Supporting information

A Coordination Strategy to Realize a Sextuply Bonded Complex

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Contents

S1. Computational method

In geometry optimization, the ωB97XD functional[1] implemented in Gaussian 09 program package is selected. The basis set with ECP proposed by Stuggart-Dresden-Bonn group[3] is used for transition metals, and cc-pVDZ C, N, O, and H. The frequency calculations show that the all the geometry do not have imaginary frequency except the $O_4(Mo_2)O_4$. The $O_4(Mo_2)O_4$ has two tiny imaginary frequencies ($20i$ cm^{-1} and $21i$ cm^{-1}) and they are very difficult to remove.

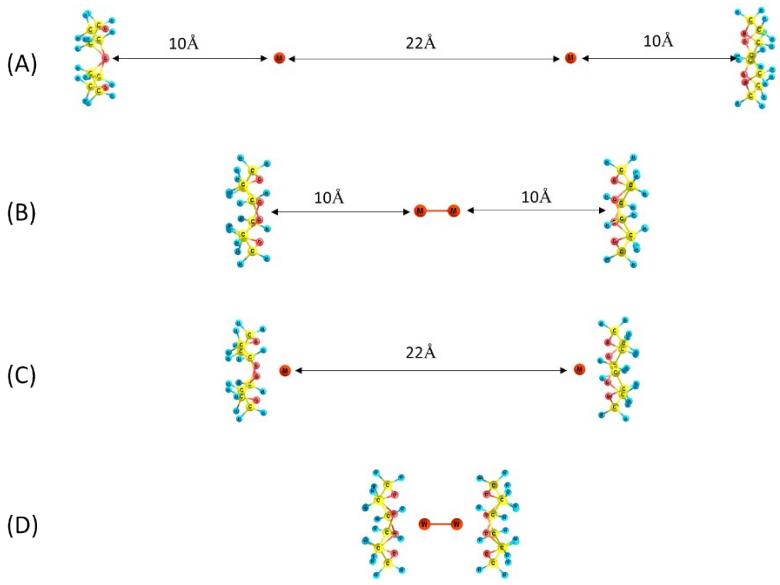
For the calculation of formation energy and binding energy, Multi-State (MS)-CASPT2/CASSCF method was used. The basis set for transition metal, N, and O atoms are the same as that used in geometry optimization by DFT method, while the cc-pVDZ basis set without d-functions are used for C atoms, and cc-pVDZ basis set without p-functions are used for H atoms in order to reduce the cost of MS-CASPT2/CASSCF calculation.

In the CASSCF calculation, the active space includes **10** n*d*-orbitals and 2 (n+1)s orbitals of two transition atoms. The imaginary shift of 0.1 is used MS-CASPT2 calculation for eliminating the intruder states. The MS-CASPT2 and CASSCF calculations are performed by MOLCAS 7.8 program.[4]

For the calculation of formation energy and binding energy by MS-CASPT2/CASSCF method, the supermolecule model are used to reduce size-extensivity error. We also expect that the supermolecule model also reduce a part of the basis set superposition error (BSSE); for the structures, see Figure below. The atomic coordinates for calculating the formation energy were optimized for each LM_2L, M, and L at their ground state by DFT(ωB97XD). For the binding energy, the coordinates of the LM_2L complex were used for the supermolecule models, and the L-M and M-M distances were just stretched. The supermolecule model (A) is used to calculate $\{2 \cdot E[M] + 2 \cdot E_{opt}[L]\}$ term in Eq. 1 (see main text). Model (B) is used to calculate the $\{E[M_2] + 2 \cdot E_{SP}[L]\}$ term in Eq. 2 (see main text). Model (C) is used to calculated the $\{2\, E_{SP}[LM]\}$ in Eq. 3 (see main text). The binding energy between L and M ($^{BE}{}_{L-M}$) is calculated by using the energy difference between model (A) and model (C). The ground-states energies of the models were used for evaluating the formation and binding energies; the high-spin state (S=6) energies of models (A) and (C) and the singlet-state of the complex (model D) are used for calculating the formation energy and $^{BE}{}_{LM-ML}$ at the CASPT2/CASSCF(14e,13o) level. In the calculation of $^{BE}{}_{L-(M_2)-L}$, the singlet-state energies of complex (D) and model (B) are used to calculate the $^{BE}{}_{L-(M_2)-L}$

at the CASPT2/CASSCF(12e,12o) level. In the calculation of bonding energies, the geometries of ML, L, and M_2 moieties are the same as that in the complex.

We did not do the EDA calculation for two reasons. The first one is that the bonding nature of the present case was interpreted as shown in the manuscript. The bonding nature of metal-metal multiple bond in $Re_2Cl_8^{2-}$.and Os_2Cl_8 is well understood via EDA method by Frenking et al.[5] The second reason comes from the computational method. As Frenking pointed out if the dispersion interaction is part of the DFT functional, the EDA results will have some difference from that calculated by usual DFT functional with dispersion interaction suggested by Grimme.[6] Because the ωB97XD functional that is used in this work includes the dispersion interaction implicitly, we are afraid that the discussion of EDA becomes complicate if more complicated DFT functionals are used.



1 Chai, J.-D. & Head-Gordon, M., *Phys. Chem. Chem. Phys.* 10, 6615-6620 (2008).

2 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,

V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

3 D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* 77, 123-141, **1990**

4 F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-Å Malmqvist, P. Neogrády, T.B. Pedersen, M. Pitonak, M. Reiher, B.O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, *J. Comput. Chem.*, 31, 224, **2010**

5 Krapp, A., Lein, M. & Frenking, G. The strength of the σ-, π- and δ-bonds in Re2Cl 8 2−. *Theor. Chem. Acc.* 120, 313-320 (**2008**).

6 Hopffgarten, M. v. & Frenking, G. Energy decomposition analysis. Wiley Interdisciplinary Reviews: Computational Molecular Science 2, 43-62 (**2012**).

Table S1. The Mo-Mo and W-W bond lengths in Å calculated by Different method[a].

	Mo-Mo	W-W
A (B3PW91)	1.956	2.038
B(wB97XD)	1.940	2.023
C(M06)	1.955	2.041
D(B3LYP)	1.965	2.048
E(M062X)	1.927	2.010
F(M06L)	1.977	2.052
CCSD	**1.932[b]**	**2.020[b]**
Expt.	**1.929[c]/1.940[d]**	**-**

a: The effective core potentials and basis set by Stuttgart-Dresden-Bonn group[1] were used for Mo and W.

b: The bond length calculated by CCSD is from ref. 2.

c. Ref. 3

d. Ref. 4

Reference:

1. Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H., *J. Chem. Phys.* 1987, **86**, 866-872.

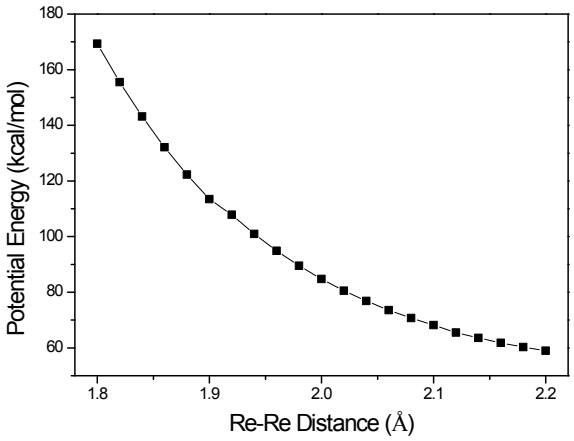
2. Wang Y-L, Hu H-S, Li, W-L, Wei F., Li J. J. Am. Chem. Soc. 2016 138, 1126-1129.

3 D. Kraus, M. Lorenz and V. E. Bondybey PhysChemComm, 2001,4, 44-48 DOI: 10.1039/B104063B

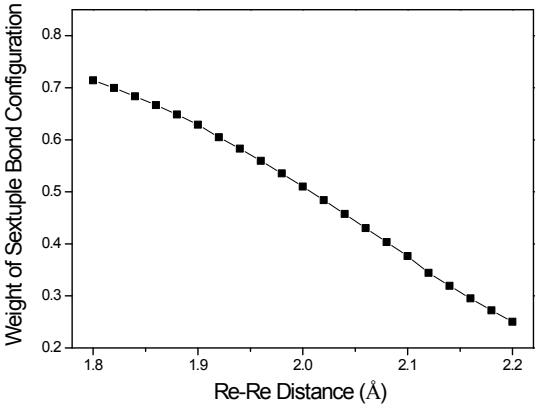
4. J. B. Hopkins1, P. R. R. Langridge‐Smith1, M. D. Morse1 and R. E. Smalley1 J. Chem. Phys. 78, 1627 (1983); http://dx.doi.org/10.1063/1.444961

S2. The sextuple bonded state of Re_2^{2+}

The optimized Re-Re distance in the close-shell singlet state, which corresponds to the sextuple boned state, is 2.005 Å by DFT method. This structure is, however, meta-stable, and the formation energy is endothermic by 96.6 kcal/mol. This endothermicity is consistent with the formation energy of 84.8 kcal/mol calculated by CASPT2/CASSCF, where the reference energy for DFT is ground state of two Re^+ ion and for CASPT2/CASSCF is the energy at Re-Re distance of 10 Å. CASPT2 calculation shows that this state is a dissociative state where the potential energy decreases and the weight of $\sigma_{(n+1)s}^{2}\sigma_{nd}^{2}\pi_{nd}^{4}\delta_{nd}^{4}\sigma_{(n+1)s}^{*0}\sigma_{nd}^{*0}\pi_{nd}^{*0}\delta_{nd}^{*0}$ decrease with increasing of Re-Re distance. These results indicate that a bare diatomic molecule Re_2^{2+} with the sextuple bonded is difficult to be fromed.



(A)



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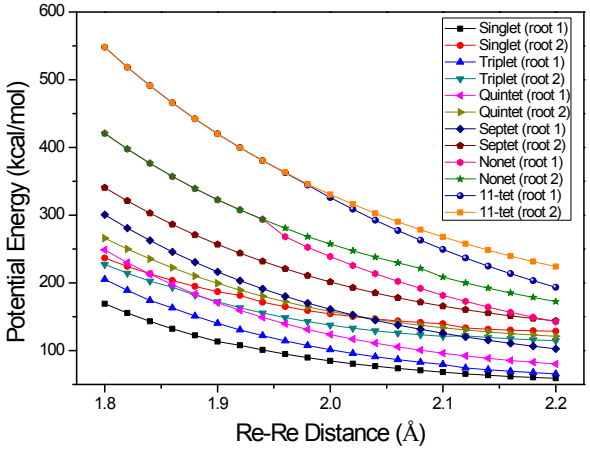


(C)

Figure S1. The potential curves of Re_2^{2+} at sextuple bonded state (A), the weight of main configuration (B), and the potential energy surfaces of different spin states by CASPT2/CASSCF.

S3. Twisted geometry of end-on $O_4(M_2)O_4$

In the geometry of end-on $O_4(M_2)O_4$ (M=W, Mo, Re^+, Tc^+) in the ground state, the two O_4 ligands shows a twisted structure where they can not overlap each other from side view; see Figure S2. Though the initial geometry is adjusted into a face-to-face one, geometry optimization finally generates the twisted one.

