

A theoretical analysis of the explanation of the significant differences in antiferromagnetic interactions between homologous μ -alkoxo and acetate bridged dicopper(II) complexes: *Ab-initio* and semi-empirical calculations

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Abstract

A magnetostructural classification of dimmers, containing the Cu(μ -alkoxo)Cu core, based on data obtained from x-ray diffraction analysis reported in the literature has been performed. In these complexes, the local geometry around the copper ions is generally a square planar and each copper ion is surrounded by one N atom and three O atoms. The influence of the overlap interactions between the bridging ligands and the metal (Cu) d orbitals on the super-exchange coupling constant has been studied by means of *ab-initio* Restricted Hatree-Fock (RHF) molecular orbital calculations. The interaction between the magnetic d orbitals and HOMOs of the acetate oxygens has been investigated in homologous μ -acetato-bridged 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 frontier orbitals, Extended Hückel molecular Orbital (EHMO) calculations are also reported. *Ab-initio* restricted Hartree-Fock calculations have shown that the acetato bridge and the alkoxide bridge contribute to the magnetic interaction countercomplementarily to reduce antiferromagnetic interaction.

Keywords: Magnetic properties; Dinuclear copper(II) complex; Antiferromagnetic coupling; *Ab-initio* calculations; Molecular orbitals

1. Introduction

Magnetisms of bis(μ -alkoxo) or bis(μ -hydroxo)dicopper(II) complexes have been the subjects of extensive investigations for the last two decades [1]. This is partly because of the use of such complexes to mimic aspects of bimetallic biosites in various proteins and enzymes [2, 3]. Most extensively studied compounds are dihydroxo bridged dinuclear copper complexes [4-8]. In these copper complexes, a good degree of success has been accomplished in correlating structure and magnetic properties. These compounds are also of theoretical interest, because they provide examples of the simplest case of magnetic interactions with only two unpaired electrons. These copper(II) complexes exhibit ferromagnetic or antiferromagnetic coupling depending on their geometry. Detailed analysis results in the linear correlation between the Cu – O – Cu angle and singlet-triplet exchange parameter J established by Hodgson and coworkers [9], who proposed: $J = -74.53\varphi + 7270 \text{ cm}^{-1}$ (in which φ is the Cu – O – Cu angle). Several theoretical calculations were performed to better understand this correlation [5, 10], and theoretical approaches were applied to understand the nature of the ferromagnetic / antiferromagnetic interaction [11].

Very recently, we studied the crystal structures and magnetic properties of (μ - hydroxo) (μ - acetato) dicopper(II) complexes, $[\text{Cu}_2(\text{L}^1)(\text{O}_2\text{CMe})]1/2.\text{H}_2\text{O}$, ($\text{L}^1 = 1,3\text{-bis(5-bromo-2-hydroxybenzylidene)propan-2-ol}$) **(1)**, $[\text{Cu}_2(\text{L}^2)(\text{O}_2\text{CMe})]1/2.\text{H}_2\text{O}$, ($\text{L}^2 = 1,3\text{-bis(5-chloro-2-hydroxybenzylidene)propan-2-ol}$) **(2)** and $[\text{Cu}_2(\text{L}^3)(\text{O}_2\text{CMe})]\text{H}_2\text{O}$, ($\text{L}^3 = 1,3\text{-bis(2-hydroxy-1-naphtylideneamino)propan-2-ol}$) **(3)** [12-14]. Antiferromagnetic interactions which were observed for these complexes show significant differences, although they have almost the same bridging ligands. In this study, we have studied the magnetostructural correlations for these and similar compounds by *ab-initio* restricted Hartree-Fock molecular orbital calculations to explain the significant differences in antiferromagnetic interactions between homologous μ - acetato bridged dicopper(II) complexes.

2. Methodology

2.1. Methods and programs

Ab-initio restricted Hartree- Fock (RHF) molecular orbital calculations for the acetate ion were carried out by using the GAUSSIAN-98 program [15]. STO-3G minimal basis sets [16] were adopted for carbon and oxygen atoms. Also the molecular orbital calculations were performed using extended Hückel molecular orbital (EHMO) method [17, 18] for the determined HOMO-LUMO energy gap by using the CACAO program [19]. The structural parameters were obtained from x-ray analysis of $[\text{Cu}_2(\text{L}^1)(\text{O}_2\text{CMe})]1/2.\text{H}_2\text{O}$, ($\text{L}^1 = 1,3\text{-bis}(5\text{-bromo-2-hydroxybenzylidene})\text{propan-2-ol}$) (**1**) [12].

2.2 Theoretical model and a 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° ($120 - 135.5^\circ$), in such systems the d_a (antisymmetric combinations of d orbitals) overlap with p_x is larger than the d_s (symmetric combinations of d orbitals) overlap with p_y , so d_a and d_s split, as illustrated in Fig. 1a. 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. 1b).

