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The Influence of f Orbitals on δ Metal Bonds

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Some δ metal bonds have been studied by using the recently proposed population analysis based on hybrid orbitals. The results show that the δ metal bonds are formed by overlap of the d-f hybrid orbitals of the metal atoms and that the f orbitals play an important role in the δ bonds. Under the influence of the f orbitals on the δ bonds, the densities of the δ electrons between the metal atoms increase and their mean kinetic energies decrease. These are of importance to the stability in the δ bonds.

INTRODUCTION

It has been proved that a metal-metal quadruple bond involves one δ bond in addition to one σ and two π bonds. Until now, all metal-metal quadruple bonds have been discovered in some transition-metal compounds. It seems very apparent that the δ bonds between two metal atoms are yielded by the d orbitals or the linear combination of the d and f orbitals of the metal atoms. In the last decades, a great number of compounds having the metal-metal quadruple bonds were synthesized and their chemical natures and structures studied, and a series of calculations were made on the metal bonds, especially on the δ metal bonds, by F. A. Cotton and other workers.¹⁻⁵ In addition, the theory of hybrid orbitals was used by L. Pauling⁶ to describe the electronic configurations of the metal bonds. But so far, the investigations of δ metal bonds have basically been limited to d orbitals and researches into the role of f orbitals in the δ metal bonds have hardly been reported. In the present paper, calculations are made on some δ metal bonds using the EHMO program containing f orbitals.^{7,8} By employing our proposed method of evaluating σ , π and δ hybrid orbitals^{9,10} and investigating the changes of the δ electronic densities and the mean kinetic energies between two metal atoms, we shall show the influence of the f orbitals on the δ metal bonds.

CALCULATION

The Slater-type orbitals are used in the present EHMO calculations. The s, p and d orbitals exponents of the metal atoms used in the calculations are taken as the best

atom values given by E. Clementi¹¹ and their ionization potentials are taken from the literature.^{12,13} Since the EHMO parameters of the f orbitals are not easily determined by experiments, their orbital exponents and ionization potentials have to be estimated approximately.

Having analyzed the 4s, 4p, 4d and 4f orbital exponents given by E. Clementi, we discovered that the ratios between the orbital exponents with the different azimuthal quantum numbers, ξ_{nl1}/ξ_{nl2} , increased linearly as the nuclear charges Z gradually increased. As a result, linear regression equations can be used to describe these correlations. The linear regression equations, the correlation coefficients r and the standard errors s are given in Table I. It can be seen from Table I that it is a good approach to employ the linear regression equations to describe the correlations between the orbital exponents. In the present calculations on orbital exponents, the correlation between the d and f orbital exponents is used to compute the 4f orbital exponents of the Mo and Tc atoms. For the W and Re atoms, we assume their correlation between the d and f orbital exponents to be the same as that of the Mo and Tc atoms since the valence electrons of W and Re are equal to those of Mo and Tc, respectively. Thus, the f orbital exponents of Mo, Tc, W and Re are 2.0561, 2.1558, 2.2130 and 2.3272, respectively.

Since the ionization potentials of the f orbitals of the Mo, Tc, W and Re atoms are not known, they have to be estimated approximately. Let us suppose that the inner

TABLE I
Linear regressions of the Clementi orbital exponents

Type	Linear regression eqn.	r	s
4p/4s	$Y = 0.8587 + 0.0016Z$	0.9247	0.0078
4d/4s	$Y = 0.5342 + 0.0053Z$	0.9662	0.0163
4f/4s	$Y = 0.0637 + 0.0107Z$	0.9859	0.0121
4d/4p	$Y = 0.6471 + 0.0040Z$	0.9670	0.0122
4f/4p	$Y = 0.1032 + 0.0104Z$	0.9862	0.0116
4f/4d	$Y = 0.3039 + 0.0085Z$	0.9793	0.0116

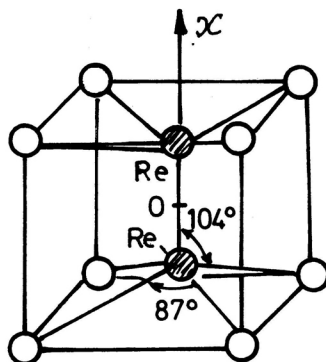


Figure 1. The structure of $\text{Re}_2\text{Cl}_8^{2-}$.

electron configuration of an atom does not change when an electron transits from d orbitals to f orbitals. Then, the difference between the total atomic energy, $E(d^{n-1}f')$, of the excited state and that of the bound state $E(d^n)$ is equal to that between the f and d orbitals $\Delta E_{d \rightarrow f}$, that is

$$\Delta E_{d \rightarrow f} = E(d^{n-1}f') - E(d^n) \quad (1)$$

According to ref. 14, the $E(d^{n-1}f')$ and $E(d^n)$ in the above equation can be evaluated approximately by the use of screening constants and effective quantum numbers. Therefore, if the ionization potentials of the d orbitals I_d are given, those of the f orbitals I_f can easily be estimated by employing the following equation

$$I_f = I_d - \Delta E_{d \rightarrow f} \quad (2)$$

The I_d , $\Delta E_{d \rightarrow f}$ and I_f of Mo, Tc, W and Re are listed in Table II.

