Importance of Orbital Complementarity in Spin Coupling through Two Different Bridging Groups in Dicopper(II) Complexes of Endogenous Alkoxo Bridging Ligand with Exogenous Carboxylate: *Ab-initio* and Semi-Empirical Calculations

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The influence of overlap interactions between the bridging ligands and the metal d orbitals on the super-exchange coupling constant are studied by means of *ab-initio* restricted Hartree-Fock molecular orbital calculations. The interaction between the magnetic d orbitals and the HOMOs of the carboxylate oxygen atoms are investigated in homologous asymmetrically dibridged dicopper(II) complexes which have significantly different $-2J$ values (the energy separation between the spin-triplet and spin-singlet states). In order to determine the nature of the fronter orbitals, extended Hückel molecular orbital (EHMO) calculations are also reported. The differences in the magnitude of the coupling constants and magnetic behaviour are rationalized in terms of the bridging ligand orbital complementary / countercomplementary concept.

Key words: Dinuclear Copper(II) Complex; Antiferromagnetic Coupling; *Ab-initio* Calculations; Molecular Orbitals; Orbital Complementary.

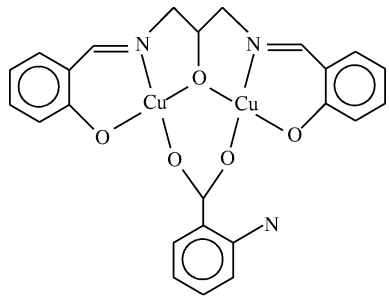
1. Introduction

Polynuclear copper(II) complexes have intensively been investigated during the last two decades. This is partly due to their relevance as active site structures of metalloproteins [1, 2], and partly because of attempts to understand the relationship between the structure and the magnetic properties [3 – 8].

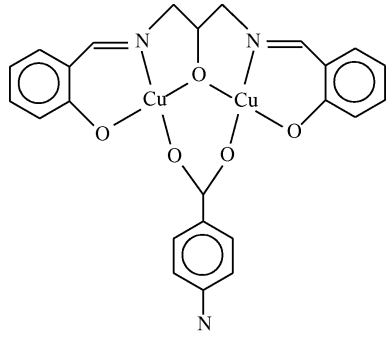
Empirical studies of the structural and magnetic properties of dicopper(II) complexes have shown some interesting magneto-structural correlations. In bis(μ-hydroxo)- and bis(μ-alkoxo)-bridged binuclear copper(II) complexes, Hatfield and Hodgson [9, 10] observed an increase in the strength of antiferromagnetic coupling with increasing Cu-O-Cu bridging angle. However, this rule is only valid in doubly bridged systems with the Cu-O-Cu angle in the range 90 – 105° [9] and in single alkoxide- or hydroxide-bridged compounds with larger Cu-O-Cu angles (120 – 135°) [11, 12]. The magnetostructural properties of binuclear copper(II) complexes which contain a second bridging ligand such as acetate or azide ions have also received considerable attention [13 – 15]. Detailed analysis results in the linear correlation between the Cu-O-Cu angle and the singlet-triplet exchange parameter J established by Hodgson [10], who proposed: $J = -74.53\varphi + 7270\,\mathrm{cm}^{-1}$, in which φ is the Cu-O-Cu angle. Several theoretical calculations were performed to better understand this correlation [16, 17], and theoretical approaches were applied to understand the nature of the ferromagnetic / antiferromagnetic interaction [18]. When a second bridging group is added to the system, the antiferromagnetic interaction is weakened or enhanced. This may show that the presence of the second bridging ligand influences the strength of the antiferromagnetic interaction. This fact has been explained, based on Hoffman's theory [19]. Accordingly the different bridging ligands can act in a complementary or countercomplementary way to enhance or attenuate the strength of the super-exchange interaction as a result of differences in symmetries of the magnetic orbitals.

