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A Coordination Strategy to Realize a Sextuply Bonded Complex

Yue Chen,a,b Jun-ya Hasegawa,a,b* Kazuya Yamaguchi,c Shigeyoshi Sakakid*

Synthesis of higher-order multiple bond is a great challenge in chemistry. However, no stable compound with a sextuple bond has been reported, except for Mo2 in an inert matrix at low temperature. Here, we propose a strategy to construct a sextuple bond in a dinuclear transition metal complex based on the complete active space second-order perturbation theory (CASPT2) and density functional theory calculations. When the dinuclear core M2 (M = W, Mo, and Re+) is capped by two neutral electron-donating ligands at both M-M ends, a sextuple bond can be realized. The proposed ligands stabilize the M-M core by the coordination, conserve the six bonding orbitals in the occupied space, and suppress the weight of the 6-6* excited electron configuration. Calculated large formation energies of these complexes indicate the large possibility of the synthesis. Electronic structure and sextuple bonding interactions are analyzed in detail.

1. Introduction

To create the highest multiple bond in a stable compound has been a great interest to chemists for decades. In main group elements, the triple bond was supposed to be the limit of multiple bond for nearly 50 years. Recently, the quadruple bond was suggested to have been synthesized. After that, many stable quadruply and quintuply bonded dinuclear transition metal complexes have been synthesized.

Though quadruple bonds do not exhibit reactivity, it is interesting that some of quintuple bonds are highly reactive, suggesting that the sextuple bond exhibits new feature. However, the synthesis of the sextuple bond is still a great challenge in chemistry. Only limited knowledge of the sextuple bond is available both in experiment and theory. A sextuple bond could be formed with five nd orbitals and one (n+1)s orbital of a transition metal in a diatomic molecule such as Cr2, Mo2, and W2. Thus, twelve atomic orbitals form six bonding molecular orbitals (MOs) (σ(n+1)s, σnd, two πnd, and two δnd) and six anti-bonding MOs (σ*(n+1)s, σ*nd, two π*nd, and two δ*nd); see Fig. 1. If the six bonding MOs are doubly occupied and their anti-bonding counterparts are unoccupied, a sextuple bond is formed. In other words, the closed-shell singlet electron configuration \( \sigma_n^2\sigma_{nd}^2\sigma_{nd}^2\delta^{6}\) provides the sextuple bond in a formal sense; hereafter, we use “S0 state” for an electronic state bearing this closed-shell electron configuration as a dominant term. The present study focuses on transition metals, but not on actinides that are also expected to be useful in forming a metal-metal multiple bond with 5f orbitals.

Roos et al. proposed a concept of effective bond order (EBO) to evaluate the bond order as follows. For a single bond, the EBO is defined as

\[ \text{EBO} = \frac{\eta_b - \eta_a}{2} \]

where \( \eta_b \) and \( \eta_a \) are occupation numbers of bonding and anti-bonding MOs, respectively. The occupation number is usually calculated by multi-configurational wave function method for strongly correlated systems. For a multiply bond, the total EBO is the summation of the contributions from each bond. In a transition metal sextuple bond, the EBOs of \( \sigma_{nd}, \pi_{nd}, \delta_{nd} \), and \( \sigma_{(n+1)s} \) contribute to the total EBO. The EBO is non-integer in many cases. A multiplicity of a bond is defined as the lowest integer value larger than the EBO. For example, the EBO of the Re-Re quadruple bond in \([\text{Re}_2\text{Cl}_6]\) was calculated to be 3.2 by a multi-configurational method.

After systematic theoretical studies, Roos et al. concluded that only Mo2 and W2, whose EBOs are both 5.2, have a sextuple bond in diatomic molecules. In the Cr2 case, the calculated EBO value (3.5) suggested that this molecule has a quadruple bond. This is true because the strong \( \delta - \delta^* \) electron correlation reduces the bond order. In experiment, only Mo2 was synthesize, but in an inert
matrix at low temperature. As far as we know, neither experimental nor theoretical studies have reported a stable sextuply bonded compound.

