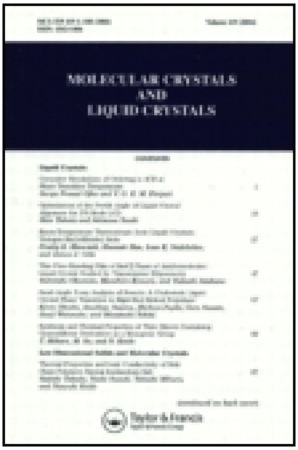

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theoretical Studies of Direct Exchange Couplings Between Transition Metal Ions II. Tetranuclear Transition Metal Systems

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Version of record first published: 04 Oct 2006.

To cite this article: Masamichi Nishino , Mitsuhiro Tanaka , Sadamu Takeda , Kazushi Mashima , Wasuke Mori , Kazuhide Tani , Akira Nakamura & Kizashi Yamaguchi (1996): Theoretical Studies of Direct Exchange Couplings Between Transition Metal Ions II. Tetranuclear Transition Metal Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 201-210

To link to this article: http://dx.doi.org/10.1080/10587259608042287

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 201–210
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THEORETICAL STUDIES OF DIRECT EXCHANGE COUPLINGS BETWEEN TRANSITION METAL IONS II. TETRANUCLEAR TRANSITION METAL SYSTEMS

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Abstract The model clusters for the tetranucler transition metal complexes synthesized by Mashima et al. were investigated theoretically. The ab-initio UHF calculations were performed for the Ni-Cr(II)-Cr(II)-Ni and Pd-Mo(II)-Mo(II)-Pd systems to study the nature of the intermetallic bonds. The bond orders and the effective exchange integrals were calculated changing the intermetallic bond distances. It is shown that the tetranuclear dσ-bonds are formed in the cases: Ni(I) and Pd(I).

INTRODUCTION

Low dimensional materials of transition metal complexes have been investigated in relation to their application for optoelectronic materials[1,2] liquid crystal[3,4] and conduction materials.[5] The interaction between organic axial ligands and quadruply bonded metal atoms has been widely investigated by F. A. Cotton and co-workers.[6,7] In these systems, the electronic conjugation between the d- and p-electrons plays an important role for controlling the strength of the metal-metal quaduple bonds.

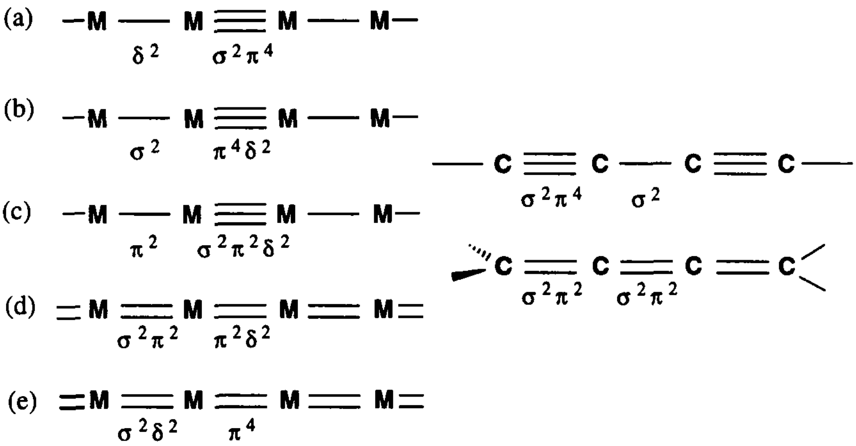
On the other hand, if transition metal atoms are used as conjugated partners at the axial position in the quadruply bonded systems, these systems would be expected to have interesting properties because of the d-d orbital interactions. Very recently, Mashima et al.[8,9] indeed synthesized the linear tetranuclear transition metal complexes:M'-M-M-M'

(M'=Pd or Pt and M=Cr(II) or Mo(II)). The magnetic measurements and solid state NMR spectroscopy [10] of these compounds have revealed that the direct exchange couplings between Cr(II) ions become weak because of the Cr(II)-M' interactions.

In order to construct the linear linkage of the multiply-bonded M-M moiety with the conjugated M-M' bonds, it is important to clarify the axial coordination effect of metal atoms M' to the Cr(II)-Cr(II) or Mo(II)-Mo(II) multiple bond. Thus elucidation of the nature of tetranuclear d-d-conjugated systems is of basic interest, together with several technological applications. As a continuation of the preceding paper (hereafter part I),[11] ab-initio UHF calculations will be performed here.