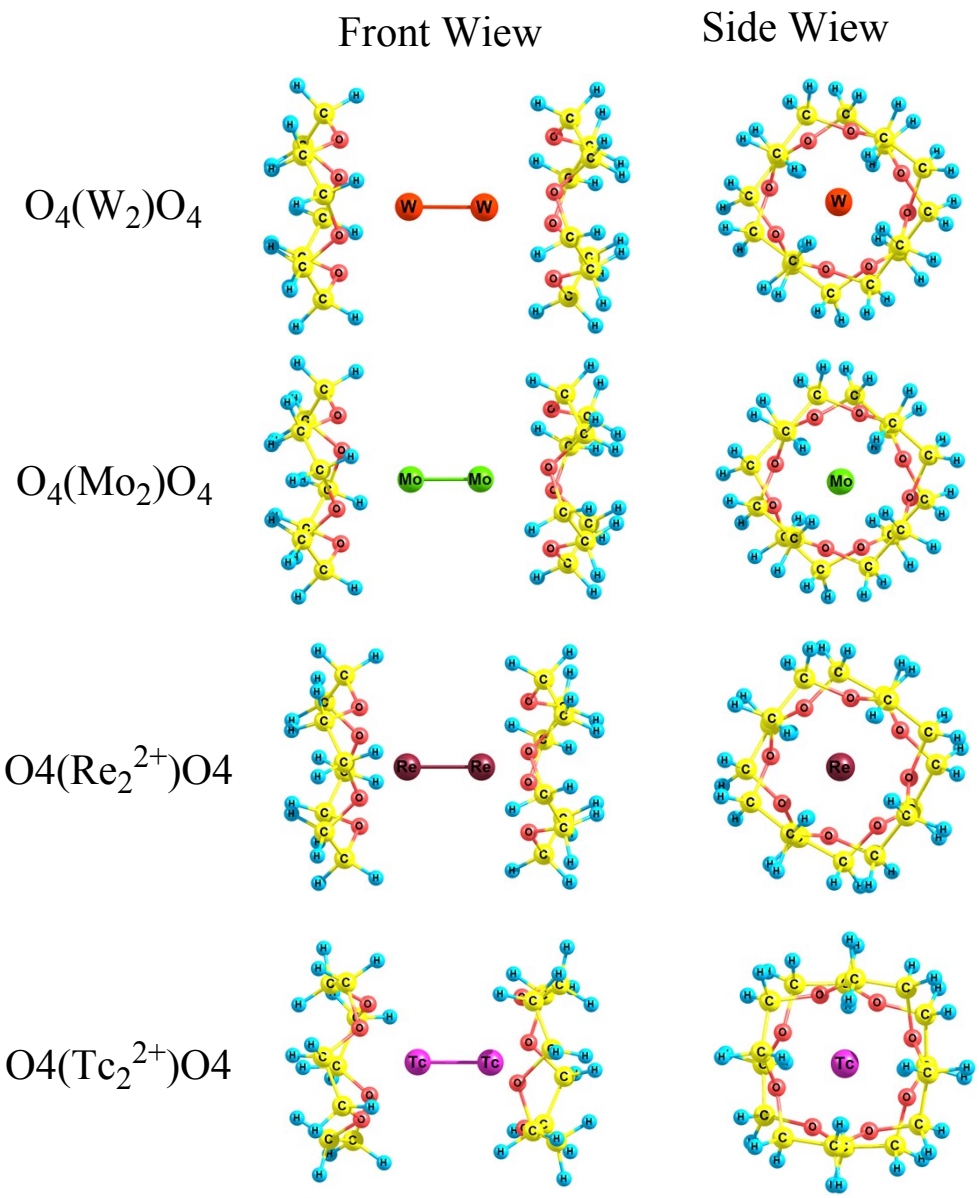


Figure S2. Geometry of end-on $O_4(M_2)O_4$ complexes.

Table S2 (A). Relative energy in kcal/mol of different spin states of end-on complex calculated by DFT.

Complex	ΔE(singlet)	ΔE(Triplet)	ΔE(Quintet)	ΔE(Septet)
O_4(W-W)O_4	0.0	9.1	17.8	9.1
O_4(Mo-Mo)O_4	0.0	22.0	30.7	50.4
$[O_4$(Re-Re)$O_4]^{2+}$	0.0	20.3	19.6	24.9
$[O_4$(Tc-Tc)$O_4]^{2+}$	0.0	-8.0	6.3	10.5
O_2N_2(W-W)O_2N_2	0.0	16.2	9.4	23.9
O_2N_2(Mo-Mo)O_2N_2	0.0	16.6	31.9	26.5
$[O_2N_2$(Re-Re)$O_2N_2]^{2+}$	0.0	10.0	32.9	36.7
$[O_2N_2$(Tc-Tc)$O_2N_2]^{2+}$	0.0	-10.3	9.5	14.0
N_4(W-W)N_4	0.0	26.4	36.3	51.3
N_4(Mo-Mo)N_4	0.0	19.5	30.1	49.0
$[N_4$(Re-Re)$N_4]^{2+}$	0.0	5.8	46.3	70.5
$[N_4$(Tc-Tc)$N_4]^{2+}$	0.0	-21.9	6.0	9.6

Table S2 (B). The weight of the S_0 configuration, $\sigma_{(n+1)s}^{2}\sigma_{nd}^{2}\pi_{nd}^{4}\delta_{nd}^{4}\sigma_{(n+1)s}^{*0}\sigma_{nd}^{*0}\pi_{nd}^{*0}\delta_{nd}^{*0}$, in the sextuple bonded state.

Complex	weight (%)
O_4(W-W)O_4	66.5
O_4(Mo-Mo)O_4	64.5
$[O_4$(Re-Re)$O_4]^{2+}$	36.9
O_2N_2(W-W)O_2N_2	58.5
O_2N_2(Mo-Mo)O_2N_2	49.3
$[O_2N_2$(Re-Re)$O_2N_2]^{2+}$	61.1
N_4(W-W)N_4	79.0
N_4(Mo-Mo)N_4	66.5
$[N_4$(Re-Re)$N_4]^{2+}$	81.7

S4. Charge transfer from O_4 ligands to M_2.

The charge transfer (CT) between ligand and M_2 moiety is an important factor to stabilize the total system. When O_4 ligands coorddinate with W_2, the electron density on O_4 has a little change. However, in the formation of $[O_4(Re_2)O_4]^{2+}$, the electron density on O_4 ligand decreases significantly; see Figures S3. These results are consistent with the Mulliken charge on the metal. Ater coordination, the Mulliken charge on W and Re decreases by 0.46 and 0.86, respectively. Based on the difference density and Mulliken charge, we can draw a conclusion that CT between O_4 and Re_2^{2+} is stronger than that between O_4 and W_2. And this is one of the reasons for the larger formation energy of cationic complexes. In addition, the distance between O_4 and Re^+/Tc^+ is much shorter than that between O_4 and W/Mo, indicating stronger interaction between O_4 and cationic ions.

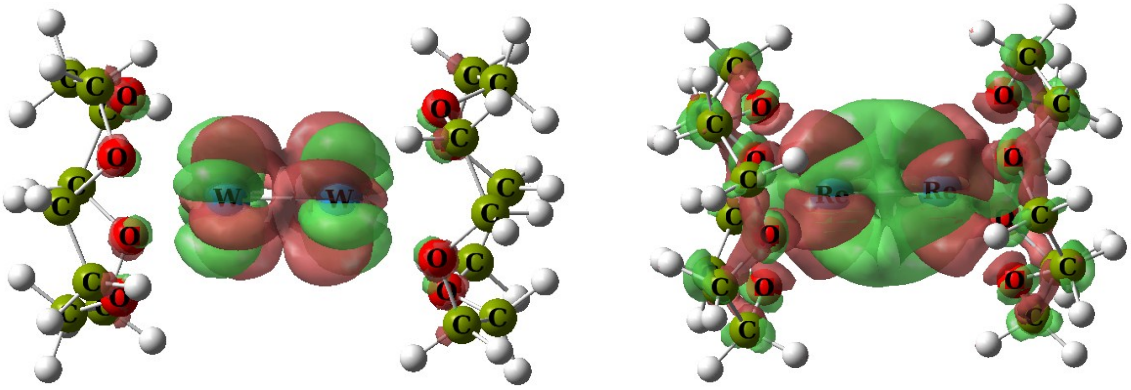


Figure S3. The differene density of $O_4(W_2)O_4$ and $[O_4(Re_2)O_4]^{2+}$. The reference of density is the total density of two O_4 ligands and M_2 moiety (M = W and Re^+). The iso-value of difference density is 0.003.

S5. The side-on complexes

The dinuclear moiety can is sandwiched by two ligands via side-on mode; see Figure 6. In side-on complexes, each metal still coordinate with four atoms on the ligands. However, in all these complexes, none of them has sextuple bonded ground state. The side-on $O_4(M_2)O_4$ with core of W_2, Mo_2, and Re_2^{2+} have quintet ground state, while side-on $O_4(Tc_2^{2+})O_4$ has singlet ground state and low-lying triplet state. All $O_2N_2(M_2)O_2N_2$ and $N_4(M_2)N_4$ complexes have triplet ground state. In potential energy, the side-on complex is more unstable than corresponding end-on structure by at least 10.0 kcal/mol; see Table S3.

Table S3. Energy of different spin states of the M_2-side complexes relative to the ground state of the M_2-end complex[a] calculated by DFT. Units are in kcal/mol.

Complex	ΔE(singlet)	ΔE(Triplet)	ΔE(Quintet)	ΔE(Septet)
$O_4(W\text{-}W)O_4$	53.2	52.5	36.5	63.9
$O_4(Mo\text{-}Mo)O_4$	48.5	46.3	37.4	53.8
$[O_4(Re\text{-}Re)O_4]^{2+}$	58.9	58.3	54.5	62.9
$[O_4(Tc\text{-}Tc)O_4]^{2+}$	5.7	17.2	30.6	33.1
$O_2N_2(W\text{-}W)O_2N_2$	37.2	16.2	61.4	76.5
$O_2N_2(Mo\text{-}Mo)O_2N_2$	28.7	27.5	33.1	59.9
$[O_2N_2(Re\text{-}Re)O_2N_2]^{2+}$	44.3	10.0	54.1	89.2
$[O_2N_2(Tc\text{-}Tc)O_2N_2]^{2+}$	25.7	12.2	28.4	30.5
$N_4(W\text{-}W)N_4$	34.2	27.6	37.6	68.8
$N_4(Mo\text{-}Mo)N_4$	37.3	21.1	43.9	71.7
$[N_4(Re\text{-}Re)N_4]^{2+}$	38.1	31.9	67.1	78.5
$[N_4(Tc\text{-}Tc)N_4]^{2+}$	22.4	12.6	29.9	42.0

a. ΔE = E(spin state, end-on) – E (ground state, side-on), unit in kcal/mol.

Table S4. The metal-metal (R_{M-M}) and averaged metal-ligand (R_{M-L}) distances [a] in end-on complexes. [b]

	M_2	$O_4(M_2)O_4$		$O_2N_2(M_2)O_2N_2$			$N_4(M_2)N_4$	
	R_{M-M}	R_{M-M}	R_{M-O}	R_{M-M}	R_{M-O}	R_{M-N}	R_{M-L}[c]	R_{M-M}	R_{M-N}
W	2.024	2.093	2.800	2.196	2.550	2.431	2.491	2.275	2.354
Mo	1.940	1.996	2.861	2.086	2.555	2.438	2.496	2.147	2.375
Re^+	2.005	2.122	2.346	2.153	2.354	2.290	2.322	2.187	2.311
Tc^+	1.968	2.013	2.381	2.070	2.404	2.296	2.349	2.226	2.249

a: R_{M-L} is the averaged distance between metal and coordinating atoms (O or N atoms).

b: Unit of distances is Å.

c: The M-O and M-N distances are averaged.

Table S5. The orbital energies (eV) in the end-on complexes calculated by DFT.

	σ_{nd}	$\sigma_{(n+1)s}$	π_{nd}	π_{nd}	δ_{nd}	δ_{nd}	δ_{nd}^{*}	δ_{nd}^{*}	π_{nd}^{*}	π_{nd}^{*}	σ_{nd}^{*}
O_4(W-W)O_4	-4.60	-4.07	-4.89	-4.89	-3.09	-3.08	3.79	3.81	4.91	4.91	4.59
O_4(Mo-Mo)O_4	-5.69	-3.19	-6.00	-6.00	-3.98	-3.96	3.10	3.11	4.52	4.52	4.59
$[O_4(Re\text{-}Re)O_4]^{2+}$	-14.81	-11.64	-14.11	-14.11	-13.06	-13.06	-5.13	-5.10	-3.45	-3.45	-5.14
$[O_4(Tc\text{-}Tc)O_4]^{2+}$	-15.13	-11.18	-14.23	-14.23	-13.70	-12.76	-12.98	-4.49	-4.49	-4.07	-5.03
O_2N_2(W-W)O_2N_2	-4.45	-3.26	-4.24	-4.09	-3.02	-2.97	4.23	4.45	6.84	6.28	3.93
O_2N_2(Mo-Mo)O_2N_2	-5.40	-2.50	-5.06	-5.30	-3.81	-3.84	3.56	3.63	5.56	5.52	3.93
$[O_2N_2(Re\text{-}Re)O_2N_2]^{2+}$	-14.38	-10.81	-13.36	-13.27	-12.35	-12.29	-4.14	-4.74	-2.89	-2.59	-4.78
$[O_2N_2(Tc\text{-}Tc)O_2N_2]^{2+}$	-14.02	-11.04	-13.90	-13.91	-12.24	-12.94	-11.17	-4.68	-4.68	-3.44	-4.67
N_4(W-W)N_4	-4.80	-3.10	-4.14	-4.14	-3.32	-3.31	4.75	4.77	6.19	6.19	3.63
N_4(Mo-Mo)N_4	-5.57	-2.70	-5.05	-5.05	-4.01	-3.99	4.05	4.14	5.48	5.48	3.63
$[N_4(Re\text{-}Re)N_4]^{2+}$	-14.29	-10.22	-12.85	-12.85	-12.07	-12.04	-3.51	-3.47	-2.45	-2.45	-4.80
$[N_4(Tc\text{-}Tc)N_4]^{2+}$	-14.85	-9.67	-12.84	-12.84	-12.38	-12.35	-3.57	-3.47	-3.47	-3.25	-10.57

Table S6. The relative energies (kcal/mol) of different spin states of M calculated by DFT.

	Septet	Quintet	Triplet	Singlet
W	0.0	-0.5	32.0	89.5
Mo	0.0	56.4	116.9	97.1
Re^+	0.0	46.1	116.9	122.9
Tc^+	0.0	7.8	47.4	62.2

Table S7. The relative energies (kcal/mol) of different spin states of ML moiety[a] in the complexes calculated by DFT.