In this work, we propose a strategy to realize a sextuply bond in stable dinuclear transition metal complexes. In our strategy, the M$_2$ core (M = W, Mo, Re$^+$, and Tc$^+$) is capped by two neutral electron-donating tetradentate ligands at both M-M ends. The complete active space self-consistent field (CASSCF) with second-order perturbation theory (CASPT2) calculations and the EBO analysis clearly show that a sextuple bond can be realized in dinuclear W, Mo, and Re$^+$ complexes. Both CASPT2/CASSCF and density-functional theory (DFT) results show that these complexes have large formation energies, indicating the large possibility of the synthesis.

2. Results and discussion

2.1. Sextuple bond in diatomic molecules

First, we show the bare metal dimer cases as the starting point. It is believed that among many transition metals, Cr, Mo, W, Mn$^+$, Tc$^+$, and Re$^+$ meet the requirements to form a sextuple bond. Previous theoretical studies demonstrated that the ground state of W$_2$ and Mo$_2$ is the S$_0$ state with a sextuple bond. Our DFT and CASPT2 calculations confirmed this conclusion. As shown in Table 1, the EBOs calculated with CASSCF for W$_2$ and Mo$_2$ in the S$_0$ state were 5.15 and 5.11, respectively. To our knowledge, Re$_2^{2+}$ and Tc$_2^{2+}$ have not been studied. At the DFT level, Re$_2^{2+}$ has a meta-stable S$_0$ ground state with an equilibrium Re-Re distance of 2.005 Å, but its formation from two Re$^+$ cations is endothermic by 115.2 and 125.3 kcal/mol at the DFT and CASPT2 levels, respectively. The instability of Re$_2^{2+}$ in the S$_0$ state is attributed to the Coulomb repulsion between the two Re$^+$ cations. Our coordination strategy works for stabilizing the Re$_2^{2+}$ structure, as will be described below.

In the case of Tc$_2^{2+}$, the lowest energy triplet state is more stable than the S$_0$ state by 13.2 and 14.5 kcal/mol at the DFT and CASPT2 levels, respectively. The $\delta_{nd}$ MOs have a lot of electron occupation because the energy level of the $\sigma_{(n+1)s}$ MO is higher than that of the $\sigma_{nd}$ MO; see Fig. 2. As a result, the EBO of Tc$_2^{2+}$ calculated by CASSCF is only 4.11; see Table 1. The formation of Tc$_2^{2+}$ is endothermic by 115.2 and 125.3 kcal/mol at the DFT and CASPT2 levels, respectively. From these results, a sextuple bond is formed in diatomic W$_2$ and Mo$_2$ molecules, but not in diatomic Re$_2^{2+}$ and Tc$_2^{2+}$.

2.2. Coordination strategies to realize a sextuple bond in a stable complex

Coordination of M$_2$ with electron-accepting ligand. To make a sextuple bond in a dinuclear complex by utilizing the coordination of ligands, the use of an electron-accepting ligand such as cyclopentadienyl (Cp)$^{56}$ and benzene(C$_6$H$_6$)$^{57}$ was theoretically proposed in pioneering works. The computational results certainly showed that CpRe$_2$Cp in the singlet state has a sextuple bond. However, a triplet state with a quintuple bond was calculated to be the ground state.$^{56}$