THEORETICAL BACKGROUNDS

First, let us theoretically consider what kinds of bonding patterns are feasible in the tetranuclear transition metal-metal conjugated systems. Since quadruply-bonded dinuclear complexes such as $Mo_2(pyphos)_4$ (pyphos = 6-(diphenylphosphino)-2-pyridonate) have one σ–bond, two π–bonds, and one δ–bond,[11] these four kinds of metal-metal bonding make it possible for us to anticipate a wide variety of tetranuclear conjugation systems. FIGURE I shows possible linear chains compounds with conjugated metal-metal bonds, together with possible organic analogs.

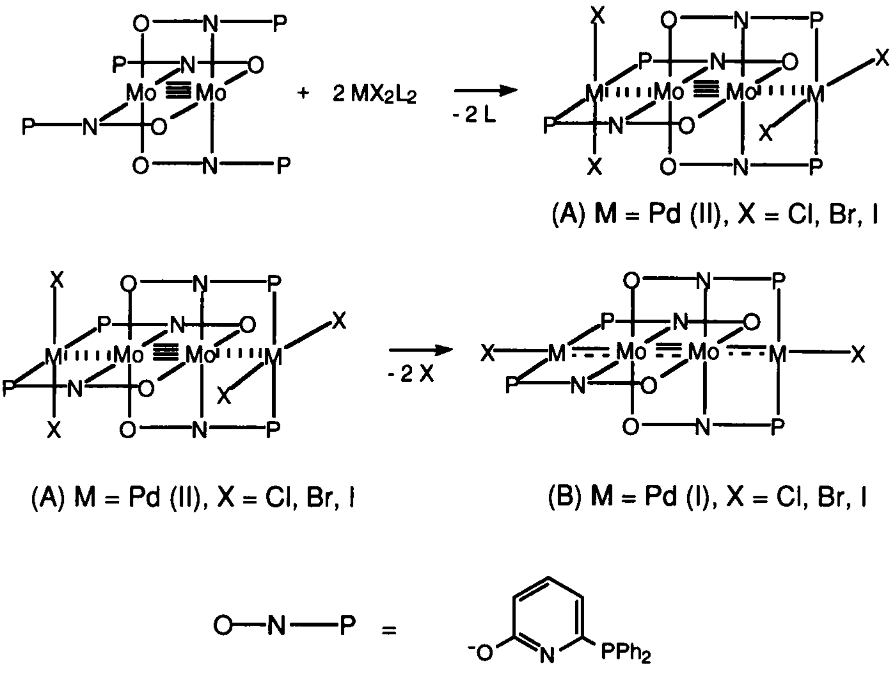


(A) organometallic sytems (B) organic sytems

FIGURE 1 Possible linear tetranuclear transition-metal complexes (A) and isoelectrc organic systems (B)

From FIGURE 1, three different metal-metal single bonds (σ^2, π^2 and δ^2) are feasible between the axitial metal ligand and the central Cr(II) (or Mo(II)) ion. The metal-metal double bonds are also possible if axial transition metals have two unpaired electrons. These bonding features can be easily understood from their organic analogs.

Synthesis of linear tetranuclear complexes in FIGURE 1 has been a challenging and interesting problem. Very recently, Mashima et al.[8,9] really synthesized the multiply-bonded linear tetranuclear transition metal complexes: $Mo_2Pd_2Cl_2(pyphos)_4$[8] (I) and $Mo_2Pd_2Cl_4(pyphos)_4$[9] (**II**) and determined their constructions experimentally as shown in FIGURE 2. **I** is composed of a straight linear Cl-Pd(I)-Mo(II)-Mo(II)-Pd(I)-Cl and four pyphos. **II** is composed of a straight linear Pd(II)-Mo(II)-Mo(II)-Pd(II), four pyphos and four chloride ions. It was found that the distance Mo(II)-Pd(I) is shorter than that of Mo(II)-Pd(II) by more than 0.2Å and the distance Mo(II)-Mo(II) in Pd(I)-Mo(II)-Mo(II)-Pd(I) is longer than that in Pd(II)-Mo(II)-Mo(II)-Pd(II). This result clearly indicates that the σ-bond can be formed between Mo(II) and Pd(I).