M	L	Septet	Quintet	Triplet	Singlet
W	O_4	0.0	2.8	26.3	38.8
Mo	O_4	0.0	50.7	57.5	99.6
Re^+	O_4	0.0	19.9	27.2	51.6
Tc^+	O_4	0.0	3.4	11.9	41.9
W	O_2N_2	0.0	3.8	13.9	19.1
Mo	O_2N_2	0.0	21.8	32.5	57.2
Re^+	O_2N_2	0.0	-1.0	7.6	32.1
Tc^+	O_2N_2	0.0	-12.3	6.8	48.0
W	N_4	0.0	-8.8	26.6	-2.3
Mo	N_4	0.0	12.1	25.2	36.8
Re^+	N_4	0.0	-5.9	-21.8	4.7
Tc^+	N_4	0.0	-14.0	-32.4	75.3

a.Since two ML moieties have little difference in geometry and energy, the averaged energy is shown in the table.

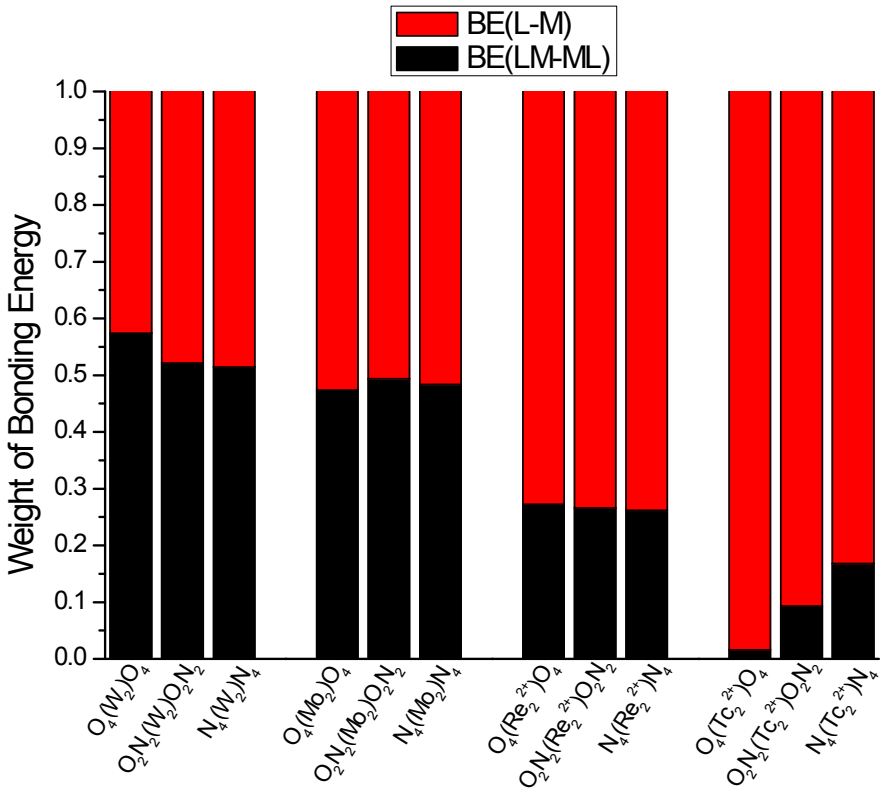


Figure S4. The contribution of $BE_{L\text{-}M}$ and $BE_{LM\text{-}ML}$ to formation energy.

Table S8A. The energy[a] of different spin state of mono-nuclear complex $O_4(M)O_4$ calculated by DFT. (unit: kcal/mol).

M	Septet	Quintet	Triplet	Singlet
W	-19.1	-24.4	8.9	57.0
Mo	-14.0	-9.6	9.6	21.8
Re^+	-124.9	-89.1	-116.3	-125.9

a: the reference is the total energy of two O_4 ligands and one M atom/cation.

Table S8B. The formation energy and formation free energy of mono-nuclear and dinuclear W complex with O_4 ligand calculated by DFT (unit: kcal/mol) .

M	Formation Energy		Formation Free Energy	
	$O_4(M)O_4$	$O_4(M_2)O_4$	$O_4(M)O_4$	$O_4(M_2)O_4$
W	-24.4	-130.5	0.6	-101.2
Mo	-14.0	-84.6	5.3	-52.8
Re^+	-125.9	-234.8	-95.6	-195.7

Table S9. The energies (eV) of the HOMO and LUMO

	HOMO	LUMO	ΔHOMO-LUMO
$O_4(W\text{-}W)O_4$	-3.08	1.18	4.26
$O_4(Mo\text{-}Mo)O_4$	-3.19	1.13	4.32
$[O_4(Re\text{-}Re)O_4]^{2+}$	-11.64	-5.14	6.50
$[O_4(Tc\text{-}Tc)O_4]^{2+}$	-10.67	-5.06	5.61
$O_2N_2(W\text{-}W)O_2N_2$	-2.97	1.13	4.10
$O_2N_2(Mo\text{-}Mo)O_2N_2$	-2.50	1.05	3.55
$[O_2N_2(Re\text{-}Re)O_2N_2]^{2+}$	-10.81	-4.78	6.03
$[O_2N_2(Tc\text{-}Tc)O_2N_2]^{2+}$	-10.63	-4.80	5.83
$N_4(W\text{-}W)N_4$	-3.10	1.13	4.23
$N_4(Mo\text{-}Mo)N_4$	-2.51	1.03	3.54
$[N_4(Re\text{-}Re)N_4]^{2+}$	-10.34	-4.42	14.76
$[N_4(Tc\text{-}Tc)N_4]^{2+}$	-9.63	-5.34	4.29

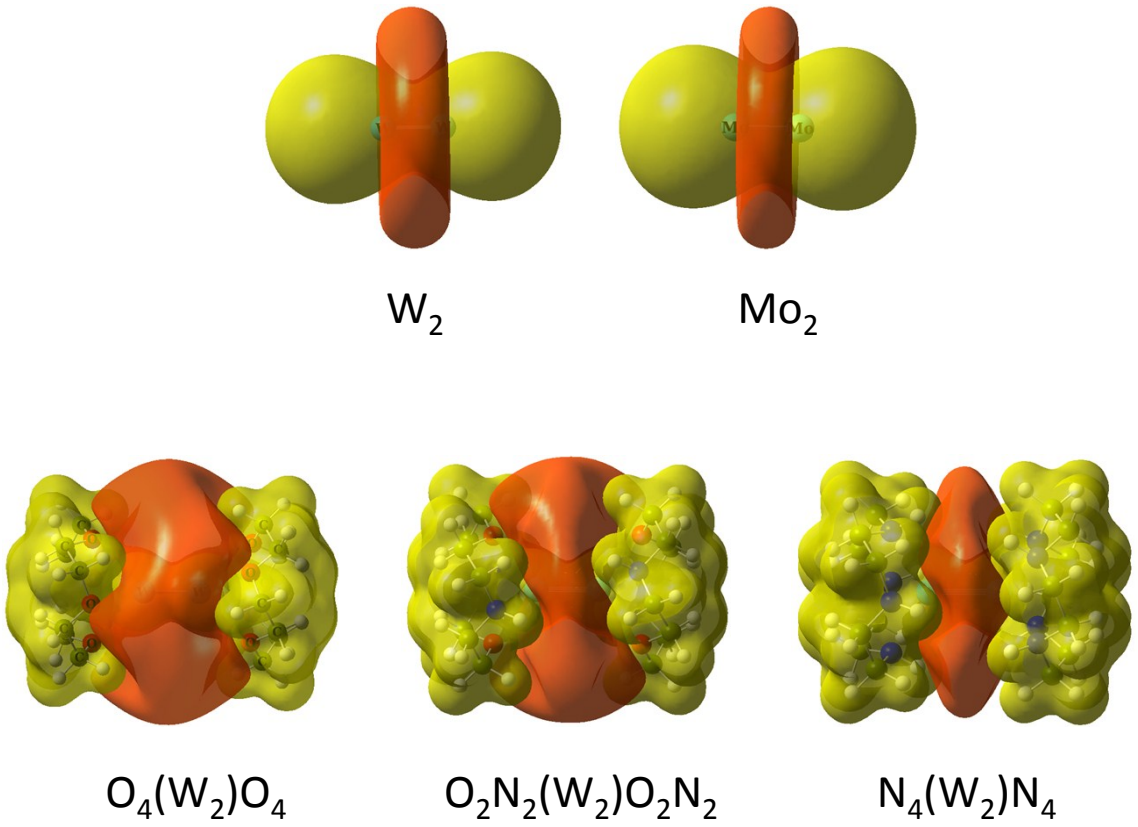
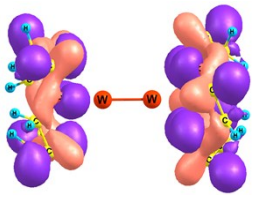
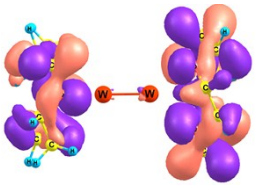
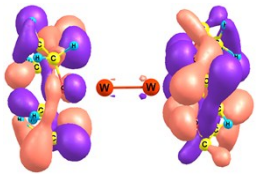


Figure S5. The electrostatic potential surface of W_2, Mo_2, and W_2 complexes. (isovalue=0.03) The orange and yellow regions show negative and positive electrostatic potential, respectively.

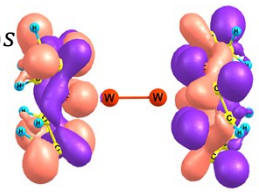
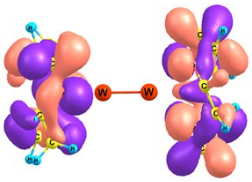
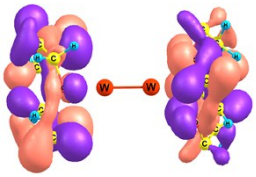
S6. Some Occupied Molecular Orbitals with the Ligand-Metal bonding characters

(a) **$O_4(W_2)O_4$**

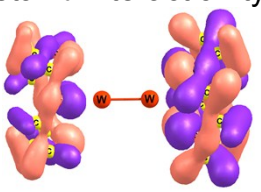
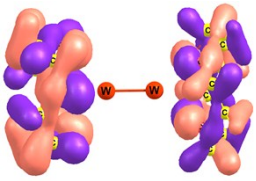
Metal-metal σ and π bonding interaction type

$\sigma_{(n+1)s}$  π_{nd}  π_{nd} 

Metal-metal σ and π anti-bonding interaction type

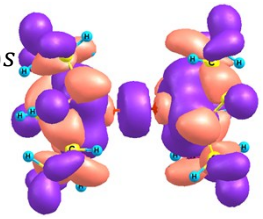
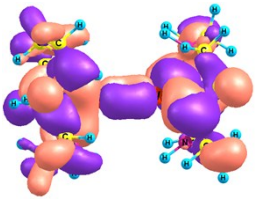
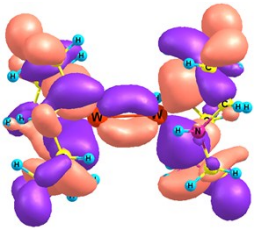
$\sigma^*_{(n+1)s}$  π^*_{nd}  π^*_{nd} 

Metal-metal δ interaction type

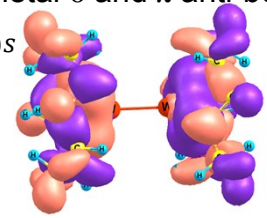
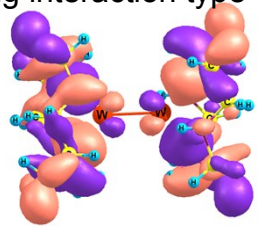
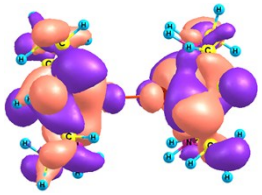
d_δ  d_δ 

(b) **$N_4(W_2)N_4$**

Metal-metal σ and π bonding interaction type

$\sigma_{(n+1)s}$  π_{nd}  π_{nd} 

Metal-metal σ and π anti-bonding interaction type

$\sigma^*_{(n+1)s}$  π^*_{nd}  π^*_{nd} 

Metal-metal δ interaction type

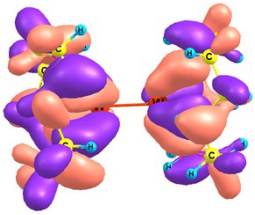
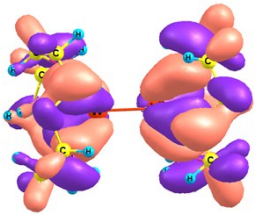
d_δ  d_δ 

Figure S6 Some occupied Kohn-Sham MOs of the tungsten complexes with the O_4 and N_4 ligands. The MOs represent lone of pair orbitals of O_4 and N_4 ligands which imply character of the interaction between tungsten and the ligands. The metal n*d* and (n+1)*s* contributions in $\mathbf{N_4(W_2)N_4}$ is much larger than those in $\mathbf{O_4(W_2)O_4}$. The isosurface value of 0.03 was used for the drawing.