| Table 1. Effective bond order$^a$ (EBO) of metal-metal bond. |
|--------------|--------|--------|--------|--------|--------|
| M$^b$ | L$^b$ | EBO$_{nd}$ | EBO$_{nd}$ | EBO$_{nd}$ | EBO$_{nd}$ |
| W | - | 0.87 | 1.81 | 1.54 (0.77) | 0.93 | 5.15 |
| Mo | - | 0.88 | 1.79 | 1.51 (0.75) | 0.93 | 5.11 |
| Re$^+$ | - | 0.87 | 1.75 | 1.20 (0.60) | 0.88 | 4.70 |
| Tc$^+$ | - | 0.86 | 1.73 | 1.04 (0.52) | 0.48 | 4.11 |
| W | O$_4$ | 0.87 | 1.82 | 1.52 (0.76) | 0.95 | 5.17 |
| Mo | O$_4$ | 0.87 | 1.79 | 1.47 (0.74) | 0.97 | 5.10 |
| Re$^+$ | O$_4$ | 0.81 | 1.76 | 1.23 (0.62) | 0.96 | 4.76 |
| Tc$^+$ | O$_4$ | 0.85 | 1.75 | 1.09 (0.55) | 0.49 | 4.18 |
| W | O$_2$N$_2$ | 0.86 | 1.83 | 1.55 (0.78) | 0.97 | 5.22 |
| Mo | O$_2$N$_2$ | 0.85 | 1.79 | 1.44 (0.72) | 0.99 | 5.07 |
| Re$^+$ | O$_2$N$_2$ | 0.85 | 1.79 | 1.53 (0.76) | 0.97 | 5.13 |
| Tc$^+$ | O$_2$N$_2$ | 0.86 | 1.74 | 1.22 (0.61) | 0.50 | 4.32 |

$^a$ EBO$_{nd}$, EBO$_{nd}$, and EBO$_{nd}$ are EBO for the $\sigma_{nd}$, $\pi_{nd}$, $\delta_{nd}$, and $\sigma_{(n+1)s}$ bonds, and EBO is for the total bond order. $^b$ "M" and "L" denote metal and ligand, respectively. For the structures of the ligands, see Scheme 1. For EBO$_{nd}$, the value in parentheses is the average value of two $\delta_{nd}$ bonds.

Fig. 2 Dominant electronic configuration of M$_2$ (M=W, Mo, Re$^+$, and Tc$^+$).

The metal-metal bond in the ground state of (C$_6$H$_6$)$_2$Cr$_2$(C$_6$H$_6$), C$_6$H$_6$(Mo$_2$)$_2$C$_6$H$_6$, and C$_6$H$_6$(W$_2$)$_2$C$_6$H$_6$ was calculated to be a quadruple bond rather than a sextuple bond.$^{53}$ The reason is that the metal-ligand interaction significantly changes the relative energies of bonding and anti-bonding MOs of the M-M moiety. As shown in Fig. 3A, the $\delta_{nd}$ and $\delta_{nd}$ orbitals are both stabilized significantly by the $\pi^*$ orbitals of benzene through back-donation interaction. In contrast, the $\sigma_{(n+1)s}$ and $\pi_{nd}$ MOs are rather destabilized by the interactions with the $\pi$ orbitals of benzene. As clearly seen in Fig 3B, only the $\delta_{nd}$ and $\delta_{nd}$ orbitals form bonding interactions with the benzene $\pi^*$ orbitals, while the $\sigma_{(n+1)s}$ and $\pi_{nd}$ MOs have anti-bonding interactions with the benzene $\pi$ orbitals. Because of spatial symmetry of MOs, the $\delta_{nd}$ and $\delta_{nd}$ MOs are only allowed to interact with the unoccupied MOs of benzene. As a result, the $\delta_{nd}$
MO energy becomes lower than the $\sigma^*_{(n+1)s}$, and the electron population increases in the $\delta^*_{nd}$ MO rather than in the $\sigma_{(n+1)s}$ MO; see Fig. 3. See also Fig. S8 in ESI for orbital correlation diagram of the C$_6$H$_6$(M$_2$)C$_6$H$_6$ complex. To conserve the six metal-metal bonding MOs in the occupied space, an ideal condition is that the energy levels of the six bonding MOs shift uniformly by the ligand coordination. Considering the MOs of CpM$_2$Cp and C$_6$H$_6$(M$_2$)C$_6$H$_6$, the ligand used is requested not to stabilize the energy of the $\delta^*_{nd}$ MO more than that of $\sigma_{(n+1)s}$ MO. To satisfy this requirement, ligand should not have electron-accepting $\pi^*$- and $\delta^*$-type MOs.