Recently Mukherjee et al. reported the crystal structures, spectral and magnetic properties of asymmetrically dibridged analogous (μ-alkoxo)(μ-carboxylato) dicopper(II) Schiff base complexes containing *o*- and *p*-aminobenzoate ligands, [$Cu_2L(O_2CC_6H_4$-*o*-NH_2)] (**1**) and [$Cu_2L(O_2CC_6H_4$-*p*-NH_2)] (**2**), where L is the trianionic pentadentate Schiff base ligand *N*,*N*′-(2-hydroxypropane-1,3-diyl)bis(salicylal-

dimine) [20]. Very recently, the crystal structures and magnetic properties of the asymmetrically dibridged (μ-alkoxo)(μ-acetato) and (μ-alkoxo)(μ-pyrazolate) dicopper(II) complexes $[Cu_2(L^1)(O_2CMe)] \cdot 1/2H_2O$, [$L^1$ = 1,3-bis(5-bromo-2-hydroxybenzlidene)propan-2-ol] (**3**) [8, 21], $[Cu_2(L^2)(O_2CMe)] \cdot 1/2H_2O$, [$L^2$ = 1,3-bis(5-chloro-2-hydroxybenzlidene)propan-2-ol] (**4**) [22], $[Cu_2(L^3)(O_2CMe)] \cdot H_2O$, [$L^3$ = 1,3-bis(2-hydroxy-1-naphthylideneamino)propan-2-ol] (**5**) [23], $[Cu_2(L^1)(3,5\ prz)]$ [L^1 = 1,3-bis(2-hydroxy-3,5-chlorosalicylideneamino)propan-2-ol] (**6**) [24], $[Cu_2(L^3)(3,5\ prz)]$ (**7**) [24, 25], $[Cu_2(L^4)(3,5\ prz)]$ (**8**) [24, 26], $[Cu_2(L^5)(3,5\ prz)]$ [L^5 = 1,3-bis(2-hydroxy-4-methoxybenzylideneamino)-propan-2-ol] (**9**) [24, 27] were also studied by our group. Antiferromagnetic interactions, which were observed for these complexes, show significant differences, although they have almost the same bridging ligands. In this paper we have studied the magnetostructural correlations for these and similar compounds by *ab-initio* restricted Hartree-Fock (RHF) molecular orbital calculations to explain the significant differences in antiferromagnetic interactions between homologous dibridged dicopper(II) complexes.



$[Cu_2L(O_2CC_6H_4\text{-}o\text{-}NH_2)]$ **(1)**



$[Cu_2L(O_2CC_6H_4\text{-}p\text{-}NH_2)]$ **(2)**

Fig. 1. Chemical structure of the compounds **1** and **2**.

2. Methodology

2.1. Methods and Programs

Ab-initio RHF molecular orbital calculations for the carboxylate ligands were carried out by using the GAUSSIAN-98 program [28]. STO-3G minimal basis sets [29] were adopted for carbon and oxygen atoms. Also the molecular orbital calculations were performed using the extended Hückel molecular orbital (EHMO) method [30, 31] for the determined HOMO-LUMO energy gap by using the CACAO program [32]. The structural parameters were obtained from X-ray analysis of the asymmetrically dibridged (μ-alkoxo)(μ-carboxylato) dicopper(II) complexes **1** and **2** (Fig. 1).

2.2. Theoretical Model and Qualitative Relationship

The sign and magnitude of the coupling constant is influenced by bridging ligands between the metal ions depending on the various types of overlap interactions between the metal d orbitals and the ligand orbitals. By symmetry, a given bridging ligand orbital generally interacts with one combination of magnetic orbitals, whether symmetric (d_s) or antisymmetric (d_a) in preference to the other combination. In the single μ-alkoxo- or μ-hydroxo-bridged dinuclear copper complexes, when the Cu-O-Cu angle is larger than 90° (120 – 135.5°), the d_a overlap with p_x is larger than the d_s overlap with p_y, so d_a and d_s split, as illustrated in Figure 2a. Thus, d'_a and d'_s gives a stronger antiferromagnetic interaction. In the presence of a second bridging ligand, d_a and d_s interact with antisymmetric (ψ_a) and symmetric (ψ_s) combinations of this ligand, respectively. This interaction forms new molecular orbitals d''_a and d''_s (Fig. 2b). A large energy separation of d'_a and d'_s leads to a strong antiferromagnetic interaction. In the presence of a second bridging ligand, either a complementary or a countercomplementary effect on the spin exchange interaction may arise due to further interactions of the symmetric (ψ_a) and antisymmetric (ψ_s) combinations with the d'_a and d'_s molecular orbitals. This interaction results in the formation of d''_a and d''_s (Fig. 2b).