In case of the acetate bridge, the separation of d_a'' and d_s'' is effected by the highest occupied molecular orbital (HOMO) of the acetate ion, as shown in Figure 2. The countercomplementary effect

by the orbital interactions with an acetate ligand makes the energy difference between d_a'' and d_s'' smaller than that between d_a' and d_s' . Therefore, the $-2J$ values of (μ -alkoxo) (μ -acetato) or (μ -hydroxo) (μ -acetato) dicopper(II) complexes are smaller than those of the single alkoxo-or hydroxo-bridged compounds. However, the larger the energy separation between the antisymmetric (d_a'') and the symmetric (d_s'') molecular orbitals, the stronger are the antiferromagnetic interactions.

The exchange coupling constant ($-2J$) for the hydroxo-bridged copper(II) complexes was evaluated by calculating the energy difference between triplet and singlet states [4] (using $H = -2JS_1.S_2$),

$$E_T - E_S = -2J = -2K_{ab} + \frac{[E(d_a'') - E(d_s'')]^2}{J_{aa} - J_{ab}} \quad (1)$$

where K_{ab} , J_{aa} and J_{ab} 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. Since the denominator of the second term varies very little and K_{ab} 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. 1b) is the determining factor for the magnitude of the coupling constant.

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. To gain a reasonable explanation for these facts we examined the super-exchange mechanism of this system in terms of Hoffman's theory [4]. In planar copper(II) complexes, an unpaired electron resides in a d_{xy} orbital, and the symmetric and antisymmetric combinations of these orbitals are expressed as in equations (2) and (3) (for the definition of x and y coordinates, see Figure 2).

$$\psi_s = d_x + d_{xy} \quad (2)$$

$$\psi_a = d_x - d_{xy} \quad (3)$$

According to Hoffman in bimetallic complexes strong antiferromagnetism is observed if the energy separation of the symmetric (ψ_s) and antisymmetric (ψ_a) combination of the two magnetic orbitals is large (Fig. 2), irrespective of the fact which combination is lower in energy. Spin exchange interaction in binuclear copper(II) complexes in which two copper(II) ions are linked by alkoxide and acetate oxygens thus can be explained in the following manner. The p_x orbital of the alkoxide oxygen atom interacts with the ψ_a orbital to raise its energy. In the case of an acetate bridge the energy of the ψ_s orbital is raised, because the highest occupied molecular orbital (HOMO) of an acetate ion has mainly oxygen $2p$ character and this orbital interacts with the ψ_s orbital. Consequently, the presence of the acetate bridge reduces the energy separation between ψ_a and ψ_s orbitals caused by the interaction through the alkoxide bridge only, and decreases the strength of the antiferromagnetic interaction. If both bridging ligands interact with the same combination of magnetic orbitals to raise the orbital energy, the super-exchange interaction through the two bridges work in a complementary fashion and the antiferromagnetic exchange interaction is enhanced. Conversely, if one of the bridging ligand interacts with an ψ_s orbital and the other with an ψ_a orbital to raise each of the orbital energies, the super-exchange interactions through the bridges work in a countercomplementary fashion and the antiferromagnetic exchange interactions attenuate.

Nishida et. al. [20] show for ψ_s higher in energy than ψ_a , a decrease in the energy difference between d_a'' and d_s'' . In other words, the energies of the interacting orbitals cause the acetate bridge to act in a countercomplementary fashion with the alkoxide bridge. In addition, if ψ_s overlaps more effectively with d_s than ψ_a with d_a , the overlap integrals of the interacting orbitals may affect the acetate bridge to work in a countercomplementary fashion with the alkoxide bridge again.

2.3 Magnetostructural Correlations

In general, binuclear 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 [21-26]. Some interesting correlations between structural and magnetic parameters emerge from the data in Table 1. When we consider dinuclear copper(II) complexes in which single hydroxide bridged and double hetero bridged (pyrazolate or pyridazine instead of acetate bridge), we notice that, although the structural properties of the compounds **(1)**, **(2)**, **(3)**, **(4)** and **(5)** are almost identical with those of other complexes, their antiferromagnetic super-exchange interactions are weaker (Table 1). This may show that the presence of second bridging ligand affects the strength of the antiferromagnetic super-exchange interaction differently. In addition, although the second bridging ligands of **(4)** and **(5)** are the same as those of **(1)**, **(2)** and **(3)**, 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 acetate ion.

3. Results and Discussion

3.1 *Ab-Initio Restricted Hartree-Fock Molecular Orbital Calculations*

In compound **(1)**, since the orbital energy of ψ_s is higher than that of ψ_a by 0.202 eV, respectively, the energies of the interacting orbitals cause the acetate bridge to work in a countercomplementary fashion with the hydroxide bridge in the compound.

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)**.