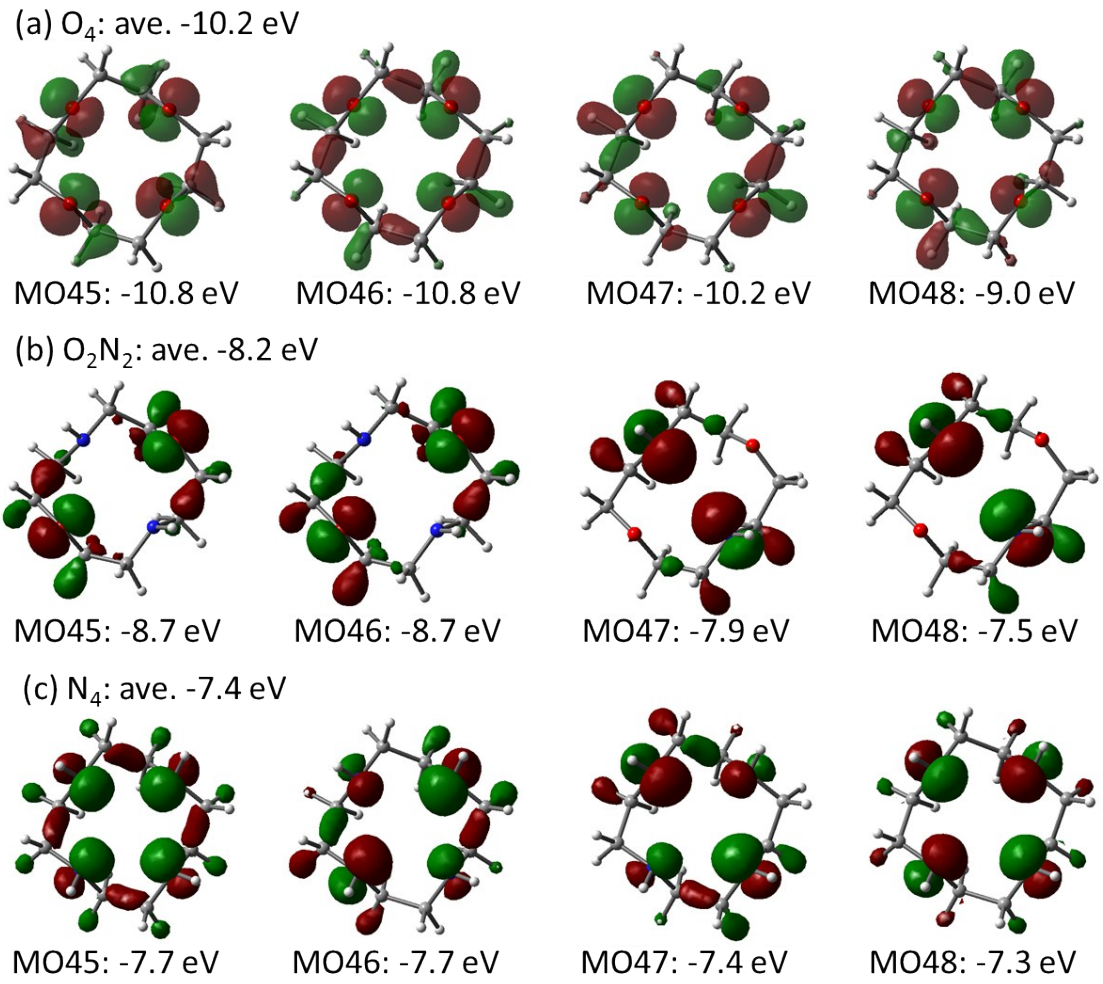


Fig. S7 Energy levels of the lone-pair orbitals in (a) O_4, (b) O_2N_2, and (c) N_4 ligands. The blue and red balls represent the N and O atoms, respectively. Calculations were performed at the ωB97XD/6-31G* level.

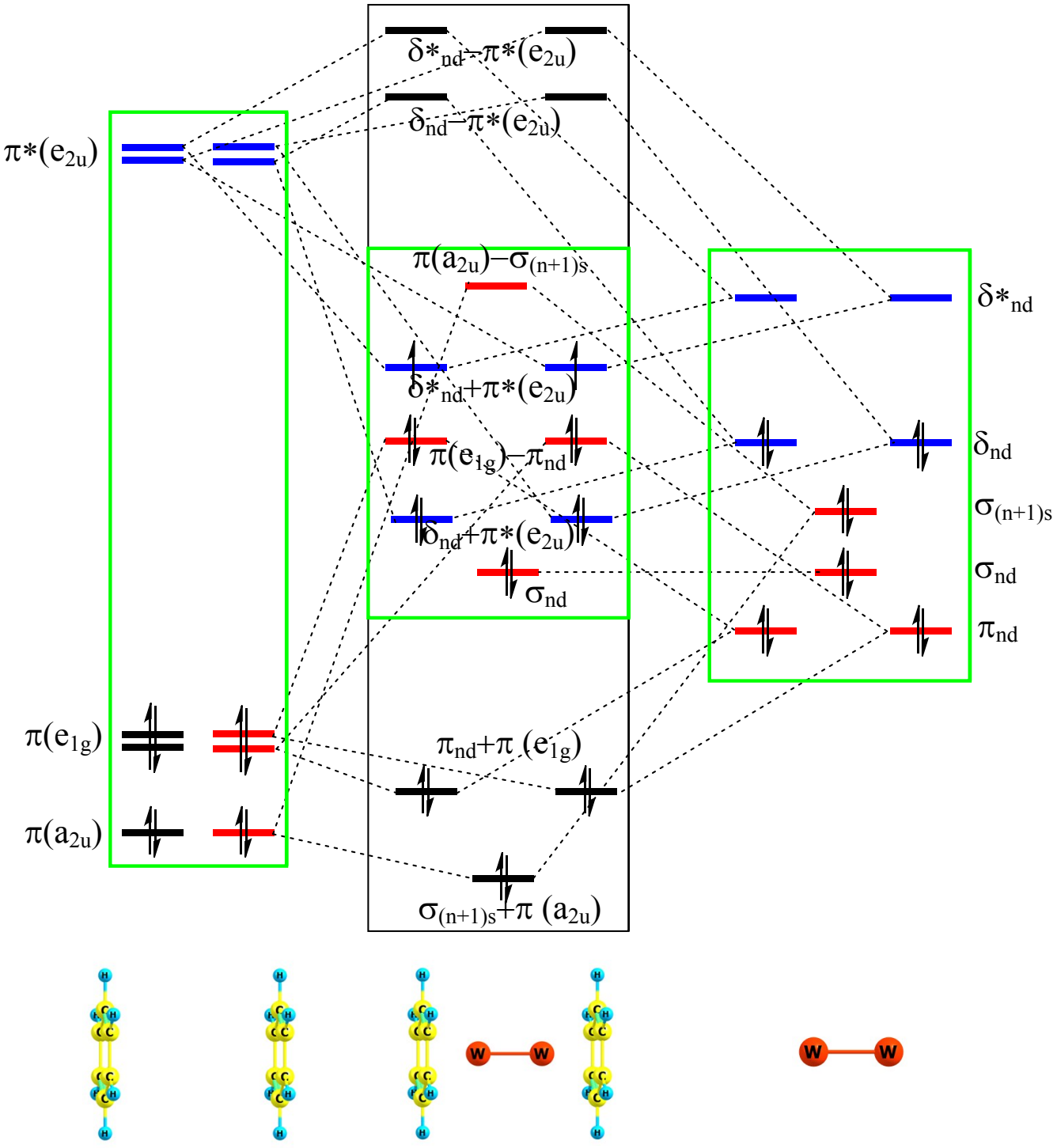


Figure S8 (A) The orbital interaction between benzene moiety and W_2.

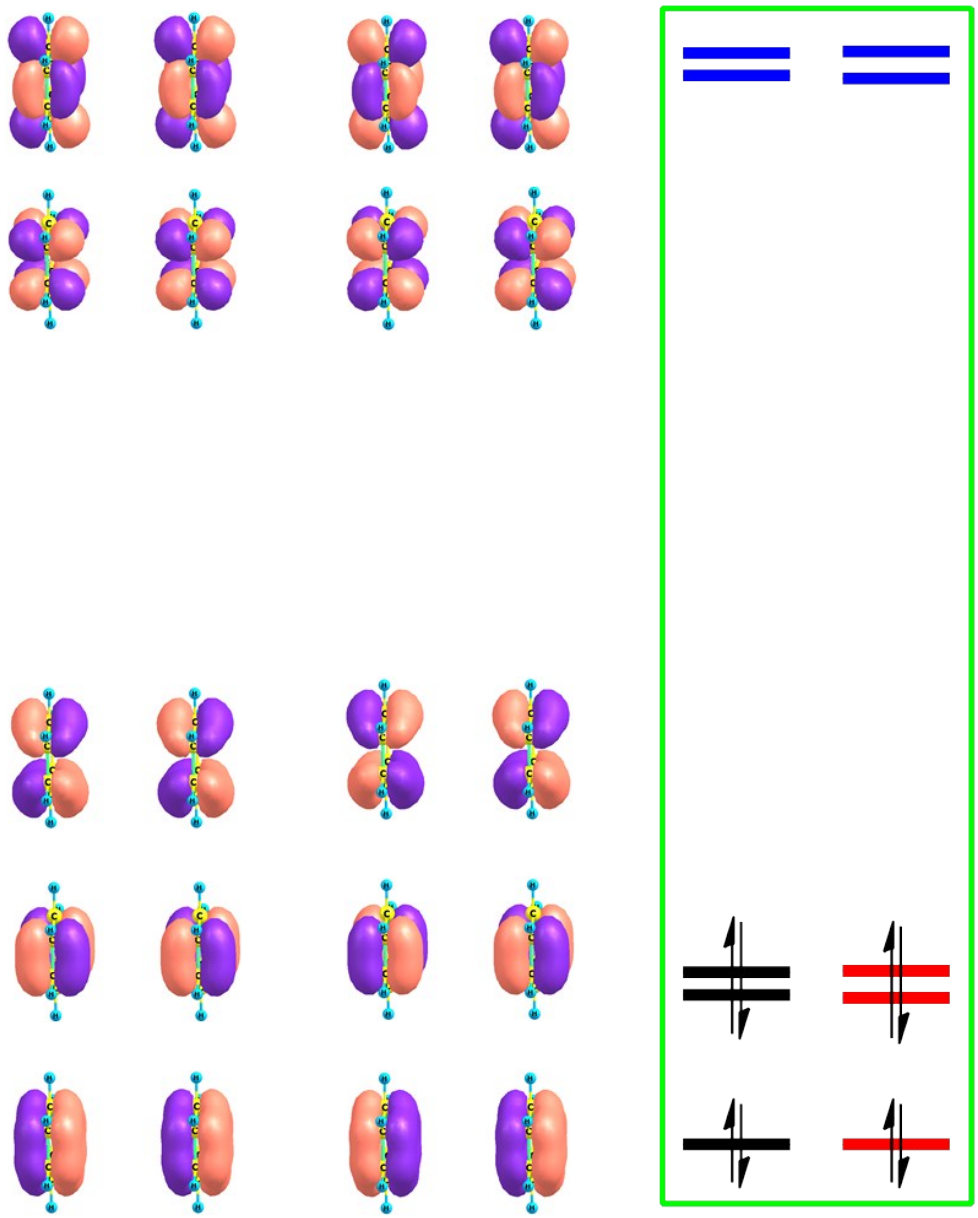


Figure S8 (B) The MOs of two benzenes moiety

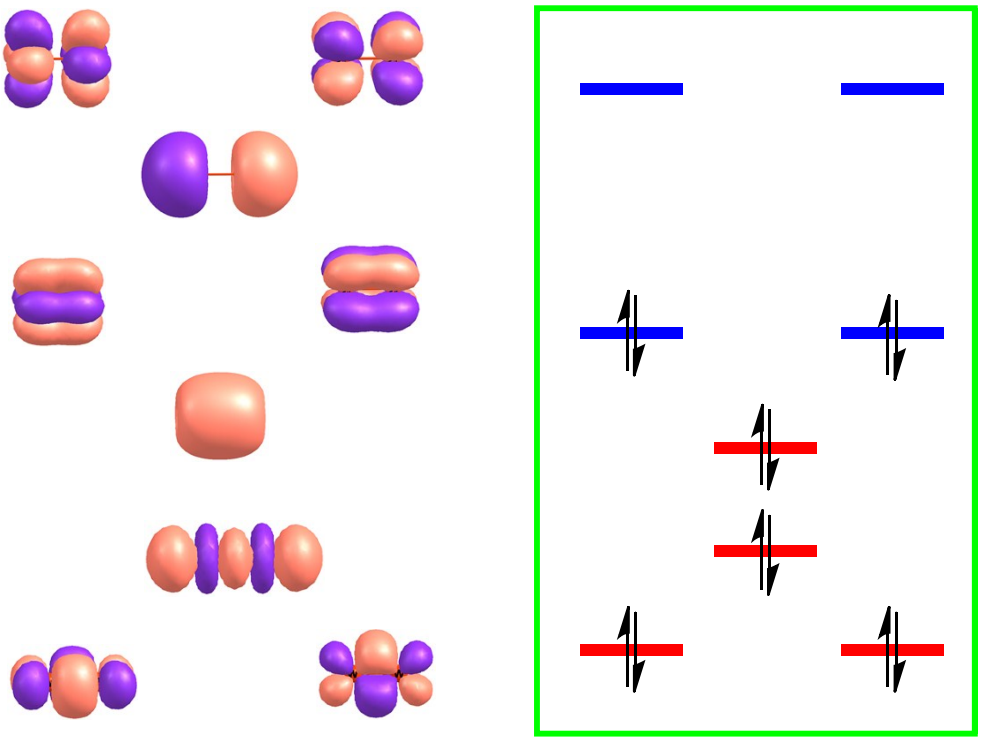


Figure S8 (C) The MOs of M_2.