**Sextuply bonded complexes with electron-donating ligand.** On the basis of the previous studies and above consideration, we propose a strategy to achieve the sextuple bond in a dinuclear complex. The basic idea is to keep the $\sigma_{(n+1)s}$ MO being more stable in energy than the $\delta^*_{nd}$ MO by employing an electron-donating ligand (L) without electron-accepting MO; see Fig. 4A. In this work, we employed a neutral tetradentate ligand with an electron-donating property, such as 12-crown-4 ether (referred as L = O$_4$), considering four factors: (1) The tetradentate electron-donating ligand interacts uniformly with all these bonding and anti-bonding MOs, and the six bonding MOs are kept in the occupied space. (2) A neutral ligand must be used to suppress the formation of too strong metal-ligand interaction. Because the $\sigma_{(n+1)s}$ orbital is more diffuse than the nd orbitals, a strong coordination would destabilize the $\delta^*_{nd}$ MO much more than the $\sigma^*_{nd}$ MOs. (3) The charge transfer (CT) from ligand to metal can stabilize the total system, particularly in the Re$_2^{2+}$ case. And, (4) The crown and aza-crown ether ligands, which are neutral tetradeinate ligand, are easily available and widely used in the transition metal complex.\(^{58,59}\) See Scheme 1 for the structures.

As shown in Fig. 5A, the M$_2$ (M = W, Mo, Re$^+$, or Tc$^+$) moiety with two O$_4$ ligands affords an O$_4$(M$_2$)O$_4$ complex. Calculated potential energy change by the ligand coordination shows that the ligand binding stabilizes the total energy as shown in Fig. 5B. In all of the W$_2$, Mo$^+_2$, and Re$_2^{2+}$ complexes, the ground-state has singlet spin multiplicity as shown in Table S2A in ESI. The S$_0$ configuration, which is illustrated in Fig. 4B, is kept being a dominant configuration in CASSCF wave function. For example, the weight of the S$_0$ configuration in the O$_4$(Mo$_2$)O$_4$ and O$_4$(W$_2$)O$_4$ complexes are 66.5% and 64.5%, respectively; see Table S2B in ESI for the other complexes.

The M-M bonding MOs of the O$_4$(W$_2$)O$_4$ complex are also shown in Fig. 4B. The MOs are dominantly localized in the M-M moiety, and the ligand MOs mix only slightly in an anti-bonding manner. These orbital interactions are apparently different from those in the benzene complex shown in Fig. 3B. The O$_4$ ligand has lone-pair orbitals on the oxygen atoms interacting with M$_2$ but no electron-accepting orbital in unoccupied space. In contrast, the benzene ligand uses both $\pi$ and $\pi^*$ MOs for the interaction with M$_2$. The $\pi$ MOs of benzene participates in weakly anti-bonding interactions with the $\sigma_{nd}$, $\pi_{nd}$, and $\sigma^*_{(n+1)s}$ MOs, while the $\pi^*$ MOs form strongly bonding MOs with the $\delta_{nd}$ and $\delta^*_{nd}$ MOs. As a result, the energy of the $\delta^*_{nd}$ MOs becomes lower than that of the $\sigma_{(n+1)s}$ MO in C$_6$H$_6$(M$_2$)C$_6$H$_6$, which is very bad for the formation of a sextuple bond.

The EBO of the M-M bond in the complexes changes little from that of naked M$_2$ as seen in Table 1. For example, the EBOs of the O$_4$(W$_2$)O$_4$ and O$_4$(Mo$_2$)O$_4$ complexes are 5.17 and 5.10, respectively. This result indicates that the W-W and Mo-Mo sextuple bonds are well maintained in these complex. The order of the occupied and unoccupied orbitals does not change with decreasing in the M–O$_4$ distance; see Fig. 5C. These results show that our ligand design works well. However, the EBO of the [O$_4$(Re$_2$)O$_4$]$^{2+}$ complex was 4.76, and showed a minor change (+0.07). This is because the weight of the S$_0$ configuration (37%) is considerably smaller than that of naked M$_2$ as seen in Table 1. For example, the EBOs of the O$_4$(W$_2$)O$_4$ and O$_4$(Mo$_2$)O$_4$ complexes are 5.17 and 5.10, respectively. This result indicates that the W-W and Mo-Mo sextuple bonds are well maintained in these complex.