The magnitude of the magnetic exchange parameter (J) may be determined according to Hoffmann's expression [19] (using $H = -2JS_1S_2$):

$$J = J_F + J_{AF} = -2K_{12} + \frac{[E(d''_a) - E(d''_s)]^2}{J_{11} - J_{12}}, \quad (1)$$

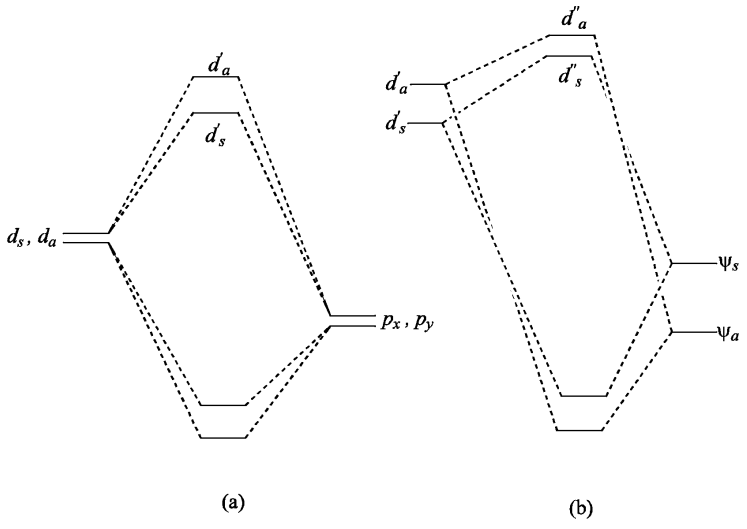


Fig. 2. Orbital energy level diagrams showing the interaction between the magnetic orbitals and bridging group orbitals: (a) for a single alkoxide- or hydroxide-bridged system; (b) for an additional bridging ligand.

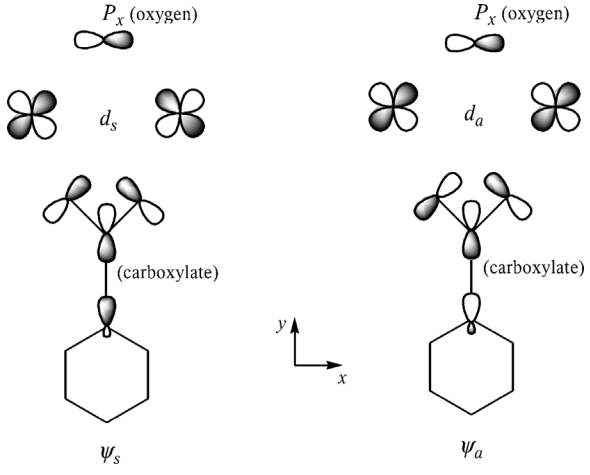


Fig. 3. Symmetric (ψ_s) and antisymmetric (ψ_a) combinations of metal and ligand orbitals.