By using the above EHMO parameters, some metal-metal quadruple bond compounds with the D_{4h} symmetry M_2L_n ($M = \text{Mo, Tc, W and Re}$) are calculated. The metal bond lengths are taken from ref. 15. The metal bond axis is taken as the X-axis and its centre as the origin point (see Figure 1.). As for the calculations on the d-f hybrid orbitals, because the method has been reported in our previous work (see refs. 9 and 10), it is not described in detail again. All the results are listed in Table III and IV.

TABLE II

Ionization potentials of the f orbitals of Mo, Tc, W and Re atoms

Atoms	I_d (eV)	$\Delta E_{d \rightarrow f}$ (eV)	I_f (eV)
Mo	10.5	6.56	3.94
Tc	12.8	8.87	3.93
W	10.37	6.09	4.28
Re	12.66	8.25	4.41

TABLE III

d-f hybrid orbitals forming δ bonds and the normalized constants of δ localized molecular orbitals

Molecule	Hybrid orbitals	Nh	Nd
$\text{Mo}_2\text{Cl}_8^{4-}$	$0.9830\varphi_{d_{yz}} + 0.1836\varphi_{f_{xyz}}$	0.6947	0.7043
$\text{Tc}_2\text{Cl}_8^{2-}$	$0.9812\varphi_{d_{yz}} + 0.1930\varphi_{f_{xyz}}$	0.6964	0.7049
$\text{W}_2\text{Cl}_8^{4-}$	$0.9316\varphi_{d_{yz}} + 0.3635\varphi_{f_{xyz}}$	0.6787	0.7038
$\text{Re}_2\text{Cl}_8^{2-}$	$0.9300\varphi_{d_{yz}} + 0.3676\varphi_{f_{xyz}}$	0.6819	0.7045
$\text{Mo}_2(\text{CH}_3)_8^{4-}$	$0.9991\varphi_{d_{yz}} + 0.0424\varphi_{f_{xyz}}$	0.7025	0.7043
$\text{Tc}_2(\text{CH}_3)_8^{2-}$	$0.9629\varphi_{d_{yz}} + 0.2699\varphi_{f_{xyz}}$	0.6945	0.7049
$\text{W}_2(\text{CH}_3)_8^{4-}$	$0.9990\varphi_{d_{yz}} + 0.0447\varphi_{f_{xyz}}$	0.7015	0.7038
$\text{Re}_2(\text{CH}_3)_8^{2-}$	$0.9568\varphi_{d_{yz}} + 0.2907\varphi_{f_{xyz}}$	0.6881	0.7038
$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$	$0.9991\varphi_{d_{yz}} + 0.0424\varphi_{f_{xyz}}$	0.7029	0.7038
$\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$	$0.9813\varphi_{d_{yz}} + 0.1925\varphi_{f_{xyz}}$	0.6948	0.7046
$\text{W}_2(\text{O}_2\text{CCH}_3)_4$	$0.9992\varphi_{d_{yz}} + 0.0400\varphi_{f_{xyz}}$	0.7021	0.7032
$\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$	$0.9826\varphi_{d_{yz}} + 0.1857\varphi_{f_{xyz}}$	0.6931	0.7042
$\text{Mo}_2(\text{SO}_4)_4^{4-}$	$0.9989\varphi_{d_{yz}} + 0.0469\varphi_{f_{xyz}}$	0.7033	0.7040
$\text{Re}_2(\text{SO}_4)_4^{2-}$	$0.9868\varphi_{d_{yz}} + 0.1619\varphi_{f_{xyz}}$	0.7042	0.7047

TABLE IV

 δ overlap integrals and bond strengths and δ electronic densities at the centres of metal bonds