(A) M = Pd (II), X = Cl, Br, I

(A) M = Pd (II), X = Cl, Br, I

(B) M = Pd (I), X = Cl, Br, I

FIGURE 2 Molecular structures of the tetranuclear transition metal complexes : (A) coordination bond between Mo(II) and M(II); (B) covalent bond between Mo(II) and M(I).[8, 9]

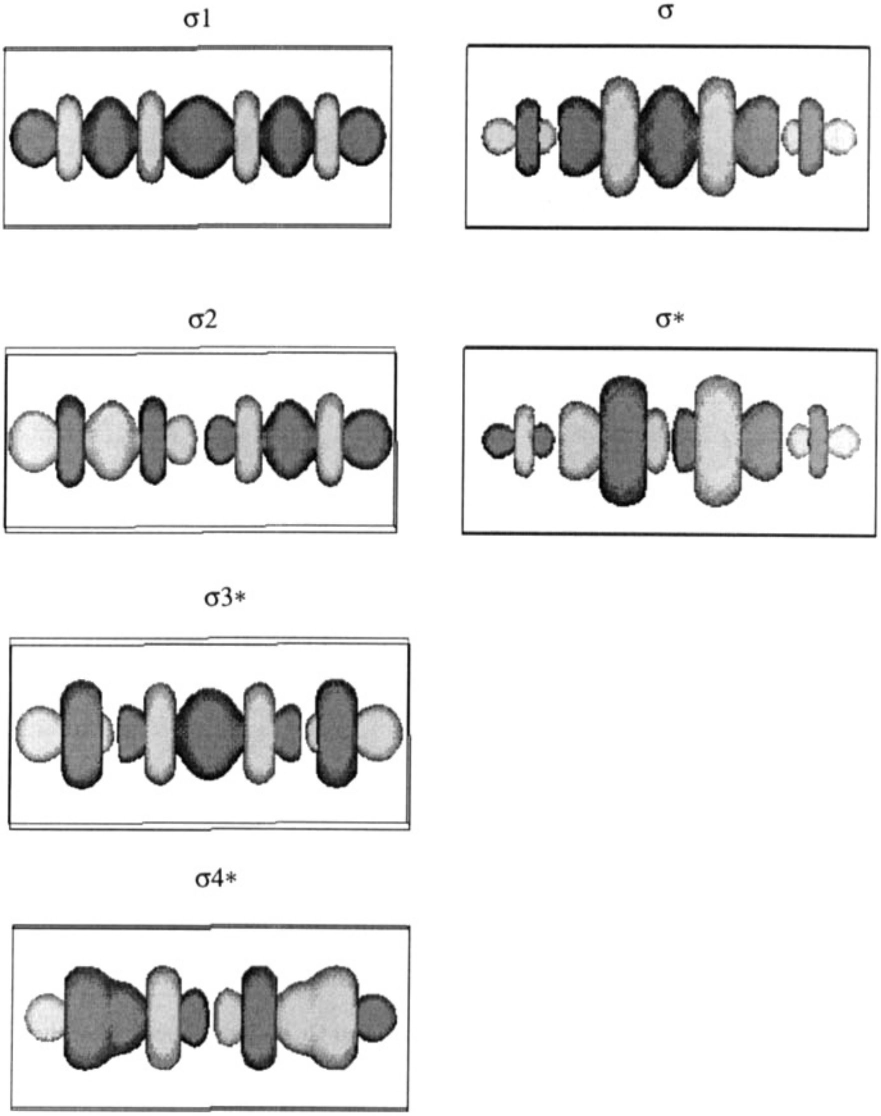
AB INITIO CALCULATIONS

In order to elucidate the nature of conjugated d-d bonds, the ab-initio MO calculations were performed for the model systems without ligands, i.e,Ni-Cr(II)-Cr(II)-Ni (**1**) and Pd(I)-Mo(II)-Mo(II)-Pd(I) (**2**) because of computational economy. We first determined the natural orbitals and their occupation numbers for elucidation of the conjugated d-d bonds. Next, we also examined variations of the effective bond orders and the effective exchange integrals for **1a** (Ni=Ni(II)), **1b** (Ni=Ni(I)) and **2**, changing the Cr(II)-Cr(II) and Mo(II)-Mo(II) intermetallic bond distances. On the other hand, the distance of Cr(II)-Ni was fixed to be 2.00 Å throughout the elongation of the metal-metal bond of **1**. Similarly, the Mo(II)-Pd(I) distance was fixed at 2.698 Å , which was the experimental value for the complex **I**. The computational methods used here have been explained in part I in this series.[11] The ab initio UHF calculations for **1** were carried out using [5333/533/5] (this is referred to as BS) and [533(21)/53(21)/(41)+ diffuse d(α=0.0912)] (BSI), whereas they were performed for **2** using basis [43333/4333/43]. (BSII).

CALCULATED RESULTS AND DISCUSSIONS

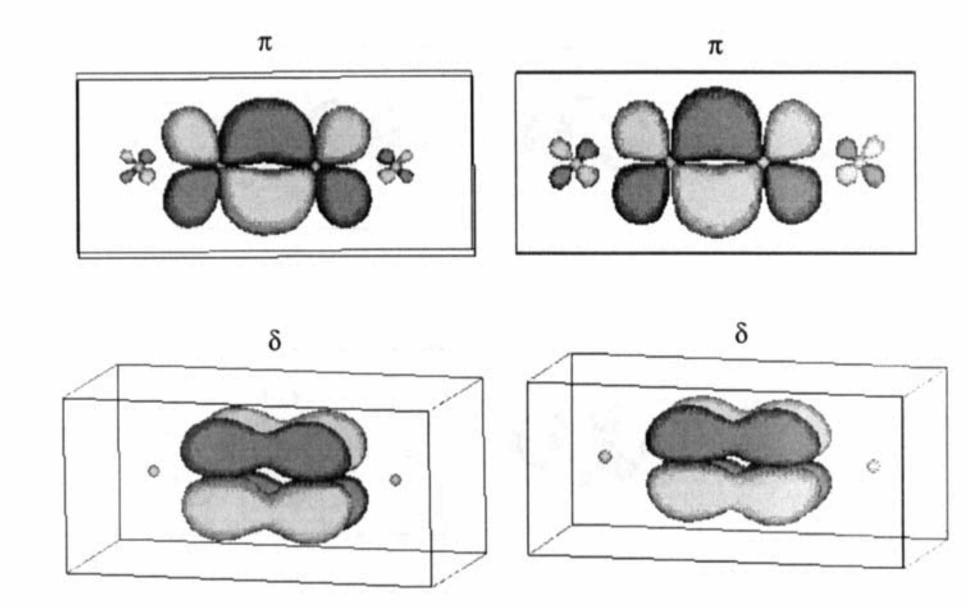