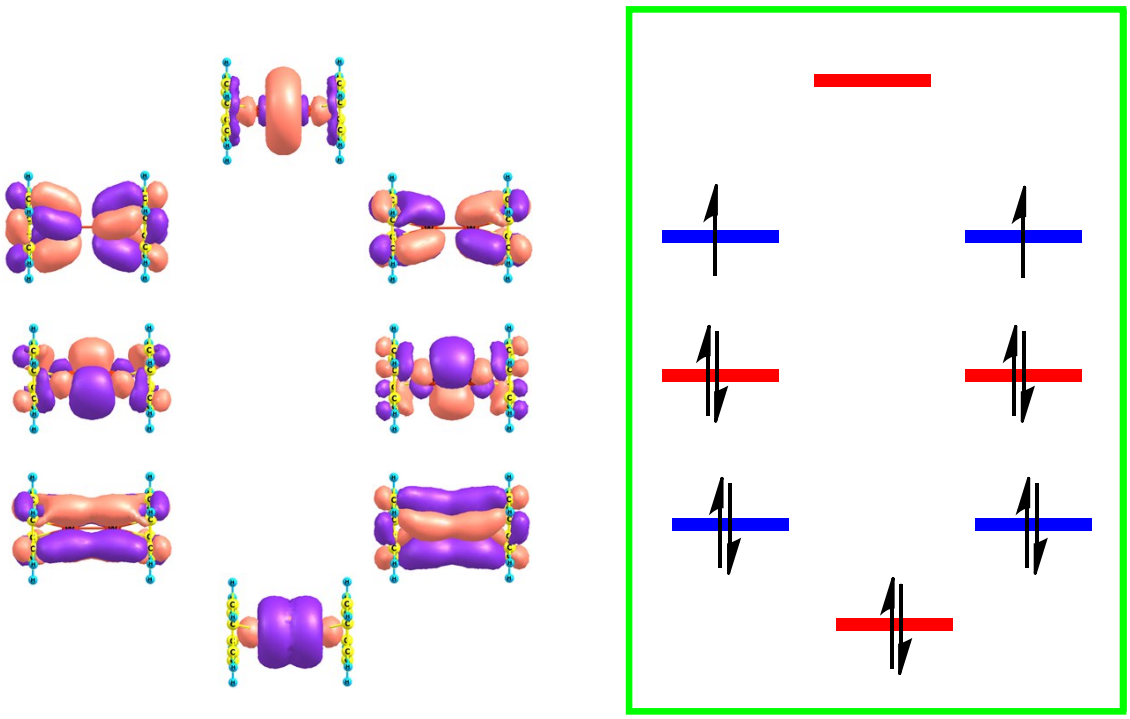
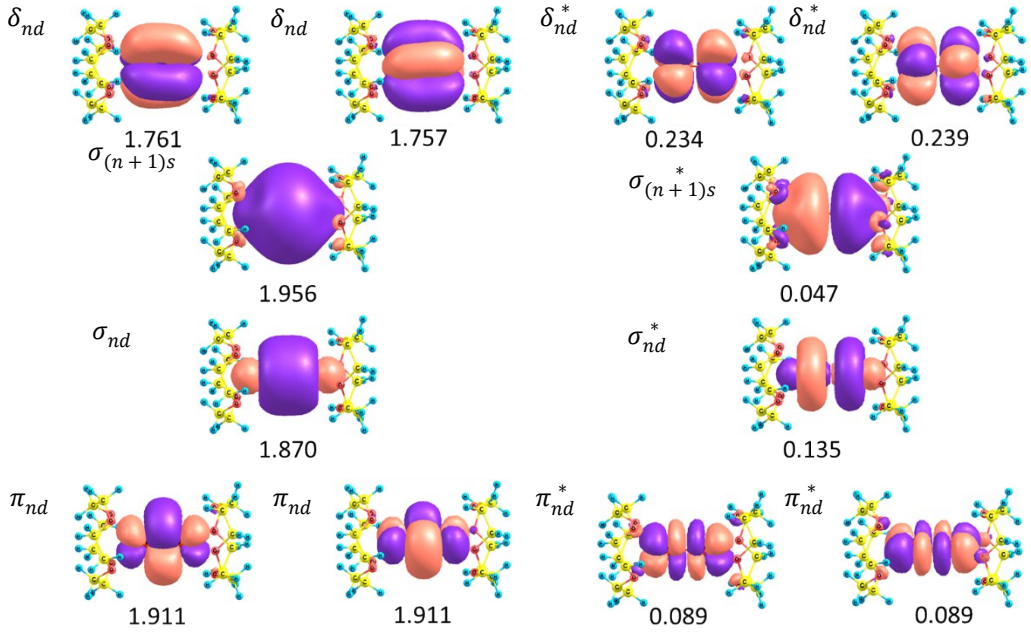


Figure S8 (D) The MOs of model complex of dibenzene and M_2.

(A) $O_4W_2O_4$



(B) $N_4W_2N_4$

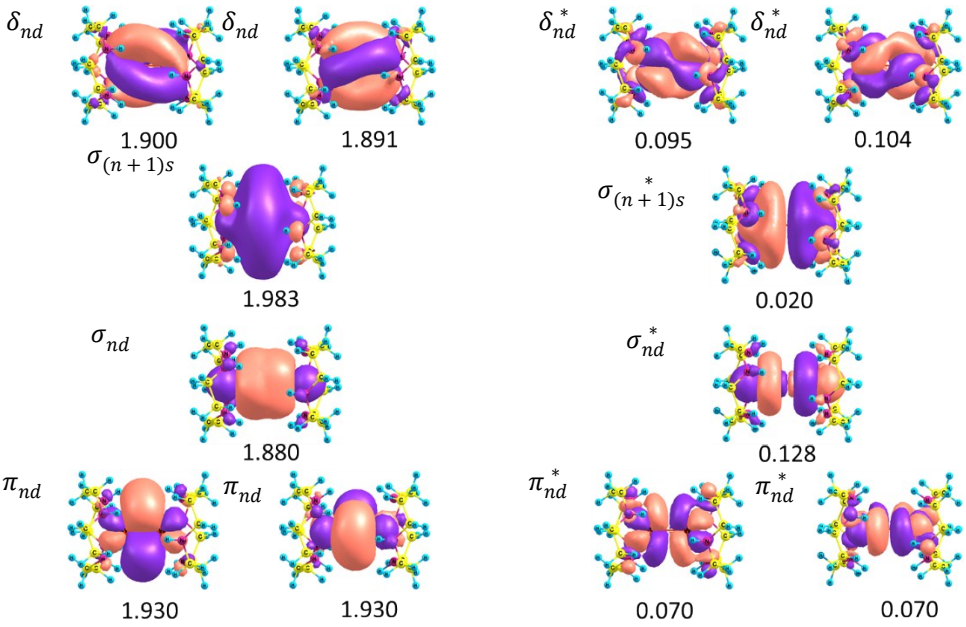


Figure S9 CASSCF natural orbitals and their occupation number for (A) $O_4W_2O_4$ and (B) $N_4W_2N_4$ complexes.

The Cartesian Coordinate of the complexes (unit: Angstrom)

$O_4(W_2)O_4$

Atom	X	Y	Z
W	1.045201067212	-0.000011525480	-0.000001910330
W	-1.047369079942	0.000063866402	0.000032316855
O	2.990660775243	-1.940120108502	0.541620650923
O	2.990512684990	0.541628196990	1.940131977947
O	2.990476536892	1.940140169611	-0.541595552046
O	2.990624441933	-0.541592175895	-1.940131173598
O	-2.988691854869	0.702287103009	-1.889853254696
O	-2.988468187521	-1.889872686085	-0.702326177457
O	-2.988731283866	-0.702347492717	1.889832050564
O	-2.988951575063	1.889853699205	0.702318472636
C	4.003899986415	-1.630466320843	1.469334536743
C	3.426741998119	-0.678674838443	2.503799867598
C	4.003735433458	1.469390110938	1.630566224216
C	3.426602374702	2.503831729360	0.678734095711
C	4.003775000041	1.630603240165	-1.469284053234
C	3.426747057053	0.678760094189	-2.503773874411
C	4.003937319870	-1.469237099336	-1.630511427912
C	3.426883050315	-2.503745595179	-0.678703826773
C	-4.002065281267	1.600182962120	-1.501886224327
C	-3.425574162140	2.552157381096	-0.467280100574
C	-4.002229601387	1.501691815190	1.600239562919
C	-3.425526165763	0.467162094047	2.552173219371
C	-4.001860611383	-1.600481994892	1.501780404753
C	-3.425071221499	-2.552306804875	0.467204417644
C	-4.001720162449	-1.501976464924	-1.600391690794
C	-3.425144666009	-0.467316338632	-2.552253776023
H	4.359864191843	-2.547945617037	1.977609855919
H	4.878021822059	-1.172429475697	0.968704241283
H	2.527101319907	-1.128947452114	2.946406475675
H	4.173431030565	-0.502013390160	3.301427946541
H	4.359599724929	1.977678511375	2.548077017039

H	4.877918489618	0.968802128491	1.172599331010
H	2.526913170936	2.946403215943	1.128944848562
H	4.173273171700	3.301486997431	0.502118431844
H	4.359651028663	2.548125188044	-1.977543587052
H	4.877934142681	1.172660535651	-0.968632733562
H	2.527074130780	1.128946727141	-2.946401697204
H	4.173478645934	0.502182827423	-3.301381188440
H	4.359905737549	-1.977487949356	-2.548002657052
H	4.878040935941	-0.968548456793	-1.172504047355
H	2.527257173190	-2.946409936494	-1.128949108439
H	4.173632096752	-3.301326307467	-0.502079066348
H	-4.359387159720	2.183534038765	-2.372950426200
H	-4.875433526174	1.062595472643	-1.086421239062
H	-2.526059650367	3.030939678354	-0.878953456765
H	-4.172635544865	3.331850642926	-0.224774566560
H	-4.359679191477	2.372690002201	2.183609256019
H	-4.875540367061	1.086091244130	1.062665567462
H	-2.526058306257	0.878972856403	3.030921262985
H	-4.172512516447	0.224523810629	3.331900078664
H	-4.359104949493	-2.183924074148	2.372816046930
H	-4.875328944874	-1.063102350363	1.086256130469
H	-2.525494637235	-3.030912965486	0.878941862491
H	-4.171949847570	-3.332147257357	0.224606452240
H	-4.358870090046	-2.373067517250	-2.183808586505
H	-4.875214901885	-1.086584791875	-1.062952259820
H	-2.525527948943	-0.878920388479	-3.030898921122
H	-4.172100594292	-0.224846629918	-3.332061371890

$O_4(Mo_2)O_4$

Atom	X	Y	Z
Mo	0.993344432656	0.000013171222	-0.000032306271
Mo	-1.002417065463	0.000141195074	-0.000835168701
O	3.034162452468	1.819403681158	-0.857919941726
O	3.034585709599	-0.859096143997	-1.818775426052
O	3.032792343778	-1.819674535241	0.859563508052
O	3.032438959211	0.858574242936	1.820303065518