Molecule	Ph	Pd	Sh	Sd	BSh	BSd
$\text{Mo}_2\text{Cl}_8^{4-}$	0.051	0.013	0.0360	0.0081	2.684	2.236
$\text{Tc}_2\text{Cl}_8^{2-}$	0.044	0.010	0.0308	0.0062	2.705	2.236
$\text{W}_2\text{Cl}_8^{4-}$	0.122	0.016	0.0855	0.0093	3.045	2.236
$\text{Re}_2\text{Cl}_8^{2-}$	0.109	0.013	0.0752	0.0073	3.052	2.236
$\text{Mo}_2(\text{CH}_3)_8^{4-}$	0.020	0.013	0.0131	0.0081	2.346	2.236
$\text{Tc}_2(\text{CH}_3)_8^{2-}$	0.064	0.010	0.0366	0.0062	2.867	2.236
$\text{W}_2(\text{CH}_3)_8^{4-}$	0.024	0.016	0.0161	0.0093	2.352	2.236
$\text{Re}_2(\text{CH}_3)_8^{2-}$	0.099	0.017	0.0560	0.0095	2.909	2.236
$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$	0.023	0.016	0.0121	0.0094	2.346	2.236
$\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$	0.050	0.012	0.0357	0.0072	2.704	2.236
$\text{W}_2(\text{O}_2\text{CCH}_3)_4$	0.027	0.019	0.0143	0.0111	2.340	2.236
$\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$	0.055	0.014	0.0408	0.0082	2.688	2.236
$\text{Mo}_2(\text{SO}_4)_4^{4-}$	0.023	0.015	0.0109	0.0087	2.358	2.236
$\text{Re}_2(\text{SO}_4)_4^{2-}$	0.043	0.012	0.0082	0.0068	2.635	2.236

In Table III, Nd and Nh represent the normalized constants of the δ localized molecular orbitals which are formed by the d orbitals and the d-f hybrid orbitals of the metal atoms, respectively. In the calculation on both Nd and Nh, it has been assumed that the δ metal bonds can be well localized. In Table IV, Sd and Sh represent the δ overlap integrals of the d orbitals and the d-f hybrid orbitals of the metal atoms, the BSd and BSh their bond strengths¹⁶ (d: $\sqrt{5}$, f: $\sqrt{7}$) and the Pd and Ph their δ electronic densities in the planes perpendicular to the metal bonds and involving their centres, respectively.

DISCUSSION

The σ and δ overlap populations, M_σ and M_δ , of the metal-metal bonds obtained by the EHMO method and the ratios, M_σ/M_δ , between them are listed in Table V. It is known that overlap populations can be used to describe chemical bonds. It is, therefore, shown by the data in Table V that the metal bonds in the metal-metal quadruple bonds compounds with the D_{4h} symmetry are proved to have the δ nominal bonds although the EHMO approach without introduction of configuration interaction has been employed. In addition, we also make calculations on the staggered configurations on these compounds. The results indicate that the δ overlap populations of their metal-metal bonds are about zero. Therefore, they do not have the δ metal bonds. This conclusion is in accord with our previous work.¹⁰

It can be seen from Table III that the δ metal-metal bonds are formed partly by overlap of the f orbitals although the d characters in the δ bonds are larger than the f characters. Consequently, the δ bonds are yielded by the d-f hybrid orbitals of the metal atoms. In what follows, we shall show that the f orbitals play an important part in the δ metal-metal bonds.

Because of the influence of the f orbitals on the δ bonds, first of all, the δ electronic densities between the metal atoms are larger than those without the f orbitals involved in the δ bonds. Let the δ localized molecular orbitals be $\Psi_\delta = N(\varphi_a + \varphi_b)$ where the φ_a and φ_b are the d orbitals or the d-f hybrid orbitals of the A and B metal

TABLE V
 σ and δ overlap populations and ratios between them

Molecule	M σ	M δ	M δ /M σ
Mo ₂ Cl ₈ ⁴⁻	0.226	0.016	0.071
Tc ₂ Cl ₈ ²⁻	0.198	0.011	0.056
W ₂ Cl ₈ ⁴⁻	0.259	0.017	0.066
Re ₂ Cl ₈ ²⁻	0.230	0.012	0.052
Mo ₂ (CH ₃) ₈ ⁴⁻	0.227	0.023	0.101
Tc ₂ (CH ₃) ₈ ²⁻	0.202	0.017	0.084
W ₂ (CH ₃) ₈ ⁴⁻	0.248	0.023	0.093
Re ₂ (CH ₃) ₈ ²⁻	0.227	0.013	0.057
Mo ₂ (O ₂ CCH ₃) ₄	0.242	0.019	0.079
Tc ₂ (O ₂ CCH ₃) ₄ Cl ₂	0.120	0.011	0.092
W ₂ (O ₂ CCH ₃) ₄	0.273	0.022	0.081
Re ₂ (O ₂ CCH ₃) ₄ Cl ₂	0.173	0.015	0.087
Mo ₂ (SO ₄) ₄ ⁴⁻	0.233	0.020	0.086
Re ₂ (SO ₄) ₄ ²⁻	0.210	0.015	0.071

atoms, respectively. Thus, the distribution functions, P(x), of the δ electronic densities along the X-axis (the metal bond axis) are given by

$$P(x) = 2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} |\Psi_{\delta}|^2 dydz = 2N^2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (\varphi_a + \varphi_b)^2 dydz \quad (3)$$