where K_{12}, J_{11} and J_{12} are the exchange integral and one-centre and two-centre Coulomb repulsion integrals, respectively, and $E(d''_a)$ and $E(d''_s)$ are orbital energies of d''_a and d''_s, respectively. J can be written as the sum of two terms: J_F being the term defined by the exchange integral between the two localized molecular orbitals, which is always ferromagnetic, and J_{AF} comprising the difference in energy between the two molecular orbitals $[E(d''_a) - E(d''_s)]^2$. Since the denominator of the second term varies very little, and K_{12} is approximately constant for compounds with similar bridging structures, the energy difference between the antisymmetric (d''_a) and symmetric (d''_s) combinations of the magnetic orbitals (see Fig. 2b) is the determining factor for the magnitude of the coupling constant. The energy difference between two molecular orbitals $[E(d''_a) - E(d''_s)]$, which corresponds to the HOMO-LUMO energy gap, determines the magnitude of the antiferromagnetic interaction. A stronger antiferromagnetic interaction is expected for the system with the larger HOMO-LUMO energy gap. The numerator of the second term $[E(d''_a) - E(d''_s)]^2$ is proportional to the overlap integral between the magnetic orbitals. The overlap integrals of interacting orbitals are an important factor to increase or decrease the energy separation. If ψ_a overlaps more effectively with d_a than ψ_s with d_s, the overlap integrals of the interacting orbitals may affect the carboxylate bridge to act in a complementary fashion with the alkoxide bridge, and strong antiferromagnetic interactions arise (Fig. 3). Nishida and Kida [33] showed that the energies of d''_a and d''_s depend on two factors, the energy differences between the interacting orbitals, $E(d_a)$ and $E(\psi_a)$, $E(d_s)$ and $E(\psi_s)$, and the overlap integrals between the interacting orbitals, $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$.

2.3. Magnetostructural Correlations

Magnetostructural correlations have been established for dinuclear copper(II) complexes in the last two decades [34–37]. In general, dinuclear copper(II) complexes have several structural features to affect the strength of exchange coupling interactions, such as the dihedral angle between the two coordination planes, the planarity of the bonds around the bridging oxygen atom, the length of the copper-oxygen

bridging bonds, and the Cu-O-Cu bridging angle [38–42]. When we consider dinuclear copper(II) complexes in which single hydroxide bridged and double hetero bridged (pyrazolate, pyridazine or acetato instead of carboxylate bridge), we notice that, although the structural properties of the acetate-bridged compounds **3**–**5** and pyrazolate-bridged compounds **6**–**11** are almost identical with those of other complexes, their antiferromagnetic super-exchange interactions are weaker (Table 1). This may show that the presence of the second bridging ligand affects the strength of the antiferromagnetic super-exchange interaction differently. In addition, although the second bridging ligands of **12** and **13** are the same as those of **3**–**5**, there is a significant difference in $-2J$ values for these complexes. Clearly, the variation of the strength of the super-exchange interaction cannot be explained completely by the structural features of binuclear copper(II) complexes. A different approach must be discussed to clarify the origin of the super-exchange mechanism of this system. Since it is difficult to explain this fact in terms of structural factors, we consider overlap interactions between the metal d orbitals and HOMOs of the second bridging ligands in the compounds.

Table 1. Structural and magnetic data for a series of related homologous asymmetrically dibridged μ-alkoxo dicopper(II) complexes **1**–**15**.

Compound[a]	Cu···Cu [Å]	Cu-O-Cu [°]	$-2J$ [cm^{-1}]
1	3.472(1)	131.0(2)	130
2	3.511(1)	132.2(2)	150
3	3.491(2)	132.0(1)	174.4
4	3.495(2)	133.3(2)	179.2
5	3.492(2)	133.5(1)	163.6
6	3.403(1)	127.1(3)	210
7	3.365(1)	125.7(1)	444
8	3.335(1)	124.7(2)	164
9	3.368(1)	126.0(2)	472
10	3.349	121.7	310
11	3.401	121.3	595
12	3.395(7)	123.6(2)	20.2
13	3.339(2)	120.1(2)	55.6
14	3.642	143.7(2)	1000
15	3.331	129.1	586