**Scheme 1.** Structures of (a) 12-crown-4 ether (O$_4$), (b) 1,7-diaza-12-crown-4 ether (O$_4$N$_2$), and (c) 1,4,7,10-tetraaza-12-crown-4 ether (N$_4$).
Though Tc’ and Mo are isoelectronic pair, their end-on complexes have different spin multiplicities in their ground states. Figure 2 show a schematic diagram of the orbital energy levels and their occupation. Because of the stronger charge transfer interaction between O4 and Tc’, the Tc-O distance is shorter than Mo-O distance by 0.48 Å. As a result, the 5s orbital is more destabilized than the 4d orbital, and the σ_{5s} becomes comparable with the δ_{nd}. For the Re’ and W isoelectronic pair, the trend similar to the Tc’-Mo pair was observed. However, their end-on O4(M2)O4 complexes both have singlet ground state because 6s orbital of the 5d transition element becomes more stable due to relativistic effects.42

Because the O4 ligand successfully maintains the sextuple bond, we examined similar neutral tetradentate ligands by substituting two or four O atoms in O4 with NH groups; they are named O2N2 and N4 ligands, respectively; see Scheme 1 and Fig. 5A for the structures. Similar to the O4 complexes, all O2N2 and N4 complexes with the W2, Mo2, and Re2+ cores have the S0 ground state, while the Tc2+ analogues have a triplet ground state. Figure 2 show a schematic diagram of the orbital energy levels and their occupation. Because of the stronger charge transfer interaction between O4 and Tc’, the Tc-O distance is shorter than Mo-O distance by 0.48 Å. As a result, the 5s orbital is more destabilized than the 4d orbital, and the σ_{5s} becomes comparable with the δ_{nd}. For the Re’ and W isoelectronic pair, the trend similar to the Tc’-Mo pair was observed. However, their end-on O4(M2)O4 complexes both have singlet ground state because 6s orbital of the 5d transition element becomes more stable due to relativistic effects.42

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Fig. 5 (A) Structures of the bare M2 and the dinuclear complexes. The numbers are the metal-metal bond lengths in Å. (B) Potential energy curve of the W–O4 coordination in S0 state. (C) Change in orbital energies against W-O4 distance. The W–O4 distance is defined as that between W and X (the center of the four O atoms). Calculations were performed with DFT; see section S1 in ESI for computational details.
Fig. 6. The structures of the M2-side O4(M2)O4, O2N2(M2)O2N2, and N4(M2)N4 complexes.

Fig. 7 Formation energy (eq. 2) and binding energy (eqs. 3 and 4) calculated with CASPT2 method. The values in parentheses are calculated by the DFT method. The negative values of the formation energy and the binding energy correspond to the exothermicity. (A) Formation energy. (B) Binding energy, $BE_{\text{L-}(\text{M}_2)}$. (C) Binding energy, $BE_{\text{LM-ML}}$.

2.3. Thermodynamic stability of sextuply bonded complexes

The formation energy of the complexes. Thermodynamic stability is an important factor to be considered. We evaluated the formation energy of the complexes as follows.

$$\Delta E = E_{\text{opt}}[\text{L(M}_2]\text{L}] - \left[2 \cdot E[\text{M}] + 2 \cdot E_{\text{opt}}[\text{L}] \right]$$  \hspace{1cm} (2)