In the light of eqn. (3), the P(x) of the δ metal bonds yielded by the d orbitals and the d-f hybrid orbitals of the metal atoms are calculated at the centres of the metal bonds (see Pd and Ph in Table IV). As seen, when there are the f characters in the δ bonds, the δ electronic densities increase. Further, let us observe the distributions of the δ electronic densities between the metal atoms. For example, for Re₂Cl₈²⁻, the P(x) are given by the following data

x(a.u.)	-3.6	-2.8	-2.1	-1.8	-1.5	-0.8	0.0	0.8	1.5	1.8	2.1	2.8	3.6
P(x) _d	0.04	0.37	0.65	0.58	0.38	0.08	0.01	0.08	0.38	0.58	0.65	0.37	0.04
P(x) _{d-f}	0.00	0.15	0.53	0.62	0.54	0.25	0.11	0.25	0.54	0.62	0.53	0.15	0.00

where P(x)_d and P(x)_{d-f} are the P(x) of the δ bonds formed by overlap of the d orbitals and the d-f hybrid orbitals of the Re atoms, respectively. Figure 2 represents the distribution curves of P(x)_d and P(x)_{d-f}.

It is demonstrated by the above data and Figure 2 that, compared with that of the δ bond yielded by their d orbitals, the electronic density of the δ bond yielded by the d-f hybrid orbitals of the Re atoms is large between the Re atoms.

Now let us observe the change of the mean kinetic energy, \bar{T}_x , of an electron along the x-axis. The \bar{T}_x has the following form

$$\bar{T}_x = 1/2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left| \frac{\partial \Psi_{\delta}}{\partial x} \right|^2 dydz \quad (4)$$

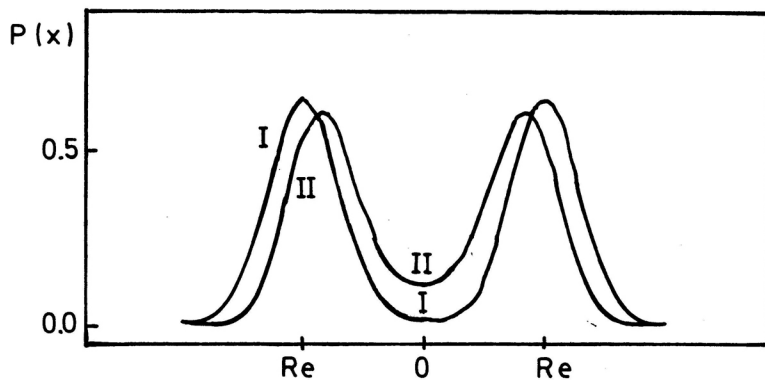


Figure 2. The distribution curves of the δ electronic density, $P(x)$, of $\text{Re}_2\text{Cl}_8^{2-}$ along the Re-Re bond. Curves I and II represent, respectively, the electronic density distributions of the δ bonds formed by the d orbitals and the d-f hybrid orbitals of Re.

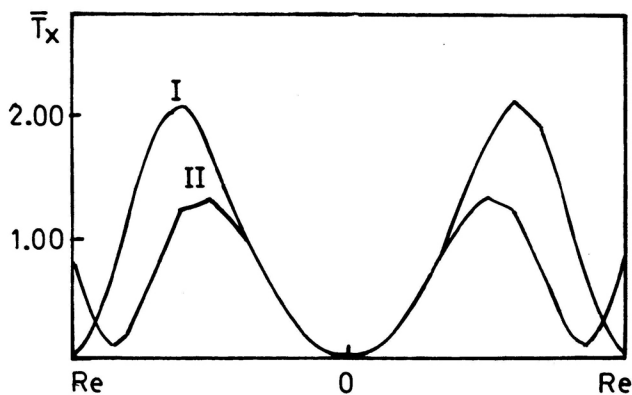


Figure 3. The distribution curves of the mean kinetic energy, \bar{T}_x , of the δ electron of $\text{Re}_2\text{Cl}_8^{2-}$ between the Re atoms. Curves I and II represent the mean kinetic energy distributions of the electrons occupying the δ MO yielded by the d orbitals and the d-f hybrid orbitals of Re, respectively.