O	-3.033286923418	-0.298960777073	1.991867293327
O	-3.028214008055	1.993297045585	0.299397136632
O	-3.024529346870	0.298291055638	-1.989311605344
O	-3.029104909704	-1.993476553092	-0.298672354305
C	4.047013252832	1.360788820994	-1.720752733281
C	3.471430561704	0.247245374633	-2.578623091099
C	4.046595800776	-1.722658131218	-1.359715871787
C	3.469731193638	-2.580004889315	-0.246434320539
C	4.044678877358	-1.361374720752	1.723695016995
C	3.468183127930	-0.247752061849	2.580829575016
C	4.045207689475	1.721952319895	1.362532317152
C	3.469962544639	2.579558015004	0.248623140519
C	-4.046733074646	-1.255444336554	1.795345436590
C	-3.469638947460	-2.399765880031	0.980039773593
C	-4.040200603761	-1.798514451588	-1.258059853317
C	-3.461303723149	-0.980138565694	-2.399308760848
C	-4.036603844209	1.257076403858	-1.799778708953
C	-3.462370692653	2.400348102008	-0.981262421752
C	-4.044042388255	1.798355624328	1.253777370010
C	-3.471023513273	0.980581825725	2.398397655212
H	4.401257309402	2.179937639053	-2.377538334740
H	4.924534840630	0.996915696448	-1.152441117475
H	2.573605649387	0.617448369262	-3.094071354968
H	4.216586075525	-0.061646445413	-3.336679850999
H	4.400750458141	-2.379727160011	-2.178675773569
H	4.924362196552	-1.155011373708	-0.995408668436
H	2.571737346775	-3.094828126060	-0.617095254575
H	4.214138524913	-3.338564817402	0.063018930109
H	4.397914750725	-2.180642989992	2.380872770546
H	4.922995670391	-0.997636975622	1.156519200778
H	2.569662014148	-0.617790175431	3.095182606023
H	4.212458852824	0.061132937102	3.339743385096
H	4.398508011339	2.378852795151	2.181995376536
H	4.923287532811	1.154104078147	0.999257099396
H	2.571671379539	3.094624810869	0.618229053874
H	4.214980250121	3.337911389335	-0.059859239214

H	-4.409254950378	-1.646550827371	2.766838960569
H	-4.919468439438	-0.814017042310	1.277056639209
H	-2.573207348255	-2.786530439770	1.485388155195
H	-4.216036985336	-3.213537717480	0.902484476748
H	-4.398849923343	-2.770571274165	-1.651193955557
H	-4.915658839505	-1.282803811056	-0.819006755135
H	-2.562561688450	-1.482895994941	-2.783822676829
H	-4.205212246658	-0.903237972233	-3.215578897007
H	-4.392226941982	1.649574202207	-2.773354868206
H	-4.914108297248	0.818709077057	-1.286748864489
H	-2.563343875925	2.786875394544	-1.482196655456
H	-4.208765814763	3.214331636815	-0.907000702937
H	-4.404907452355	2.770361391885	1.645065215163
H	-4.917130354432	1.282579170022	0.810139548936
H	-2.573864713401	1.483308112891	2.786878881822
H	-4.218874121531	0.904458127967	3.210996047402

$O_4(Re_2)O_4$

Atom	X	Y	Z
Re	1.059353394142	-0.000017441682	-0.000002836390
Re	-1.062484657635	0.000006667633	0.000007604277
O	2.420892715478	-1.717310980329	0.841729737334
O	2.420758696048	0.841739431861	1.717330522845
O	2.420752218918	1.717342963802	-0.841709723851
O	2.420886354767	-0.841703648896	-1.717328596640
O	-2.419361022514	0.485426445709	-1.850268288171
O	-2.419272856293	-1.850312326302	-0.485459900295
O	-2.419392519144	-0.485460704644	1.850245930432
O	-2.419425111171	1.850306478893	0.485455508124
C	3.415635546640	-1.357622901683	1.812022298839
C	2.849592582494	-0.200166983090	2.607318955118
C	3.415485419055	1.812077365023	1.357714687477
C	2.849488726167	2.607351060301	0.200220350615
C	3.415556466392	1.357755063701	-1.811979165601
C	2.849650035268	0.200246851812	-2.607296777299
C	3.415700571941	-1.811933576981	-1.357668754891

C	2.849745186629	-2.607266619488	-0.200195172362
C	-3.413387030175	1.508756469050	-1.690498601018
C	-2.846619199033	2.516706426616	-0.712495397818
C	-3.413461723544	1.690436327439	1.508757606781
C	-2.846652082107	0.712443956498	2.516691778990
C	-3.413326354712	-1.508876237737	1.690461267563
C	-2.846456799827	-2.516774452351	0.712462953961
C	-3.413271235609	-1.690551455242	-1.508820155532
C	-2.846502526033	-0.712509288721	-2.516731229154
H	3.614988501660	-2.215016132126	2.473455452404
H	4.354429541496	-1.077853208513	1.302756031763
H	1.950163929730	-0.510407321394	3.154207957145
H	3.590084875269	0.187671076200	3.322418010836
H	3.614745831557	2.473516493000	2.215124370040
H	4.354320753237	1.302850966161	1.078012199817
H	1.950020988372	3.154208989041	0.510401770325
H	3.589981336448	3.322473352193	-0.187573882215
H	3.614840236778	2.215172133579	-2.473401788539
H	4.354363822973	1.078077950091	-1.302687000591
H	1.950210343867	0.510404532630	-3.154214672405
H	3.590203061716	-0.187514873660	-3.322374401339
H	3.615069555739	-2.473354612387	-2.215067711032
H	4.354471272413	-1.302607851549	-1.077928801483
H	1.950339441948	-3.154209280088	-0.510408035784
H	3.590293323479	-3.322324875640	0.187611850682
H	-3.610385098810	1.987723957178	-2.662112126522
H	-4.352946612215	1.065929971950	-1.316130817394
H	-1.945362799802	2.988618775491	-1.124087387716
H	-3.585854992181	3.295484746274	-0.474101930870
H	-3.610545047926	2.662022827861	1.987745462941
H	-4.352984390179	1.316004322865	1.065907153827
H	-1.945423798063	1.124068803011	2.988629888213
H	-3.585884933030	0.473980410606	3.295449847035
H	-3.610298387826	-1.987862940291	2.662070586108
H	-4.352917819681	-1.066130461335	1.316077010652
H	-1.945181508968	-2.988636518804	1.124071687027

H	-3.585633515627	-3.295593852040	0.474024094188
H	-3.610225467201	-2.662163043957	-1.987809117673
H	-4.352854567125	-1.316214194562	-1.066017979419
H	-1.945226573703	-1.124061410404	-2.988641159688
H	-3.585729635383	-0.474104132247	-3.295513348305

$O_4(Tc_2)O_4$

Atom	X	Y	Z
Tc	1.006751000	0.000000000	0.000000000
Tc	-1.006230000	0.000000000	0.000000000
O	2.389428000	-1.738487000	-0.861245000
O	2.387194000	-0.860803000	1.735278000
O	2.389428000	1.738487000	0.861245000
O	2.387194000	0.860803000	-1.735278000
O	-2.387250000	-0.797141000	-1.765821000
O	-2.389321000	-1.768971000	0.797581000
O	-2.387250000	0.797141000	1.765821000
O	-2.389321000	1.768970000	-0.797581000
C	3.393012000	-2.251191000	0.020232000
C	2.828743000	-2.187343000	1.425908000
C	3.391487000	0.019590000	2.249470000
C	2.830353000	1.426541000	2.186986000
C	3.393012000	2.251192000	-0.020232000
C	2.828743000	2.187343000	-1.425908000
C	3.391487000	-0.019590000	-2.249470000
C	2.830354000	-1.426541000	-2.186986000
C	-3.391889000	0.101577000	-2.246349000
C	-2.830520000	1.505212000	-2.133636000
C	-3.393319000	2.247925000	0.102155000
C	-2.829022000	2.133877000	1.504554000
C	-3.391890000	-0.101577000	2.246349000
C	-2.830520000	-1.505212000	2.133636000
C	-3.393318000	-2.247925000	-0.102155000
C	-2.829021000	-2.133877000	-1.504554000
H	3.629580000	-3.294551000	-0.244430000
H	4.316730000	-1.652929000	-0.066179000

H	1.937173000	-2.823334000	1.508709000
H	3.574838000	-2.530100000	2.159293000
H	3.626950000	-0.246714000	3.292649000
H	4.315315000	-0.067998000	1.651592000
H	1.939074000	1.510784000	2.823219000
H	3.578373000	2.157454000	2.530948000
H	3.629580000	3.294551000	0.244430000
H	4.316730000	1.652929000	0.066179000
H	1.937173000	2.823334000	-1.508709000
H	3.574838000	2.530100000	-2.159293000
H	3.626951000	0.246714000	-3.292649000
H	4.315315000	0.067999000	-1.651592000
H	1.939074000	-1.510784000	-2.823219000
H	3.578373000	-2.157453000	-2.530947000
H	-3.629243000	-0.126593000	-3.298098000
H	-4.314820000	-0.006956000	-1.650422000
H	-1.939356000	1.612117000	-2.766673000
H	-3.578552000	2.248230000	-2.450671000
H	-3.631772000	3.299805000	-0.124332000
H	-4.316118000	1.651561000	-0.005352000
H	-1.937594000	2.766739000	1.610172000
H	-3.575272000	2.449659000	2.249841000
H	-3.629244000	0.126592000	3.298098000
H	-4.314820000	0.006956000	1.650421000
H	-1.939356000	-1.612117000	2.766673000
H	-3.578552000	-2.248230000	2.450671000
H	-3.631772000	-3.299805000	0.124332000
H	-4.316118000	-1.651561000	0.005352000
H	-1.937593000	-2.766740000	-1.610172000
H	-3.575272000	-2.449659000	-2.249841000

$O_2N_2(W_2)O_2N_2$

Atom	X	Y	Z
W	1.095905079634	0.000038000218	-0.000033999638
W	-1.100270077549	-0.000019997608	0.000017002465
O	2.618127188757	1.930617138172	-0.690384049267

O	2.617807189983	-1.930645136941	0.690409047600
O	-2.614847189415	-1.906688134564	-0.747595052689
O	-2.614693188252	1.906721139349	0.747547056313
N	-2.507667179602	-0.710722050772	1.848681132140
N	-2.507503182281	0.710760050990	-1.848683132430
N	2.511760180411	-0.653346044592	-1.866799134542
N	2.511674178524	0.653279045460	1.866829133600
C	3.486444251611	1.704461122653	1.585203113099
C	2.999065215937	2.634528190907	0.478408036649
C	3.662675261827	1.494330107681	-1.536932109498
C	3.058499218898	0.522070038705	-2.541221181813
C	3.486373251899	-1.704653124034	-1.585081116576
C	2.998766214916	-2.634644191851	-0.478324035052
C	3.662332265010	-1.494544106960	1.537083110226
C	3.058189221574	-0.522204036968	2.541315184860
C	-3.660774261353	-1.443837104686	-1.578480111946
C	-3.056761220892	-0.444421029861	-2.555813186245
C	-3.480890250627	1.754473124695	-1.535309112292
C	-2.994418214175	2.648153192709	-0.398444030802
C	-3.660720264107	1.443987105269	1.578371112017
C	-3.056865220097	0.444530029791	2.555755183127
C	-3.481169248748	-1.754309127374	1.535211108665
C	-2.994722215921	-2.648053188792	0.398387027828
H	3.732005270935	2.312868165234	2.478325179579
H	4.427320320811	1.221130086556	1.272813092764
H	2.084122149879	3.151902226036	0.798440059098
H	3.778829271100	3.384607243937	0.245753015414
H	4.113540294721	2.356250169025	-2.063301147132
H	4.464306323238	0.998842070971	-0.953493067720
H	2.223549157600	1.028781072891	-3.045649218344
H	3.825286276259	0.259738016499	-3.297163238299
H	3.731938266512	-2.313092165964	-2.478180179721
H	4.427281320448	-1.221441089317	-1.272603094065
H	2.083787148930	-3.151904226326	-0.798436058518
H	3.778411273991	-3.384814242201	-0.245569015193
H	4.112997295362	-2.356547169756	2.063485147353

H	4.464109321132	-0.999168070615	0.953747067508
H	2.223122159186	-1.028801075791	3.045662220229
H	3.824940273714	-0.259972018678	3.297328235765
H	-4.114727297500	-2.289297165910	-2.128338152890
H	-4.459558322705	-0.963782067351	-0.978532068234
H	-2.222865158964	-0.937900066312	-3.074784220102
H	-3.823891275070	-0.159571012847	-3.303120239508
H	-3.723776268374	2.391611173956	-2.408801174091
H	-4.423185319204	1.263011089663	-1.240310089487
H	-2.079031147238	3.175504229855	-0.700294052153
H	-3.774444270285	3.390053245136	-0.141952008715
H	-4.114619297715	2.289499163449	2.128193153032
H	-4.459516321907	0.964012068951	0.978377072218
H	-2.222954161285	0.937940066820	3.074766222784
H	-3.824070274566	0.159766009371	3.303019235447
H	-3.724215268528	-2.391415171995	2.408681172567
H	-4.423370319570	-1.262720089802	1.240133090281
H	-2.079413149710	-3.175503229710	0.700304048311
H	-3.774812270727	-3.389876245930	0.141863011685
H	-1.665228117208	1.074949078479	-2.307722165201
H	-1.665546120984	-1.075043076233	2.307880166944
H	1.668696122643	1.005130072550	2.334310168067
H	1.668801121993	-1.005096072912	-2.334388168793

$O_2N_2(Mo_2)O_2N_2$

Atom	X	Y	Z
Mo	1.043082077462	-0.000002000290	-0.000012001740
Mo	-1.042569077161	-0.000020997753	0.000018997463
O	2.565075185131	1.942070137248	-0.663614046470
O	2.564988183099	-1.942083139133	0.663640050240
O	-2.567178183144	-1.896865139001	-0.775641055295
O	-2.567138182636	1.896888137044	0.775618057252
N	-2.459541175859	-0.745545051777	1.839463134343
N	-2.459377178537	0.745558053662	-1.839467134923
N	2.461734176339	-0.634262044997	-1.877439137442
N	2.461655175467	0.634254043837	1.877454134326