[a] **1**, $[Cu_2L(O_2CC_6H_4\text{-}o\text{-}NH_2)]$ [20]; **2**, $[Cu_2L(O_2CC_6H_4\text{-}p\text{-}NH_2)]$ [20]; **3**, $[Cu_2(L^1)(O_2CMe)]\cdot 1/2H_2O$ [8]; **4**, $[Cu_2(L^2)(O_2CMe)]\cdot 1/2H_2O$ [22]; **5**, $[Cu_2(L^3)(O_2CMe)]\cdot H_2O$ [23]; **6**, $[Cu_2(L^1)(3,5\ prz)]$ [24]; **7**, $[Cu_2(L^3)(3,5,prz)]$ [25]; **8**, $[Cu_2(L^4)(3,5,prz)]$ [26]; **9**, $[Cu_2(L^5)(3,5,prz)]$ [27]; **10**, $[Cu_2(L^1)(prz)]$ [33]; **11**, $[Cu_2(L^2)(prz)]$ [33]; **12**, $[Cu_2(OH)(O_2CMe)(dmen_2)(ClO_4)_2]$ [15, 22]; **13**, $[Cu_2(OH)(O_2CMe)(tmen_2)(ClO_4)_2]$ [15, 22]; **14**, $[Cu_2(OH)(ClO_4)A](ClO_4)_2\cdot CHCl_3$ (A = binucleating macrocycle) [11]; **15**, $[Cu_2(L_1)(pyd)]BF_4\cdot H_2O$ [36].

3. Results and Discussion

3.1. Ab-initio Restricted Hartree-Fock Molecular Orbital Calculations

First we carried out molecular orbital calculations of the carboxylate ligand bridges by *ab-initio* RHF methods and investigated the interaction between the d orbitals and the HOMOs of the carboxylate ligands in order to clarify the influence of the second bridging ligand on the super-exchange interaction. We determined approximate values for the overlap integrals between the interaction orbitals, $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$, and calculated the difference between $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ for the compounds **1** and **2**.

We obtained the HOMOs of the carboxylate ligands of the compounds **1** and **2** by using the GAUSSIAN-98 program [28]. The overlap integrals between the interacting orbitals are expressed as $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$. We determined approximate values for $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ for the compound **1**.

The HOMOs are expressed in terms of linear combination of atomic orbitals (LCAOs):

$$\begin{aligned}\psi_s = {} & 0.007445[s(O1) + s(O2)] \\ & + 0.25288[p_x(O1) - p_x(O2)] \\ & + 0.080175[p_y(O1) + p_y(O2)] \\ & + (\text{terms of carbon orbitals}), \qquad (2)\end{aligned}$$

$$\begin{aligned}\psi_a = {} & 0.00607[s(O1) - s(O2)] \\ & + 0.44039[p_x(O1) + p_x(O2)] \\ & + 0.19565[p_y(O1) - p_y(O2)] \\ & + (\text{terms of carbon orbitals}). \qquad (3)\end{aligned}$$

The overlap integrals $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ are given as functions of the angle α between the Cu-carboxylate O bond vector and nearest lobe of the local magnetic d orbital (see Fig. 4). Figure 4 shows the projection of Cu and donor atoms onto the coordination plane, together with axes of the magnetic d orbital (broken lines). The angles formed by the coordinative bonds and axes of the d orbitals are denoted as α, β, γ and δ. In order to fulfill the requirement of maximum overlap, the following function was minimized:

$$\begin{aligned}F(\alpha) &= \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \\ &= \alpha^2 + (\alpha + 90 - 86.40)^2 \\ &\quad + (\alpha + 180 - 86.40 - 94.51)^2 \qquad (4) \\ &\quad + (\alpha + 270 - 86.40 - 94.51 - 84.17)^2.\end{aligned}$$

If $\frac{dF(\alpha)}{d\alpha} = 0$, then $\alpha = -1.90°$.

