$ exists in solution as a mixture of isomers XIII and XIV with the equilibrium favoring XIV.

On the basis of UV-visible and photoelectron spectroscopic data and cyclic voltametric studies, the $M_2R_2(O_2CR')_4$ compounds of structural type XIV have a valence MO configuration M-M $\pi^4\delta^2$.⁵⁷ The HOMO

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Scheme I
Coordination Chemistry: Substitution Reactions



is a δ^2 orbital just as is found in the d^4-d^4 $M_2(O_2CR)_4$ compounds that have M-M quadruple bonds. Formally the d^3-d^3 dinuclear compounds lack a M-M σ bond though in reality there is extensive mixing of M-C and M-M σ orbitals.

The bonding in XIV may be related to that of the well-known quadruple bond by the schematic MO correlation diagram shown in Figure 2 where two alkyl radicals are brought up along the M-M axis.⁵⁸ The in-phase and out-of-phase combinations of the C_{sp^3} orbitals interact with the tungsten $5d_{z^2}$ and $6s$ orbital combinations to produce a set of M-M and M-C σ and σ^* orbitals such that the net M-M bonding retains the π and δ orbitals of the M-M quadruply bonded tetracarboxylates. There is an interesting analogy here with the bonding in the diatomic C_2 which has a double bond of valence MO configuration π^4 (formally lacking a σ bond as a result of occupied σ and σ^* orbitals derived from $1s^2-1s^2$, $2s^2-2s^2$ overlap)⁵⁹ and ethylene which contains a C-C double bond of configuration $\sigma^2\pi^2$. Despite the lack of a formal σ bond, the bond distance in C_2 , 1.24 Å,⁶⁰ is shorter than that in ethylene, 1.34 Å.⁶¹

Reactions of d^3-d^3 M_2 Compounds. The extremely diverse structural chemistry of M_2^{6+} -containing compounds might lead one to anticipate that the reaction chemistry would be extraordinarily rich and complex, and this is indeed so.⁶² (1) There is a large number of ligand substitution reactions wherein the various ground-state geometries of the M_2 unit compounds are interrelated. In certain cases the rates of isomerizations are sufficiently slow that separate chemistries of the isomers can be investigated. This is the case for 1,1- and 1,2- $M_2X_2Y_4$ compounds. (2) The dinuclear centers are redox active. The d^3-d^3 M-M bonding electrons take the place of those in ligand field split metal d orbitals in mononuclear complexes. Oxidative addition

and reductive elimination reactions can lead to stepwise changes in M-M bond order. The redox activity of a d^3-d^3 M_2 center is greatly influenced by its coordination geometry as well as the nature of the attendant ligands. A more detailed discussion of the organometallic chemistry⁶³ and the reactivity⁶⁴ of d^3-d^3 M_2^{6+} containing compounds is presented elsewhere. Herein the general concepts of reactivity are described.

Scheme I shows some of the commonly observed reaction patterns of $(M\equiv M)^{6+}$ -containing compounds having a triple bond of configuration $\sigma^2\pi^4$. Many of these reactions are not found in mononuclear chemistry and point to the importance of the $(M\equiv M)^{6+}$ unit as an inorganic functional group or synthon. For instance, the reductive cleavage of $C\equiv C$ and $C\equiv N$ bonds in the reactions between alkynes or nitriles and certain $W_2(OR)_6$ compounds provides examples of six-electron redox reactions!^{65,66} The reductive coupling of ketones/aldehydes to give olefins proceeds by an initial four-electron reduction of the $R_2C=O$ ligand to give a d^1-d^1 bridging alkylidene oxo compound.⁶⁷ A reduction of carbon monoxide can be brought about in a stepwise manner.⁶⁸ CO first adds across the $(M\equiv M)^{6+}$ unit to give an inorganic analogue of cyclopropenone, $M_2(\mu-C=O)$ [$\bar{\nu}(CO) = 1575$ cm^{-1} in $W_2(O-t-Bu)_6(\mu-CO)$], and then further reduction by another $(M\equiv M)^{6+}$ unit gives $W_4(\mu_4-C)$ -containing compounds.

While the above reactions are impressive because they involve the rupture of strong bonds, reactions involving C-H bond cleavage are intriguing because of their mechanistic possibilities. For example, 1,2-dialkyl $(M\equiv M)^{6+}$ containing compounds undergo reductive elimination reactions with loss of alkane and alkene and formation of d^4-d^4 (M^4-M) compounds^{69,70} or oxidative addition reactions with elimination of alkanes and formation of d^1-d^1 ($M-M$) containing compounds supported by hydrido and alkylidyne ligands.^{71,72} These competing pathways involve β - and α -CH activation processes, respectively.