(A) Orbital Interactions and Delocalized σ-Bonds

FIGURE 3 illustrates the natural molecular orbitals obtained for the singlet ground state of **1a** and **1b** by the UHF/BSI method. From FIGURE 3, the σ-bonding and -antibonding molecular orbitals (MO) for the Cr(II)-Cr(II) core in **1a** have small dz^2-type tails on the Ni(II) atoms, showing that weak coordination bonds are formed between the dz^2-type lone-pair orbital of Ni(II) and the σ-MO of the core. This in turn indicates that the strong σ-bond between Ni(II) and Cr(II) cannot be formed because of the exchange repulsion if the axial Ni(II) ion has the octahedral ligand field as can be recognized from FIGURE 2. On the other hand, the four σ-type molecular orbitals (MO) are constructed of the four dz^2-type atomic orbitals (AO) in the case of **1b** as shown in FIGURE 3, since the Ni(II) ion with the square planar configuration provides the dz^2 -type unpaired electron for covalent-bond formation. The $\sigma 1$ and $\sigma 2$ orbitals are the bonding MOs with the zero- and one-nodes, respectively, whereas the $\sigma 3^*$ and $\sigma 4^*$ orbitals are the antibonding MOs. The orbital interaction schemes between $d\sigma$-type AOs in **1b** are quite similar in the $p\pi$-type AO interactions in butadiene.



(B) Ni(I)-Cr(II)-Cr(II)-Cr(I): 1b **(A) Ni(II)-Cr(II)-Cr(II)-Ni(II): 1a**

FIGURE 3 The σ-type molecular orbitals for the linear tetranuclear transition-metal complexes **1a** and **1b**; (A) The σ and σ* illustrate the bonding and antibonding MOs in **1a** , respectively and (B) the four σ–type MOs in **1b**.