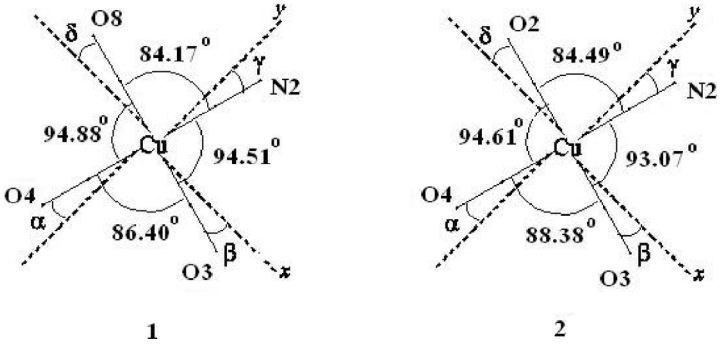


Fig. 4. Projection of Cu and donor atoms onto the best plane formed by these atoms (the broken lines are the axes of the magnetic d orbital) for **1** and **2**.

For compound **2** in a similar way, the value of α is obtained as $\alpha = 1.06°$.

Finally, we determined the overlap integrals between d_s and ψ_s, and between d_a and ψ_a. When the *x*- and *y*-axes in Fig. 4 are rotated by α, the d_1 orbital is expressed in terms of the new coordinate system as

$$d_1 = (\cos(2\alpha))d_{x^2-y^2} + (\sin(2\alpha))d_{xy}. \quad (5)$$

The ψ_s and ψ_a orbitals of the carboxylate ion can be expressed as the sum of the orbitals on O4 and O5 and the neighbouring carbon atoms:

$$\psi_s = \phi_{s1} + \phi_{s2} + \phi_{sC}, \quad (6)$$

$$\psi_a = \phi_{a1} + \phi_{a2} + \phi_{aC}. \quad (7)$$

These orbitals can be expressed in terms of the new coordinate system in which the *y*-axis is on the Cu-O4 bond (for compound **1**):

$$\begin{aligned}\phi_{s1} &= 0.007448s + 0.25288[(\cos 30)p_x + (\sin 30)p_y] \\ &\quad + 0.080175[-(\cos 60)p_x + (\sin 60)p_y], \quad (8)\\ \phi_{s1} &= 0.007448s + 0.178906p_x + 0.19587p_y.\end{aligned}$$

From (5) and (8) follows:

$$\begin{aligned}S(d_1, \phi_{s1}) &= 0.007448(\cos 2\alpha)S(3d, 2s) \\ &\quad + 0.178906(\sin 2\alpha)S(3d_\pi, 2p_\pi) \\ &\quad + 0.19587(\cos 2\alpha)S(3d_\sigma, 2p_\sigma).\end{aligned}$$

Since $d_s = (d_1 - d_2)/2^{1/2}$ and $S(d_2, \phi_{s2}) = -S(d_1, \phi_{s1})$,

$$S(d_s, \psi_s) = 2S(d_1, \phi_{s1})/2^{1/2}, \quad (9)$$

$$\begin{aligned}S(d_s, \psi_s) &= 0.01053(\cos 2\alpha)S(3d, 2s) \\ &\quad + 0.25297(\sin 2\alpha)S(3d_\pi, 2p_\pi) \quad (10)\\ &\quad + 0.27696(\cos 2\alpha)S(3d_\sigma, 2p_\sigma).\end{aligned}$$

In a similar way, $S(d_a, \psi_a)$ is obtained:

$$\begin{aligned}S(d_a, \psi_a) &= 0.008583(\cos(2\alpha))S(3d, 2s) \\ &\quad + 0.40093(\sin(2\alpha))S(3d_\pi, 2p_\pi) \quad (11)\\ &\quad + 0.550894(\cos(2\alpha))S(3d_\sigma, 2p_\sigma).\end{aligned}$$

The difference between $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ is calculated for **1**. The rough overlap integrals are evaluated by using data from Jaffe and Kuroda [43, 44], $S(3d, 2s) \approx 0.04$, $S(3d_\pi, 2p_\pi) \approx 0.02$, $S(3d_\sigma, 2p_\sigma) \approx 0.06$. In the case of **1**, $\alpha = -1.9°$; hence

$$S(a - s) = S(d_a, \psi_a) - S(d_s, \psi_s) = 0.0165. \quad (12)$$

In the case of compound **2** the overlap integrals were obtained in the same way:

$$\begin{aligned}S(d_s, \psi_s) &= 0.005634(\cos 2\alpha)S(3d, 2s) \\ &\quad - 0.033949(\sin 2\alpha)S(3d_\pi, 2p_\pi) \quad (13)\\ &\quad + 0.096923(\cos 2\alpha)S(3d_\sigma, 2p_\sigma),\end{aligned}$$

$$\begin{aligned}S(d_a, \psi_a) &= 0.002362(\cos 2\alpha)S(3d, 2s) \\ &\quad - 0.17989(\sin 2\alpha)S(3d_\pi, 2p_\pi) \quad (14)\\ &\quad + 0.513962(\cos 2\alpha)S(3d_\sigma, 2p_\sigma).\end{aligned}$$

In the case of compound **2**

$$S(a - s) = S(d_a, \psi_a) - S(d_s, \psi_s) = 0.0250. \quad (15)$$

3.2. Extended Hückel Molecular Orbital (EHMO) Calculations

In addition to the above calculations, we have also carried out EHMO calculations. EHMO calculations have been performed in order to gain insight into the molecular orbitals that participate in the superexchange pathway. Using the crystallographic coordinates for the compounds **1** and **2**, energy differences

($\Delta\varepsilon$) of 0.483 eV for **1** and 0.558 eV for **2** are obtained between the d''_a and d''_s orbitals, respectively.

At the end of our *ab-initio* restricted Hartree-Fock molecular orbital calculation for the compounds **1** and **2** we noticed that $S(a-s)$ of the compound is positive. This shows that the ψ_a overlap with d_a is more effective than the ψ_s overlap with d_s, $S(d_a, \psi_a) > S(d_s, \psi_s)$. Since the overlap of the antisymmetric molecular orbitals is more effective, the carboxylate bridge acts in a complementary fashion to reduce the energy separation between d''_a and d''_s.

The $S(a-s)$ and $\Delta\varepsilon$ values of **1**–**8** are given in Table 2. A natural question arises from the above explanation. Although each group of asymmetrically dibridged dicopper(II) compounds [groups i: **1**, **2** (μ-alkoxo)(μ-carboxylato), ii: **3**, **4**, **5** (μ-alkoxo)(μ-acetato) and iii: **6**, **7**, **8** (μ-alkoxo)(μ-pyrazolate)] have almost the same bridging ligands, why is there a significant difference between their antiferromagnetic super-exchange coupling constants? The answer can be easily found from Table 2, in which the $S(a-s)$ and $\Delta\varepsilon$ values of the compounds are compared. As seen in Table 2, the $S(a-s)$ values of compounds **1** and **2** for the group i and **6**, **7**, **8** for the group iii are positive. This shows that the ψ_a overlap with d_a is more effective than the ψ_s overlap with d_s, $S(d_a, \psi_a) > S(d_s, \psi_s)$. Since the overlap of the antisymmetric molecular orbitals is more effective, the carboxylate bridge and pyrazolate bridge act in a complementary fashion to reduce the energy separation between d''_a and d''_s for the groups i and iii, respectively. When the $S(d_s, \psi_s)$ overlap is more effective since the energy separation between d''_a and d''_s attenuates, the antiferromagnetic super-exchange interaction is stronger:

$$S(a-s)(\mathbf{2}) > S(a-s)(\mathbf{1})$$
$$\text{when } -J(\mathbf{2}) > -J(\mathbf{1}) \text{ for the group i.}$$

In the case of group iii,

$$S(a-s)(\mathbf{8}) > S(a-s)(\mathbf{7}) > S(a-s)(\mathbf{6})$$
$$\text{when } -J(\mathbf{8}) > -J(\mathbf{7}) > -J(\mathbf{8}).$$

The calculations show that the values of $S(a-s)$ correlate very well with these values.