C	3.451860248218	1.671680121400	1.596537116087
C	2.961469215020	2.624227189535	0.511995038353
C	3.603224261693	1.518657110790	-1.523524107410
C	2.999031216299	0.555379042434	-2.534776183928
C	3.451895248001	-1.671718121618	-1.596463115940
C	2.961419213062	-2.624250187578	-0.511951037265
C	3.603099259444	-1.518707107456	1.523616110167
C	2.998877215136	-0.555404040767	2.534825180450
C	-3.607165261629	-1.418698100255	-1.603949116601
C	-3.000546213721	-0.404062030482	-2.561848182890
C	-3.447611245956	1.767169129378	-1.499862105475
C	-2.961189211462	2.650385188260	-0.356392024066
C	-3.607208257281	1.418766099532	1.603843117107
C	-3.000702215174	0.404109026714	2.561793185498
C	-3.447808248062	-1.767093128942	1.499770108010
C	-2.961348213350	-2.650339192174	0.356340027110
H	3.719369269661	2.261153164969	2.495839179069
H	4.380798316811	1.179344086640	1.263485089600
H	2.055053147108	3.144211227400	0.852520063616
H	3.741311270909	3.375172241133	0.284935018756
H	4.044099290684	2.388461172296	-2.045563146913
H	4.415273320274	1.025152075861	-0.952974066549
H	2.159382156282	1.064427076813	-3.029827215482
H	3.762155271700	0.309508020493	-3.299622235015
H	3.719438269082	-2.261201161346	-2.495750182039
H	4.380829316014	-1.179408085336	-1.263359092497
H	2.055001150151	-3.144201225950	-0.852522063906
H	3.741223268733	-3.375223243237	-0.284852022597
H	4.043898293290	-2.388527171283	2.045692149742
H	4.415209316285	-1.025242073036	0.953118066262
H	2.159183153886	-1.064422076088	3.029829215772
H	3.761965270608	-0.309555022017	3.299715237916
H	-4.056891293412	-2.254599161863	-2.171912158062
H	-4.412182316586	-0.952316066391	-1.001444072547
H	-2.162272157284	-0.888439064789	-3.083177219985
H	-3.762483271634	-0.113538005667	-3.311980238313

H	-3.709453265905	2.411729175311	-2.362189167625
H	-4.379550315770	1.257713088757	-1.202740087048
H	-2.054374149196	3.191686232000	-0.660827049820
H	-3.742633266804	3.384583245749	-0.084686007901
H	-4.056947290948	2.254686163894	2.171768158349
H	-4.412195318471	0.952414070017	1.001277069499
H	-2.162440155185	0.888454061672	3.083174219550
H	-3.762703271783	0.113634009003	3.311880239688
H	-3.709772264534	-2.411635172265	2.362075172262
H	-4.379687314468	-1.257577090204	1.202563087842
H	-2.054583147750	-3.191688232290	0.660842046703
H	-3.742810271302	-3.384497243862	0.084580008407
H	-1.650234117987	1.142633081754	-2.330122169358
H	-1.650469120312	-1.142671081972	2.330188168345
H	1.652394118974	1.005200072117	2.388103173304
H	1.652499118324	-1.005192070957	-2.388141173522

$O_2N_2(Re_2)O_2N_2$

Atom	X	Y	Z
Re	1.074338079843	0.000002000290	-0.000003000435
Re	-1.078428080217	-0.000003000435	-0.000003000435
O	2.435234175649	-0.738034052783	-1.776042130068
O	2.435210177461	0.738030052203	1.776053126371
O	-2.432107177325	-0.739787052964	1.774962126928
O	-2.432117173483	0.739794053979	-1.774962126928
N	-2.221834157638	1.836026133402	0.749615054543
N	-2.221863161843	-1.836021132677	-0.749620055268
N	2.224789157481	-1.835819129846	0.747054053621
N	2.224817161541	1.835814134413	-0.747058054201
C	3.311375240548	1.495744106332	-1.703673124812
C	2.891945209533	0.342570025449	-2.595252184518
C	3.379793244418	-1.756339125386	-1.439387105030
C	2.712200197794	-2.640380187475	-0.401415027673
C	3.311342235763	-1.495755107927	1.703677120100
C	2.891912210039	-0.342584022188	2.595259185533
C	3.379792244273	1.756319127778	1.439400101623

C	2.712226196272	2.640367190882	0.401417027963
C	-3.375564245056	-1.759582124655	1.438250104209
C	-2.708361196773	-2.641961189175	0.398419027177
C	-3.308777239552	-1.494391105942	-1.705469120644
C	-2.889646209558	-0.339818023291	-2.595624185541
C	-3.375555243751	1.759602127555	-1.438239102614
C	-2.708328197279	2.641973190915	-0.398418027032
C	-3.308739239334	1.494413109132	1.705479122094
C	-2.889614210210	0.339833025466	2.595628186121
H	3.594514258180	2.371266171436	-2.309916165826
H	4.198322300667	1.204252084034	-1.120641078547
H	2.039543147151	0.617418042114	-3.231964230218
H	3.721771268695	0.017614003406	-3.240386234305
H	3.629035263021	-2.348620168651	-2.333529165949
H	4.311188309437	-1.300564094929	-1.057601076600
H	1.839121132378	-3.127144223933	-0.854982060767
H	3.417037247213	-3.421348247881	-0.072207002933
H	3.594474257672	-2.371280168174	2.309919166261
H	4.198294301898	-1.204266086064	1.120652080142
H	2.039507147223	-0.617428043564	3.231968230798
H	3.721740269492	-0.017635001160	3.240396235755
H	3.629036263166	2.348598170753	2.333541167689
H	4.311181308422	1.300523094276	1.057623074498
H	1.839150131292	3.127148224513	0.854973059462
H	3.417081248301	3.421325244546	0.072220004818
H	-3.622595260569	-2.352954167363	2.332238169257
H	-4.308096310895	-1.304601092910	1.058324075600
H	-1.834778132362	-3.129202226005	0.850487059877
H	-3.413400243731	-3.422650246168	0.068943005911
H	-3.592053255882	-2.368938172548	-2.313034168137
H	-4.195608304018	-1.203824085475	-1.121738078860
H	-2.037752146752	-0.613727046677	-3.233398231770
H	-3.719926265758	-0.013600003469	-3.239508233997
H	-3.622592260134	2.352975170408	-2.332226167517
H	-4.308087309590	1.304635092548	-1.058299077267
H	-1.834740132143	3.129197225280	-0.850494060892

H	-3.413351247209	3.422675244501	-0.068936004896
H	-3.591993257766	2.368962170736	2.313051165310
H	-4.195583300393	1.203863085839	1.121760082050
H	-2.037708145664	0.613731041966	3.233392230900
H	-3.719891265975	0.013627002092	3.239523230880
H	-1.511051108604	-2.377601169246	-1.245436091912
H	-1.510998106211	2.377584172073	1.245421089737
H	1.514408108528	2.378633170717	-1.242050087783
H	1.514367107875	-2.378625169557	1.242040091625

$O_2N_2(Tc_2)O_2N_2$

Atom	X	Y	Z
Tc	1.035081076210	0.000000000000	0.000001000145
Tc	-1.035301076359	0.000001000145	0.000000000000
O	2.395693173170	-0.971586071788	-1.727455122980
O	2.395697173750	0.971586071788	1.727454122835
O	-2.396007171074	-0.969660067689	1.728400122420
O	-2.396008171219	0.969659067544	-1.728398122130
N	-2.166944157380	1.756578128291	0.950133067361
N	-2.166942157090	-1.756578128291	-0.950132067216
N	2.167266156444	-1.755659127329	0.952025066530
N	2.167264156154	1.755659127329	-0.952025066530
C	3.277274238398	1.272167089054	-1.815895130161
C	2.877543206192	0.040273002785	-2.609406188941
C	3.333773239123	-1.925474138574	-1.242123087784
C	2.657149190066	-2.676819195255	-0.105115006726
C	3.277278233686	-1.272167089054	1.815893129871
C	2.877549207062	-0.040273002785	2.609404188651
C	3.333776239558	1.925473138429	1.242120087349
C	2.657150190211	2.676819195255	0.105114006581
C	-3.333887239778	-1.924112136879	1.244043091013
C	-2.656917193469	-2.676606190829	0.107990005553
C	-3.276943238028	-1.274351093521	-1.814808131299
C	-2.877500205249	-0.043070000885	-2.609434187709
C	-3.333888239923	1.924111136734	-1.244042090868
C	-2.656920188612	2.676606190829	-0.107990005553

C	-3.276944238173	1.274349093231	1.814808131299
C	-2.877500205249	0.043069000740	2.609435187854
H	3.624497261188	2.067697149542	-2.495907178345
H	4.126031296137	1.018101074774	-1.163589082909
H	2.048556146974	0.262072016257	-3.296597235605
H	3.728117268101	-0.325932025978	-3.205247229814
H	3.606568259732	-2.635352188676	-2.039479148455
H	4.258869306260	-1.422360102070	-0.907986062726
H	1.785811128384	-3.214475229061	-0.502795037875
H	3.362217241230	-3.419995247491	0.305164020332
H	3.624501261768	-2.067698149687	2.495904177910
H	4.126033296427	-1.018101074774	1.163585082329
H	2.048563147989	-0.262071021404	3.296597235605
H	3.728124269116	0.325932025978	3.205243229234
H	3.606573260457	2.635351188531	2.039476148020
H	4.258872306695	1.422360102070	0.907982067437
H	1.785813128674	3.214475229061	0.502795037875
H	3.362217241230	3.419995247491	-0.305166020622
H	-3.606771257417	-2.633235188633	2.042061147131
H	-4.259059307351	-1.421549100894	0.909247065651
H	-1.785584127219	-3.213658232306	0.506465035558
H	-3.361812240714	-3.420322247280	-0.301607023158
H	-3.623647259648	-2.070728149822	-2.494079177873
H	-4.125939298672	-1.019986072928	-1.162927082171
H	-2.048365145738	-0.265350020601	-3.296305235599
H	-3.728049268824	0.322336023149	-3.205807231638
H	-3.606772257562	2.633233188343	-2.042060146986
H	-4.259061307641	1.421548100749	-0.909247065651
H	-1.785587127654	3.213658232306	-0.506464035413
H	-3.361815241149	3.420321247135	0.301608023303
H	-3.623650260083	2.070726149532	2.494078177728
H	-4.125939298672	1.019983072493	1.162927082171
H	-2.048365145738	0.265351020746	3.296306235744
H	-3.728049268824	-0.322337023294	3.205808231783
H	-1.514392111500	-2.276645162315	-1.539040108237
H	-1.514394106498	2.276645162315	1.539041108382

H	1.514931110278	2.275174165982	-1.541677109596
H	1.514934110713	-2.275174165982	1.541678109741

$N_4(W_2)N_4$

Atom	X	Y	Z
W	-1.128072000	0.000469000	-0.000110000
W	1.145776000	-0.000287000	0.000916000
N	-2.390709000	1.764197000	0.947237000
N	-2.389590000	-0.947294000	1.764517000
N	-2.389227000	0.946207000	-1.763830000
N	2.378614000	-1.932850000	0.520004000
N	-2.386983000	-1.764215000	-0.946488000
N	2.378854000	0.520644000	1.933006000
N	2.376549000	1.933225000	-0.520192000
N	2.376781000	-0.519664000	-1.933275000
C	-3.399274000	1.891992000	-1.291380000
C	-2.870528000	2.674343000	-0.089948000
C	-3.400109000	1.290581000	1.892866000
C	-2.869844000	0.089604000	2.674786000
C	-3.397490000	-1.894730000	1.290972000
C	-2.866119000	-2.675659000	0.089686000
C	-3.397288000	-1.292706000	-1.892526000
C	-2.869215000	-0.090844000	-2.674382000
C	3.382578000	-1.554654000	-1.695602000
C	2.857375000	-2.585583000	-0.696669000
C	3.385292000	-1.693495000	1.553966000
C	2.858679000	-0.695893000	2.585484000
C	3.384080000	1.556003000	1.693337000
C	2.855780000	2.586706000	0.695743000
C	3.380569000	1.696408000	-1.557089000
C	2.854171000	0.696881000	-2.587007000
H	-3.726078000	2.596048000	-2.080939000
H	-4.292522000	1.314132000	-0.993870000
H	-2.007157000	3.275593000	-0.410737000
H	-3.656244000	3.362403000	0.279740000
H	-1.545601000	2.116936000	1.411106000