For the Re-Re bond of $\text{Re}_2\text{Cl}_8^{2-}$, the \bar{T}_x between the Re atoms are

$x(\text{a.u.})$	-2.1	-1.7	-1.3	-1.1	-0.6	0.0	0.6	1.1	1.3	1.7	2.1
$T_{x,d}$	0.00	1.17	2.13	1.79	0.66	0.00	0.66	1.79	2.13	1.17	0.00
$T_{x,d-f}$	0.84	0.20	1.23	1.34	0.70	0.00	0.70	1.34	1.23	0.20	0.84

where \bar{T}_x are given in terms of eV.

Figure 3 is the distribution graph of the $\bar{T}_{x,d}$ and $\bar{T}_{x,d-f}$. Obviously, under the influence of the f orbitals of Re on the δ metal bond, the mean kinetic energy of the δ electron decreases. Because of this, the probability of the δ electrons discovered be-

tween the Re atoms increases. It seems that the δ electrons form an electronic bridge between two Re atoms which makes the Re-Re bond more stable.

In addition, since the f orbitals have an effect on the δ metal bonds, the δ overlap integrals and the bond strengths of the d-f hybrid orbitals of the metal atoms are all larger than those of their d orbitals.

Finally, it must be pointed out that the electronic spectra (cm^{-1}) evaluated by us using the EHMO method, when a δ electron transits from a δ bonding MO to a δ antibonding MO, are smaller than the experiments because the EHMO results depend mostly on the EHMO parameters, especially on the d orbital exponents of transition metal atoms. Nevertheless, the results calculated by employing the δ MO formed by the d-f hybrid orbitals of the metal atoms instead of their d orbitals are better. This is because addition of the f orbitals to the basis set results in a decrease in the energies of the δ bonding molecular orbitals, compared with the results for a basis set having only s, p and d atomic orbitals. For example, for $\text{Mo}_2\text{Cl}_8^{4-}$, $E_d - E_{df} = 0.027$ eV and, for $\text{Re}_2\text{Cl}_8^{2-}$, $E_d - E_{df} = 0.03$ eV.

As before, under the influence of f orbitals, the densities of the δ electrons between two metal atoms increase and their mean kinetic energies decrease although the f orbitals in the δ bonds are small in character. These are of importance to the stability in the δ bonds.

REFERENCES

1. F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Bonds*, Wiley, New York, 1982.
2. J. L. Templeton, *Progr. Inorg. Chem.* **26** (1979) 211.
3. F. L. Campbell III, F. A. Cotton, and G. L. Powell, *Inorg. Chem.* **24** (1985) 177.
4. D. L. Lichtenberger and C. H. Blevins II, *J. Amer. Chem. Soc.* **106** (1984) 1636.
5. J. G. Norman, Jr. and H. J. Kolari, *J. Amer. Chem. Soc.* **97** (1975) 33.
6. L. Pauling, *Proc. Nat. Acad. Sci. US* **72** (1975) 3799, 4200.
7. C. Yang, L. Ming, and C. Guoxian, *Chem. Phys.* **103** (1986) 111.
8. C. Yang, C. Guoxian, and L. Ming, *Computers and Applied Chem.* **3** (1986) 219, (in Chinese).
9. L. Ming, *Int. J. Quantum Chem.* **38** (1990) 597.
10. L. Ming and C. Yang, *J. Mol. Struct.* **205** (1990) 167.
11. E. Clementi, D. L. Riamondi, and W. P. Reinhardt, *J. Chem. Phys.* **47** (1967) 1300.
12. R. H. Summerville and R. Hoffmann, *J. Amer. Chem. Soc.* **98** (1976) 7240.
13. H. Berke and R. Hoffmann, *J. Amer. Chem. Soc.* **100** (1978) 7224.
14. X. Guangxian and Z. Xuezhuan, *Acta Chem. Sinica (China)* **22** (1956) 441, (in Chinese).
15. X. Sifen, *Inorganic Chemistry — Introduction to New Fields*, Beijing University Press, Beijing, 1988, (in Chinese).
16. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1960.

SAŽETAK

Utjecaj f-orbitala na δ veze metala

Li Ming i Shan Zian

Pokazano je da d-f hibridi igraju važnu ulogu u ostvarivanju δ -veza metalnih atoma. Primjese f-orbitala povećava elektronsku gustoću između atoma metala i smanjuje prosječnu kinetičku energiju elektrona.