An energy differences $\Delta\varepsilon = [E(d''_a) - E(d''_s)]$ of 0.483 and 0.558 eV is also obtained between the d''_a and d''_s orbitals by EHMO calculations for the compounds **1** and **2**. From the expression (1) for the exchange parameter it is seen that the binuclear complex with the greater antiferromagnetic interaction has the larger $\Delta\varepsilon = [E(d''_a) - E(d''_s)]$ energy difference (Table 2):

$$-J(\mathbf{2}) > -J(\mathbf{1}),$$
$$\Delta\varepsilon(\mathbf{2}) > \Delta\varepsilon(\mathbf{1}),$$

and, for the group iii

$$-J(\mathbf{8}) > -J(\mathbf{6}) > -J(\mathbf{7}),$$
$$\Delta\varepsilon(\mathbf{8}) > \Delta\varepsilon(\mathbf{6}) > \Delta\varepsilon(\mathbf{7}).$$

These results also indicate that a large energy separation of d''_a and d''_s orbitals leads to a strong antiferromagnetic interaction.

Table 2. Comparison of the values of $S(a-s)$, $\Delta\varepsilon$ and J for the compounds **1**–**8**.

Compound	$-2J$ [cm^{-1}]	$S(a-s)$	$\Delta\varepsilon$ [eV]	Second bridge
1	130	0.0170	0.483	(μ-carboxylato)
2	150	0.0250	0.558	(μ-carboxylato)
3	174.4	−0.0163	0.615	(μ-acetato)
4	179.2	−0.0161	0.645	(μ-acetato)
5	163.6	−0.0169	0.605	(μ-acetato)
6	444	0.01074	0.220	(μ-pyrazolate)
7	164	0.00419	0.190	(μ-pyrazolate)
8	472	0.01296	0.230	(μ-pyrazolate)

As seen in Table 2, the $S(a-s)$ values of the compounds **3**, **4** and **5** for the group ii are negative. This shows that the ψ_s overlap with d_s is more effective than the ψ_a overlap with d_a, $S(d_s, \psi_s) > S(d_a, \psi_a)$. Since the overlap of the symmetric molecular orbitals is more effective, the acetate bridge acts in a countercomplementary fashion to reduce the energy separation between d''_a and d''_s. The value of $-S(a-s)$ for **5** is shown to be the biggest in the group ii. This indicates that the $S(d_s, \psi_s)$ overlap for **5** is the most effective one. Consequently, the antiferromagnetic coupling of **5** is weaker than that of compounds **3** and **4**. The bigger the value of $-S(a-s)$, the weaker is the antiferromagnetic interaction. When the $S(d_s, \psi_s)$ overlap is more effective, since the energy separation between d''_a and d''_s attenuates, the antiferromagnetic super-exchange interaction is weaker:

$$-S(a-s)(\mathbf{5}) > -S(a-s)(\mathbf{3}) > -S(a-s)(\mathbf{4}),$$
$$-J(\mathbf{5}) < -J(\mathbf{3}) < -J(\mathbf{4}),$$

and again, from the expression (1) for the exchange parameter, it is seen that the dinuclear complex with the greater antiferromagnetic interaction has the larger $\Delta\varepsilon = [E(d''_a) - E(d''_s)]$ energy difference:

$$-J(\mathbf{5}) < -J(\mathbf{3}) < -J(\mathbf{4}),$$
$$-\Delta\varepsilon(\mathbf{5}) < -\Delta\varepsilon(\mathbf{3}) < -\Delta\varepsilon(\mathbf{4}).$$

The calculations show that the values of $S(\mathrm{a}-\mathrm{s})$ and $\Delta\varepsilon$ correlate very well with the values in each of the groups.

4. Conclusion

In dinuclear copper(II) complexes which contain two different bridging ligands, the bridging units may act in a complementary or countercomplementary fashion to increase or decrease the strength of the super-exchange process. The reason of the weak antiferromagnetic coupling of the (μ-alkoxo)(μ-carboxylato)-bridged dinuclear copper(II) complexes **1** and **2** is explained by the complementary fashion of the carboxylate bridge. In addition, our calculations show that because of the significant difference in the values of $S(\mathrm{a}-\mathrm{s})$ and $\Delta\varepsilon$, there is a significant difference in the J values of these complexes.

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