H	-3.728555000	2.079675000	2.596732000
H	-4.292842000	0.991281000	1.315036000
H	-2.006676000	0.410853000	3.276043000
H	-3.655296000	-0.280811000	3.362740000
H	-1.543127000	-1.409718000	2.116285000
H	-3.723624000	-2.599743000	2.080032000
H	-4.291728000	-1.318729000	0.992638000
H	-2.002088000	-3.275827000	0.410836000
H	-3.650380000	-3.364679000	-0.281276000
H	-1.541231000	-2.116065000	-1.410362000
H	-3.722513000	-2.082517000	-2.597093000
H	-4.291366000	-0.996550000	-1.315211000
H	-2.006117000	-0.411356000	-3.276268000
H	-3.655135000	0.279169000	-3.361967000
H	-1.544573000	1.410062000	-2.117053000
H	3.696228000	-2.064584000	-2.626931000
H	4.283766000	-1.065060000	-1.284734000
H	1.994877000	-3.102595000	-1.142458000
H	3.645026000	-3.337258000	-0.492244000
H	1.524615000	-2.371479000	0.886041000
H	3.701291000	-2.624504000	2.062922000
H	4.284966000	-1.280545000	1.063476000
H	1.996202000	-1.143143000	3.101356000
H	3.645605000	-0.491086000	3.337850000
H	1.524109000	0.885768000	2.371598000
H	3.699739000	2.065397000	2.624234000
H	4.284248000	1.066836000	1.279937000
H	1.992801000	3.101557000	1.143021000
H	3.641641000	3.340017000	0.490543000
H	1.519053000	2.367679000	-0.883857000
H	3.692499000	2.628090000	-2.067329000
H	4.282861000	1.286038000	-1.069226000
H	1.990779000	1.142313000	-3.102774000
H	3.640706000	0.492313000	-3.339742000
H	1.519798000	-0.884833000	-2.368063000

$N_4(Mo_2)N_4$

Atom	X	Y	Z
Mo	-1.073473076129	0.000017002465	-0.000005000725
Mo	1.073688075553	0.000002000290	-0.000002000290
N	-2.328218168449	1.020672071854	-1.738899126043
N	-2.328131166418	1.739008125972	1.020679072869
N	-2.328149169028	-1.738996124232	-1.020672071854
N	2.327193167993	0.443814031806	1.967298144000
N	-2.328182168521	-1.020687074029	1.738939126551
N	2.327211165311	1.967286142260	-0.443835029559
N	2.327165169225	-0.443824033256	-1.967316141318
N	2.327183166543	-1.967289142695	0.443819032531
C	-3.348420240946	-1.210750089605	-1.925484140024
C	-2.814271202355	0.007606002186	-2.673015194017
C	-3.348357242395	1.925624139157	-1.210611085325
C	-2.813955204161	2.673196193803	0.007570002258
C	-3.348338239640	1.210705088371	1.925540137561
C	-2.814121201772	-0.007604001896	2.673082193148
C	-3.348344240510	-1.925579137924	1.210604089602
C	-2.813965200319	-2.673179191338	-0.007576997981
C	3.347286240561	-1.738228123999	1.466571104356
C	2.815554203179	-0.803685057611	2.550001184893
C	3.347335242374	1.466521107689	1.738260123347
C	2.815665203399	2.549949182645	0.803653058263
C	3.347297242156	1.738206126101	-1.466598102979
C	2.815539201004	0.803672055726	-2.550021182502
C	3.347288240851	-1.466550106603	-1.738291122551
C	2.815609200571	-2.549966185110	-0.803674056016
H	-3.702428268588	-1.967034142762	-2.652700190555
H	-4.226536306465	-0.922713065565	-1.321008095929
H	-1.953846140824	-0.304657020901	-3.284468233761
H	-3.596620256628	0.396723029969	-3.353828241927
H	-1.535122111636	1.537946108359	-2.131985152530
H	-3.702480265544	2.652841189833	-1.966840141091
H	-4.226495305812	1.321346097313	-0.922226063743

H	-1.953567142703	3.284628235794	-0.304878021196
H	-3.596246260608	3.354026238887	0.396749028447
H	-1.535034109459	2.132016151733	1.537990109447
H	-3.702344266991	1.966958142326	2.652792193311
H	-4.226483304072	0.922613066941	1.321131092597
H	-1.953699140676	0.304660021336	3.284550235067
H	-3.596448258147	-0.396794029680	3.353875243451
H	-1.535087111852	-1.537953109374	2.132013151298
H	-3.702376266340	-2.652834188818	1.966841141236
H	-4.226505301970	-1.321261095572	0.922353066283
H	-1.953543139223	-3.284608238186	0.304787023876
H	-3.596261257491	-3.354003240844	-0.396760030042
H	-1.535068109097	-2.132018152023	-1.537997110462
H	3.704038263909	-2.679523190454	1.927567140429
H	4.223495304736	-1.278371094328	0.976668067833
H	1.958203142871	-1.285459090197	3.043915220918
H	3.600539258666	-0.637571043253	3.313743239944
H	1.529610111450	0.815830056483	2.493492177426
H	3.704080264707	1.927476137818	2.679580193427
H	4.223507306476	0.976485067757	1.278474093388
H	1.958333140554	3.043924216931	1.285394091355
H	3.600680257944	3.313663238928	0.637533048326
H	1.529607111015	2.493481181123	-0.815801057570
H	3.704065267824	2.679494191540	-1.927596139343
H	4.223501305606	1.278330093675	-0.976704067762
H	1.958190140986	1.285465091067	-3.043919221498
H	3.600511259898	0.637552045789	-3.313774239147
H	1.529566110362	-0.815825061050	-2.493497178151
H	3.704007264706	-1.927522139196	-2.679612192775
H	4.223481302706	-0.976537070005	-1.278522089764
H	1.958263140987	-3.043927217366	-1.285406093095
H	3.600614258958	-3.313692237841	-0.637558046659
H	1.529573111377	-2.493470179528	0.815796056845

$N_4(Re_2)N_4$

Atom	X	Y	Z
Re	1.092623080002	0.000001000145	0.000000000000
Re	-1.094253078223	0.000000000000	0.000000000000
N	2.268687162007	1.626717115909	1.145363080722
N	2.268648161644	1.145369081592	-1.626714115474
N	2.268650161934	-1.145369081592	1.626713115329
N	-2.268170161127	-0.357126024661	-1.957223138356
N	2.268681161137	-1.626718116054	-1.145364080867
N	-2.268186163447	1.957222138211	-0.357117023356
N	-2.268166165838	0.357126024661	1.957224138501
N	-2.268186163447	-1.957221143358	0.357119023646
C	3.310682240606	-0.299094023904	2.248104162019
C	2.772379197653	1.109252078168	2.435257173693
C	3.310667238431	2.248158159266	0.299067019989
C	2.772316199101	2.435282177318	-1.109265080053
C	3.310677239881	0.299091023469	-2.248108162599
C	2.772371201785	-1.109254078458	-2.435260174128
C	3.310662237706	-2.248160159556	-0.299071020569
C	2.772315198956	-2.435284177608	1.109262079618
C	-3.309052237093	-2.168358156032	-0.672679048541
C	-2.771145198642	-1.745170125157	-2.029280145998
C	-3.309051236948	0.672662046076	-2.168345154147
C	-2.771161200962	2.029271144693	-1.745160123707
C	-3.309050236803	2.168359156177	0.672682048976
C	-2.771141198062	1.745170125157	2.029282146288
C	-3.309047236368	-0.672662046076	2.168349154727
C	-2.771157200382	-2.029270144548	1.745163124142
H	3.649163260535	-0.713850049241	3.211328233128
H	4.186364302451	-0.289356019500	1.580019112848
H	1.925526140822	1.091155078812	3.136188228250
H	3.548914255576	1.764546124757	2.862078207469
H	1.539477113392	2.316972167638	1.328034093391
H	3.649107262998	3.211403233420	0.713808053735
H	4.186388300639	1.580123112053	0.289317019136
H	1.925435138211	3.136179226945	-1.091137076202
H	3.548811256516	2.862128204136	-1.764590125846

H	1.539483108971	1.328034093391	-2.317019169161
H	3.649156264812	0.713847048806	-3.211333228562
H	4.186361302016	0.289352018920	-1.580026113863
H	1.925515139227	-1.091154078667	-3.136188228250
H	3.548903253981	-1.764550125337	-2.862083208194
H	1.539469112232	-2.316971167493	-1.328033093246
H	3.649099261838	-3.211406228563	-0.713813049168
H	4.186384300059	-1.580128112778	-0.289324020151
H	1.925432137776	-3.136179226945	1.091137076202
H	3.548811256516	-2.862130204426	1.764585125121
H	1.539487109551	-1.328033093246	2.317020169306
H	-3.643205264472	-3.218031231381	-0.702162053133
H	-4.187479300081	-1.561501110655	-0.401597027604
H	-1.923382136864	-2.387989172649	-2.307031165549
H	-3.547831257293	-1.857736132761	-2.803071202923
H	-1.537184108996	-0.233809019228	-2.658697192273
H	-3.643220261355	0.702140049943	-3.218014234208
H	-4.187465303343	0.401566028401	-1.561476112322
H	-1.923400139474	2.307031165549	-2.387979171199
H	-3.547857255772	2.803051200023	-1.857731132036
H	-1.537182108706	2.658677189373	-0.233809019228
H	-3.643203264182	3.218032231526	0.702166048422
H	-4.187478299936	1.561502110800	0.401603028474
H	-1.923377136139	2.387990172794	2.307031165549
H	-3.547825256423	1.857736132761	2.803075203503
H	-1.537178108126	0.233809019228	2.658696192128
H	-3.643213260340	-0.702140049943	3.218018229496
H	-4.187462302908	-0.401566028401	1.561481113047
H	-1.923395138749	-2.307030165404	2.387979171199
H	-3.547853255192	-2.803051200023	1.857736132761
H	-1.537181108561	-2.658677189373	0.233808019083

$N_4(Tc_2)N_4$

Atom	X	Y	Z
Tc	1.114191079937	0.000000000000	0.000000000000

Tc	-1.112158081490	0.000000000000	0.000000000000
N	2.155975154400	0.820786060717	1.814588131149
N	2.155938154327	1.814602133179	-0.820787060862
N	2.155938154327	-1.814602133179	0.820787060862
N	-2.155883156935	0.644412045640	-1.885534136449
N	2.155975154400	-0.820786060717	-1.814588131149
N	-2.155898153818	1.885531136014	0.644411045495
N	-2.155883156935	-0.644411045495	1.885534136449
N	-2.155898153818	-1.885531136014	-0.644411045495
C	3.200421228555	-1.398605102525	1.781840129389
C	2.662324189013	-0.281903018332	2.659829192369
C	3.200426229280	1.781865127723	1.398580098900
C	2.662280193216	2.659852190412	0.281902018187
C	3.200421228555	1.398606102670	-1.781840129389
C	2.662324189013	0.281903018332	-2.659829192369
C	3.200426229280	-1.781865127723	-1.398580098900
C	2.662280193216	-2.659852190412	-0.281902018187
C	-3.201068232410	-1.561979111172	-1.639722117771
C	-2.663337193021	-0.534713040995	-2.620165187929
C	-3.201067232265	1.639710116031	-1.561982111607
C	-2.663355190339	2.620158186914	-0.534711040705
C	-3.201067232265	1.561980111317	1.639723117916
C	-2.663336192876	0.534713040995	2.620166188074
C	-3.201066232120	-1.639710116031	1.561983111752
C	-2.663355190339	-2.620158186914	0.534711040705
H	3.545179253759	-2.242832159591	2.401762174744
H	4.068982295038	-1.045760074182	1.206027087405
H	1.816349132490	-0.656347045813	3.254633236338
H	3.438292249389	0.064093006463	3.362250240723
H	1.444429105858	1.328373094920	2.340600169936
H	3.545183254339	2.401795174237	2.242801160388
H	4.068998292066	1.206089085812	1.045704076646
H	1.816298130387	3.254631236048	0.656370049148
H	3.438224244821	3.362293241666	-0.064106003057
H	1.444403102088	2.340614166674	-1.328390097385
H	3.545179253759	2.242832159591	-2.401762174744

H	4.068982295038	1.045760074182	-1.206028087550
H	1.816348132345	0.656347045813	-3.254633236338
H	3.438291249244	-0.064093006463	-3.362250240723
H	1.444429105858	-1.328373094920	-2.340600169936
H	3.545183254339	-2.401795174237	-2.242802160533
H	4.068998292066	-1.206088085667	-1.045704076646
H	1.816299130532	-3.254631236048	-0.656370049148
H	3.438224244821	-3.362293241666	0.064106003057
H	1.444403102088	-2.340614166674	1.328390097385
H	-3.545140253396	-2.461437175608	-2.176571156273
H	-4.070741290797	-1.157294085607	-1.100485076973
H	-1.819462128785	-0.965159071222	-3.179119230147
H	-3.440861246180	-0.256943018689	-3.350057240183
H	-1.449128104577	1.101593078881	-2.461780177717
H	-3.545142253686	2.176557154243	-2.461440176043
H	-4.070734295074	1.100461078785	-1.157302081475
H	-1.819486132265	3.179125231017	-0.965153070352
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H	-1.449138106027	2.461776177137	1.101588078156
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H	-3.545140253396	-2.176557154243	2.461441176188
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H	-1.449139106172	-2.461776177137	-1.101589078301