(B) Ni(I)-Cr(II)-Cr(II)-Ni(I): 1b **(A) Ni(II)-Cr(II)-Cr(II)-Ni(II):1a**

FIGURE 4 The π- and δ-type molecular orbitals for the linear tetranuclear transition-metal complexes **1a** (A) and **1b** (B).

FIGURE 4 illustrates the π- and δ-MOs in **1a** and **1b**. The π-MOs are almost the same between **1a** and **1b**, being essentially localized on the Cr(II)-Cr(II) core. The π-conjugation between the axial transition metal and Cr(II) ions is negligible in **1**.

(B) Occupation Numbers

The occupation numbers of the bonding σ1 and σ2 orbitals of **1b** in FIGURE 3 are 2.0 in the closed-shell picture. However, the occupation numbers of the antibonding σ3* and σ4* orbitals might not be negligible if the electron-electron interactions are considered explicitly:the formal bond orders are reduced significantly in this situation.[11] In order to determine the occupation numbers of these σ-MOs, the natural orbital analysis of the UHF/BSI solution for **1b** was carried out as previously.[11] Table 1 summarizes the calculated results. For comparative purpose, those of the molybdenum dimer **2**

TABLE I The occupation numbers of Ni(I)-Cr(II)-Cr(II)-Ni(I) (**1b**) by the projected UHF/BS method

R(Å)	σ1	σ2	σ3*	σ4*
1.500	1.94046	1.25779	0.74221	0.05954
2.000	1.81830	1.49982	0.50018	0.18170
2.389	1.80547	1.63906	0.36094	0.19453
2.400	1.80570	1.64254	0.35746	0.19430
2.500	1.80879	1.67311	0.32689	0.19121
3.000	1.84199	1.79387	0.20613	0.15801
3.500	1.88290	1.86860	0.13140	0.11710

TABLE II The occupation numbers of Pd(I)-Mo(II)-Mo(II)-Pd(I) (**2**) by the projected UHF/BSII method.

R(Å)	σ1	σ2	σ3*	σ4*
2.0000	1.9615	1.36286	0.63714	0.03848
2.0981	1.9474	1.41526	0.58474	0.05256
2.1208	1.9444	1.42677	0.57323	0.05564
2.5000	1.9103	1.60820	0.39180	0.08974
3.0000	1.7504	1.47283	0.52717	0.24961
3.5000	1.6451	1.50654	0.49346	0.35493

are summarized in TABLE II.

From TABLES I and II, the following conclusions are drawn:

(1) The occupation numbers of σ2 and σ3* MOs are 1.26 and 0.74, respectively at the Cr(II)-Cr(II) distance (R=1.5 Å) of **1b**, although those of σ1 and σ4* are almost 2.0 and 0.0, respectively. This indicates the strong mixing of HOMO and LUMO, giving rise to the open-shell character responsible for the localization of the dσ-electrons on the Ni(I) atom: the valence-bond (VB) structure of **1b** in this specific geometry is therefore given by

Ni(I)•......Cr(II)-Cr(II).....•Ni(I).

(2) The occupation numbers of σ1 and σ2 MOs are over 1.86 at R=3.5 Å of **1b**, where the Ni(I)-Cr(II) distance is assume to be 2.0 Å. Judging from these values, the strong covalent bonds are formed between Cr(II)-Ni(I), leading to the valence-bond

(VB) structure of **1b** given by

Ni(I)-Cr(II)......Cr(II)-Ni(I).

(3) The occupation numbers of σ2 and σ3* MOs are 1.36 and 0.64, respectively at the Mo(II)-Mo(II) distance (R=2.0 Å) of **2**, although those of σ1 and σ4* are almost 2.0 and 0.0, respectively. This indicates the strong mixing of the HOMO and LUMO : the valence-bond (VB) structure of **2** at the conformation is given by

Pd(I)•......Mo(II)-Mo(II).....•Pd(I).

(4) The occupation numbers of σ1 and σ2 MOs are about 1.51-1.65 at R=3.5 Å of **2**, where the Mo(II)-Pd(I) distance is assume to be 2.683 Å. The weak open-shell characters appear in the covalent bonds between Mo(II) and Pd(I) ions because of too long Mo-Pd distance, leading to the valence-bond (VB) structure of **2** given by

Pd(I)δ•.....•δ Mo(II)......Mo(II)δ•.....•δPd(I).