$E_{\text{opt}}[\text{L(M}_2]\text{L}]$, $E[\text{M}]$, and $E_{\text{opt}}[\text{L}]$ stand for the potential energies of the entire complex, the transition metal atom/cation, and the ligand at their ground-state optimized structures, respectively; see Table S6 and S7. The formations of the O4(W2)O4, O4(Mo2)O4, [O4(Re2)O4]2+, and [O4(Tc2)O4]2+ complexes from separated M and O4 are exothermic by 124.0, 95.5, 250.2, and 208.4 kcal/mol, respectively, at the CASPT2 level, and 130.5, 84.6, 234.8, and 207.4 kcal/mol, respectively, at the DFT level; see Fig. 7A. The calculated Gibbs formation energies at 298.15 K are 101.2, 52.8, 195.7, and 171.9 kcal/mol, respectively, at the DFT level. It is noteworthy that the formations of the [O4(Re2)O4]2+ and [O4(Tc2)O4]2+ complexes are significantly exothermic despite the large endothermicity in the Re3+ and Tc3+ bond formation. In addition, these dicatonic complexes exhibit formation energies larger than those of their neutral W2 and Mo2 analogous due to stronger electrostatic interaction between O4 and the cationic metal center, which will be discussed below. Similar to the O4 complexes, the calculated formation energies of the O2N2 and N4 complexes are all exothermic as shown in Fig. 7A, indicating their thermodynamic stability.

Metal-ligand and metal-metal bond energies. As described above, the formation energies of the complexes are much larger than those of the bare metal dimers. In addition, the formation energy becomes larger when stronger electron-donating ligands (O2N2 and N4) are used. Fig. 8A shows that the charges in the metal moiety, which is relevant to the donative property of the ligands, correlates well to the formation energy of the complexes. In this subsection, the reasons are analyzed by an energy decomposition. For this purpose, the binding energy between L and M2 ($BE_{\text{L-}(\text{M}_2)}$) and the metal-metal bonding energy between two LM moieties ($BE_{\text{LM-ML}}$) were evaluated with the following equations,

$$BE_{\text{L-}(\text{M}_2)} = \frac{1}{2} \left[ E_{\text{opt}}[\text{L(M}_2]\text{L}] - E_{\text{SP}}[\text{M}_2] - 2 E_{\text{SP}}[\text{L}] \right]$$  \hspace{1cm} (3)

$$BE_{\text{LM-ML}} = E_{\text{opt}}[\text{L(M}_2]\text{L}] - 2 E_{\text{SP}}[\text{LM}]$$  \hspace{1cm} (4)

where $E_{\text{opt}}[\text{L(M}_2]\text{L}]$, $E_{\text{SP}}[\text{M}_2]$, $E_{\text{SP}}[\text{LM}]$, and $E_{\text{SP}}[\text{L}]$ are potential energies of the entire complex, the M2 moiety, the LM moiety, and the ligand, respectively. The subscript, "SP", denotes a single-point calculation, in which geometries of M2, L, and LM were taken to be the same as those of the corresponding moieties of the DFT-optimized structure of L(M2)L. The ground-state energies were used for all these equations.63

As shown in Figs. 7B and 7C, both $BE_{\text{L-}(\text{M}_2)}$ and $BE_{\text{LM-ML}}$ are negative and contribute to the stabilization of the complex. In Fig. S4 in ESI, the weight of $BE_{\text{L-}(\text{M}_2)}$ and $BE_{\text{LM-ML}}$ is compared. In neutral W2 and Mo2 complexes, the contributions of $BE_{\text{L-}(\text{M}_2)}$ and $BE_{\text{LM-ML}}$
and $BE_{LM-ML}$ are comparable, while $BE_{L-\text{Mg}_2-\text{L}}$ is significantly larger than $BE_{LM-ML}$ in cationic Re$_2^{2+}$ and Tc$_2^{2+}$ complexes. The large $BE_{L-\text{Mg}_2-\text{L}}$ contribution in the cationic complexes originates from both electrostatic and orbital interactions. As shown in Fig. S5 in ESI, the positive electrostatic potential from the metal core is extending toward outside the M-M moiety. This positive region overlaps very well with the ligand lone-pair electrons. In Fig. S3 in ESI, the electron difference density map by the complex formation is compared between O$_4$(W$_2$)O$_4$ and O$(\text{Re}_2)$O$_4$. The amount of CT from the ligands to the Re$_2$ core is apparently greater than that to the W$_2$ core, which indicates that greater orbital interaction leads to larger $BE_{L-\text{Mg}_2-\text{L}}$ in the Re complex.