Comparisons with Mononuclear Systems. In mononuclear chemistry, oxidation states and coordination numbers are often limited to changes of ± 2 . For example, organoplatinum chemistry,⁷³ which is among the richest and best developed of the transition elements, centers on L_4Pt^{II} with a range to L_2Pt^0 and L_6Pt^{IV} . The beautiful chemistry of the bent sandwich compounds Cp_2ML_n ($M =$ a group 4 or 5 element) involves a redox range of 2, e.g., $Ti^{II/IV}$ and $Nb^{III/V}$, and uses three metal orbitals that lie in one plane.⁷⁴ In

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(74) See ref 5, section 20.4 and references cited therein.

(58) Braydich, M. D.; Bursten, B. E.; Chisholm, M. H.; Clark, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4459.

(59) For simple MO descriptions of the bonding in diatomics such as C_2 and "sp" mixing, see: Gray, H. B.; DeKock, R. L. *Chemical Structure and Bonding*; W. A. Benjamin: Reading, MA, 1980; Chapter 4. See also: Mulliken, R. S.; Ermler, W. C. *Diatom Molecules. Results of ab Initio Calculations*; Academic Press: New York, 1977; Table 7, p 172.

(60) Fougere, P. F.; Nesbitt, R. K. *J. Chem. Phys.* **1966**, *44*, 285.

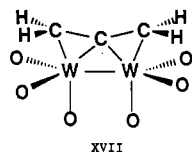
(61) Kutchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

(62) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21; *Angew. Chem.* **1986**, *98*, 21.

contrast to mononuclear templates, the M_2 unit offers a greater redox range with access to $d^4-d^4 M_2^{II,II}$ and $2M^{VI}$. The coordination number n for M_2L_n may vary from $n = 6$ to $n = 12$, and the geometries may involve bridged or unbridged M-M bonds. The frontier orbitals of the $(M\equiv M)^{6+}$ unit are therefore variable, being dependent upon the attendant ligands and their disposition about the dinuclear center.

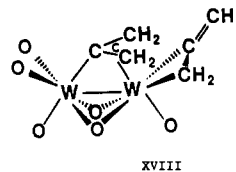
Consider the addition of allene to a mononuclear complex L_nM . What would be the geometry of the resultant 1:1 adduct? Given information concerning the d electron count, the specific metal, and the attendant ligands, this type of question is one that can be addressed readily by a fragment molecular orbital or isobal approach.^{5,6} The same question concerning the addition of allene to a $M_2(OR)_6$ compound of structural type I cannot be answered so readily, however. There is the complication of stoichiometry (i.e., one allene per M_2 or one allene per M), and the possibility of ligand bridges (alkoxide, substrate, or both) has to be confronted.

Allene forms a 1:1 adduct with $W_2(O-t-Bu)_6$ having a structure of the type shown in XVII.⁷⁵ The allene is V-shaped, $C-C-C = 145^\circ$, and aligned parallel to the $W-W$ axis. The methylene hydrogens are contained in one plane!



$W_2(O-t-Bu)_6$ also forms a 2:1 allene adduct which can be prepared by the further addition of allene to $W_2(O-t-Bu)_6(C_3H_4)$. The structure of the 2:1 allene adduct is depicted by XVIII and contains a metallaallyl ligand and an $\eta^2-C_3H_4$ ligand.⁷⁵ The latter mode of allene-metal bonding is the one observed in mononuclear chemistry.

(75) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Foltling, K.; Ellis, P. D.; Huggins, B. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *29*, 1523; *Angew. Chem.* **1989**, *101*, 1547.



The structures XVII and XVIII testify to the flexibility of the $M_2(OR)_6$ group as a template for substrate uptake. The substrate may bridge the two metal atoms or may bond to only one metal atom; the attendant alkoxide ligands can be accommodated in either unbridged or bridged structures.

Concluding Remarks

The coordination chemistry surrounding the $d^3-d^3 M_2$ centers of molybdenum and tungsten is remarkably diverse and reflects the subtle interplay of metal-ligand and metal-metal bonding. The extraordinary wealth of accessible ground-state geometries, coupled with the redox capabilities of the dinuclear center, generates a richness in reactivity that requires considerable further exploration of scope and mechanism. Also, detailed studies of the photophysics and photochemistry of $d^3-d^3 M_2$ systems are warranted. While all of the aforementioned relate to the molecular chemistry of $d^3-d^3 M_2$ containing compounds, there is also the unexplored field of M_2 subunits in ordered assemblies. One can imagine inorganic analogues of polyacetylene, copolymers with organic molecules, $\sim M_2 \sim \sim M_2 \sim \sim M_2 \sim$, and liquid crystals containing $M_2 \cdots M_2 \cdots M_2$ cores.⁷⁶ Given the redox activity and electronic flexibility of the M-M bonding in $d^3-d^3 M_2$ containing compounds, these "materials" should have interesting physicochemical properties.

I thank the National Science Foundation for support of this chemistry, 1974-present, and my many talented co-workers. Particular thanks are due to Drs. John Huffman, William Streib, and Kirsten Foltling at the Indiana University Molecular Structure Center. I am also indebted to Professor F. A. Cotton, for many enjoyable discussions.

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