EFFECTIVE EXCHANGE INTEGRALS

As shown in part I,[11] the Cr(II)-Cr(II) quadruple bond is rather weak even in the dinuclear chromium complexes.[6] Therefore, it might become very weak if the coordination bond is formed between the axial transition metal ion and Cr(II). In fact, the direct exchange integrals (J_{ab}) between Cr(II) ions are in the range; -8 - -80 cm^{-1} in the tetranuclear system **III** (Pt(II)-Cr(II)-Cr(II)-Pt(II)).[10] In order to elucidate the nature of the Cr(II)-Cr(II) bond in **III**, the ab initio UHF calculations were carried out for the model system: Ni(II)-Cr(II)-Cr(II)-Ni(II) (**1**) fixing the Cr(II)-Ni(II) distance. TABLE III summarizes the J_{ab} values calculated for **1** using both basis sets (BS and BSI).

From TABLE III, the J_{ab} values by the single zeta basis set (BS) become positive (ferromagnetic) if the Cr(II)-Cr(II) distance R is longer than 3Å, whereas they are negative (antiferromagnetic) in the whole region if the triple zeta basis set (BSI) is employed. Probably, the latter tendency is compatible with the experimental one.[11] The magnitude of J_{ab} by BSI decreases with the increase of R in an exponential manner. Therefore, the calculated J_{ab} value is only $|110|$ cm^{-1} at the experimental distance R=2.389 Å for **III**: it is noteworthy that the corresponding value is $|487|$ cm^{-1} at R=2.015 Å for the parent compound without the Pt(II) coordination.[11] Thus, the coordination of the dσ-lone pair of axial transition metal M' contributes to weaken the Cr(II)-Cr(II) σ-bond, although the weak Cr(II)-M' coordination bond is newly formed.

TABLE III The effective exchange integrals (J_{ab}) of Ni(I)-Cr(II)-Cr(II)-Ni(I) (**1a**) calculated by the UHF method

R(Å)	J_{ab}(BS)	J_{ab}(BSI)
1.5000	-3448.76286575795	-3679.2767917719
2.0000	-391.78629061789	-516.1748250803
2.0150	-364.22755393261	-487.2180276878
2.3890	-33.68910029409	-110.0498365043
2.5000	-7.30216850235	-68.6812876195
3.0000	7.69777446746	-7.5520685037
3.5000	0.80243401572	-0.7337127465

DISCUSSION AND CONCLUDING REMARKS

The ab initio MO calculations of the model systems, i.e. Ni-Cr(II)-Cr(II)-Ni (**1**) and Pd(I)-Mo(II)-Mo(II)-Pd(I) (**2**) have elucidated possible difference in bonding features which can be controlled by the ligand fields in the tetranuclear transition metal complexes synthesized by Mashima et al.[8,9] The natural molecular orbitals by these calculations in FIGURES 3 and 4 have clearly demonstrated that the dσ-bonds in **1b** (Ni=Ni(I)) should be delocalized over the whole skeleton. However, the occupation numbers for the anti-bonding σ-orbitals ($\sigma 3^*$ and $\sigma 4^*$) are quite large, showing that electron localizations occur considerably because of the electron correlation effect. Namely, the formal bond orders are significantly reduced by the effect.[11] This in turn indicates that the nature of the conjugated d-d σ-bonds is variable, depending on the kinds of transition metals and ligands employed. Probably, such correlation effect should be much more important in the double bond systems in FIGURE 1. Therefore, further theoretical studies are essential for several model complexes having realistic ligands.

The hole or electron doping into conjugated π-electron systems in FIGURE 1 has received continuous interest in relation to conductivity and nonlinear optical responses.[12] Judging from the strength of the electron correlation effect in the tetranuclear transition metal model systems examined here, such modifications of the electronic states of the systems in FIGURE 1 and 2 are particularly interesting from the same reason. Further theoretical studies are inevitable for elucidation of possible electronic states in hole or electron doped metal-metal bonds.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No.06101004). Ab initio calculations have been carried out on the IBM RS/6000 workstations by using the GAUSSIAN 94[13] program package.

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