As shown in Fig. 7B, the amount of $BE_{L-\text{Mg}_2-\text{L}}$ becomes larger with the increase in the donative property of the ligand (O$_4$ < O$_2$N$_2$ < N$_4$). This result consistently correlates to the metal-ligand distance as shown in Table S4 in ESI; the M-L distances are in the order of O$_4$(M$_2$)O$_4$ > O$_2$N$_2$(M$_2$)O$_2$N$_2$ > N$_4$(M$_2$)N$_4$. In the O$_2$N$_2$(M$_2$)O$_2$N$_2$ complex, the M-O distance is also longer than the M-N distance, but the deviation between the M-O and M-N distances becomes smaller than those in O$_4$(M$_2$)O$_4$ and N$_4$(M$_2$)N$_4$ complexes. This trend is rationalized by the orbital interactions. The bonding orbitals between M and L are shown in Fig. S6 in ESI. Apparently, the M-L orbital mixing in the N$_4$ ligand is larger than that in the O$_2$ ligand. In Fig. S7 in ESI, lone-pair MOs and their orbital energies are summarized for the O$_4$, O$_2$N$_2$, and N$_4$ ligands. The averaged energy level of the N$_4$ lone-pair orbitals (-7.4 eV) is higher than that of the O$_4$ ligand (-10.2 eV). This feature arises from the fact that the energy of the nitrogen 2p orbital is higher than that of the oxygen 2p and closer to that of the valence d-orbitals of the metal core. As a result, the $BE_{L-\text{Mg}_2-\text{L}}$ for the N$_4$ ligand becomes larger than that for the O$_2$ ligand. The orbital interaction affects the calculated M-L interaction. As shown in Table S4 in ESI, the M-N4 distance is shorter than that of the M-O4 one. For example, the calculated W-L distance for the N$_4$, O$_2$N$_2$, and O$_4$ ligands is 2.4 Å, 2.5 Å, and 2.8 Å, respectively.

As shown in Fig. 7C, the amount of $BE_{LM-ML}$ increases with the increase in the electron population around the metal moiety. This trend correlates to the EBO for the 6-bond. For instance, EBO of N$_2$W$_2$N$_4$ complex (1.80) is larger than that for O$_2$(W$_2$)O$_4$ complex (1.52). This is because the occupation number of the $\delta_{\text{ind}}$ orbitals increases and that of the $\delta^*$ orbitals decreases. The occupation number of the two $\delta_{\text{ind}}$ orbitals are 3.79 for N$_4$(W$_2$)N$_4$ and 3.52 for O$_4$(W$_2$)O$_4$, while that for the two $\delta^*$ orbitals are 0.20 for N$_4$(W$_2$)N$_4$ and 0.47 for O$_4$(W$_2$)O$_4$; see Fig S9 in ESI. These changes in the occupation number indicate that the weight of the $\delta-\delta^*$ excited configurations decreases significantly because the $\delta-\delta^*$ orbital energy gap is increased by the N$_4$ ligand. The averaged $\delta\delta^*$ gap is 8.1 eV and 6.9 eV for N$_4$W$_2$N$_4$ and O$_4$W$_2$O$_4$, respectively; see Table S5 in ESI. This increase in the gap mainly arises from the destabilization of the $\delta^*$ orbital by 0.8 eV. The CASSCF natural orbitals for O$_4$(W$_2$)O$_4$ and N$_4$(W$_2$)N$_4$ (Fig. S9 in ESI) clearly show that the metal-ligand anti-bonding interaction in N$_4$W$_2$N$_4$ is larger than that in O$_4$(W$_2$)O$_4$. The increasing order in the $\delta-\delta^*$ orbital energy gap O$_4$ < O$_2$N$_2$ < N$_4$ arises from the stronger d-donating natures of O$_2$N$_2$ and N$_4$ than that of O$_4$, indicating the use of donating ligand is crucial. We note that, in the previous study, the role of the electrostatic effect was also pointed out for the M-M bond in R$_3$M-$M'\text{R}_3$ (M, M' = Cr, Mo, W; R = Cl, NMe$_2$), [Re$_2$Cl$_6$]$^2-$, and Os$_2$Cl$_6$ complexes by using the EDA/EDA-NOCV analysis. Because the donative ligands increase the charges on the metal moiety, the electrostatic interpretation should be a rational interpretation.

In addition, the $BE_{LM-ML}$ values of the W$_2$ and Re$_2^{2+}$ complexes are larger than those of the Mo$_2$ and Tc$_2^{2+}$ complexes in most cases; see Fig. 7C. This is attributed to the stronger $\sigma_{(n+1)s}$ bonding interaction in the W$_2$ and Re$_2^{2+}$ complexes; see EBO in Table 1. This is true because their 6s orbitals are more stable than the 5s orbitals of Mo and Tc due to relativistic effects.
quintuply bonded complex Mo₂(N²N)₂. In addition, the HOMO level of those neutral complexes is higher than that of Mo₂(N²N)₂. For example, the HOMO energy of O₄(MoO)₄, O₂(N₂)₂O₂, O₂(Re²⁺)O₂ respectively, while those for the corresponding dinuclear complexes are -101.2, -52.8 and -195.7 kcal/mol at DFT level; see Table S8 in ESI. The significant difference in the Gibbs formation energy between the mono-nuclear and dinuclear complexes mainly arises from the metal-metal bonding interaction. These results also indicate the possibility of the synthesis of the dinuclear complexes.

The thermodynamic stability of mono-nuclear complex. There is a possibility that the formation of two mono-nuclear complexes competes with that of dinuclear complex. The Gibbs formation energies are 0.6, 5.3, and -95.6 kcal/mol for O₂(W)O₂, O₂(MoO)₄, O₂(Re²⁺)O₂ respectively, while those for the corresponding dinuclear complexes are -101.2, -52.8 and -195.7 kcal/mol at DFT level; see Table S8 in ESI. The significant difference in the Gibbs formation energy between the mono-nuclear and dinuclear complexes mainly arises from the metal-metal bonding interaction. These results also indicate the possibility of the synthesis of the dinuclear complexes.

3. Conclusions

We theoretically proposed a molecular-designing strategy for realizing stable metal-metal sextuply-bonded complexes for the first time. The present coordination strategy is based on the following ideas: Stabilizing the M₂ core by the ligand coordination, conserving the six bonding orbitals in the occupied space, and suppressing the δ⁻ electron correlations.

The state-of-the-art CASPT2 and DFT calculations showed that the tetradentate electron-donating ligands, such as O₄, O₂N₂, and N₄ can enhance thermodynamic stability, keeping the Mo-Mo and W-W sextuple bonds like in the bare metal dimers. Even [N₂(Re²⁺)N₂]²⁺ and [O₂N₂(Re²⁺)O₂N₂]²⁺ could have a Re-Re sextuple bond with the S₂ ground state. All these sextuply bonded complexes have a large formation energy, indicating their thermodynamic stability and possibility of being synthesized. The DFT results were consistent to those from the CASPT2/CASSCF calculations, which indicates that DFT method is applicable to the investigation of the metal-metal multiple bond that can be described by a single-reference electronic structure method. We note that verification with multi-reference methods should improve the reliability of the conclusion. We also note that only multi-reference methods are applicable to the metal-metal bond with a quasi-degenerate electronic structure (see ref. 47 for the U₂ case).

The reason of the stability has been analyzed in detail. The stabilization energy arises from both metal-metal binding and metal-ligand binding. As the donative property of the ligand increases, electron population in the δ⁻ orbitals is suppressed because the strong metal-ligand interaction by donating ligand destabilizes the δ⁻ orbital energy. The N₄ ligand can make M-L interaction stronger than does the O₄ ligand because the energy levels of the lone-pair electrons of the N₄ ligand are higher than those of the O₄ ligand and closer to those of the valence d-orbitals.

As mentioned before, quintuply bonded Mo₂(N²N)₂ was synthesized in THF solution. We hope that a series of dinuclear complexes proposed in this study are synthesized not in far future.

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Notes and references


58. The ground state of the LM fragment was in septet spin multiplicity.