We obtained the HOMOs of the acetate ion of the compound **(1)** by using the GAUSSIAN-98 program [15]. The HOMOs are expressed in terms of linear combination of atomic orbitals (LCAOs):

$$\begin{aligned} \psi_s = & 0.00447[s(O1) + s(O2)] + 0.7067[p_x(O1) - p_x(O2)] \\ & + 0.0183 [p_y(O1) + p_y(O2)] + (\text{terms of carbon orbitals}) \end{aligned} \quad (4)$$

$$\begin{aligned} \psi_a = & 0.00220 [s(O1) - s(O2)] + 0.3105 [p_x(O1) + p_x(O2)] \\ & + 0.01588 [p_y(O1) - p_y(O2)] + (\text{terms of carbon orbitals}) \end{aligned} \quad (5)$$

The overlap integrals $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ are given as a function of the angle (α) between the Cu – acetate O bond vector and nearest lobe of the local magnetic d orbital (see Fig. 3). Figure 3 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 fulfil the requirement of maximum overlap, the following function was minimised:

$$\begin{aligned} F(\alpha) &= \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \\ &= \alpha^2 + (\alpha + 90 - 86.41)^2 + (\alpha + 180 - 86.41 - 93.60)^2 \\ &\quad + (\alpha + 270 - 86.41 - 93.60 - 84.37)^2 \\ &= \alpha^2 + 4.6\alpha + 12.056 \end{aligned} \quad (6)$$

$$\text{If } \frac{dF(\alpha)}{d\alpha} = 0, \text{ then } \alpha = -2.3^\circ.$$

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.3 are rotated by α , the d_I orbital is expressed in terms of the new coordinate system as

$$d_I = (\cos(2\alpha))d_{x^2-y^2} + (\sin(2\alpha))d_{xy} \quad (7)$$

The ψ_s and ψ_a orbitals of the acetate ion can be expressed as the sum of the orbitals on O9 and O10 and the neighbouring carbon atoms:

$$\psi_s = \phi_{s1} + \phi_{s2} + \phi_{sC} \quad (8)$$

$$\psi_a = \phi_{a1} + \phi_{a2} + \phi_{aC} \quad (9)$$

These orbitals can be expressed in terms of the new coordinate system in which the y -axis is on the Cu – O10 bond.

$$\phi_{s1} = 0.00447s + 0.7067 [(cos30) p_x + (sin30) p_y] + 0.0183 [-(cos60) p_x + (sin60) p_y]$$

$$\phi_{s1} = 0.00447 s + 0.6029 p_x + 0.3692 p_y \quad (10)$$

From (7) and (10) follows

$$\begin{aligned} S(d_1, \phi_{s1}) &= 0.00447(cos(2\alpha)).S(3d,2s) + 0.6029 (sin(2\alpha)).S(3d_\pi,2p_\pi) \\ &+ 0.3692 ((cos(2\alpha)).S(3d_\sigma,2p_\sigma)) \end{aligned}$$

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

$$S(d_s, \psi_s) = 2 S(d_1, \phi_{s1})/2^{1/2} \quad (11)$$

$$\begin{aligned} S(d_s, \psi_s) &= 0.00632 (cos(2\alpha)).S(3d,2s) + 0.8525 (sin(2\alpha)).S(3d_\pi,2p_\pi) \\ &+ 0.5221 ((cos(2\alpha)).S(3d_\sigma,2p_\sigma)) \end{aligned} \quad (12)$$

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

$$\begin{aligned} S(d_a, \psi_a) &= 0.00311 (cos(2\alpha)).S(3d,2s) + 0.3691 (sin(2\alpha)).S(3d_\pi,2p_\pi) \\ &+ 0.2390 ((cos(2\alpha)).S(3d_\sigma,2p_\sigma)) \end{aligned} \quad (13)$$

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 [27, 28], $S(3d, 2s) \approx 0.04$, $S(3d_\pi, 2p_\pi) \approx 0.02$, $S(3d_\sigma, 2p_\sigma) \approx 0.06$. In the case of **1**, $\alpha = -2.3^\circ$; hence

$$S(a-s) = S(d_a, \psi_a) - S(d_s, \psi_s) = -0.0163 \quad (14)$$

3.2. Extended Hückel Molecular Orbital (EHMO) Calculations

In addition to the above calculations, we have also carried out Extended Hückel Molecular Orbital (EHMO) calculations. EHMO calculations have been performed in order to gain insight into the molecular orbitals that participate in the super-exchange pathway. Using the crystallographic coordinates for the compound, an energy difference of 0.615 eV is obtained between the d_a'' and d_s'' orbitals.

At the end of our *ab-Initio* restricted Hartree-Fock molecular orbital calculation we noticed that $S(a-s)$ of the compound is 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 $S(a-s)$ values of **(1)**, **(2)**, **(3)**, **(4)** $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})(\text{dmen}_2)(\text{ClO}_4)_2]$ [29, 30] and **(5)** $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})(\text{tmen}_2)(\text{ClO}_4)_2]$ [29, 30] are given in Table 2. The value of $-S(a-s)$ for **(4)** is shown to be the biggest. This indicates that the $S(d_s, \psi_s)$ overlap for **(4)** is the most effective one. Consequently, the weakest antiferromagnetic coupling is observed for compound **(4)**. In the case of other compounds, 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'' attenuate, the antiferromagnetic super-exchange interaction is weaker:

$$-S(a-s)(\mathbf{4}) > -S(a-s)(\mathbf{5}) > -S(a-s)(\mathbf{3}) > -S(a-s)(\mathbf{1}) > -S(a-s)(\mathbf{2})$$

$$-J(\mathbf{4}) < -J(\mathbf{5}) < -J(\mathbf{3}) < -J(\mathbf{1}) < -J(\mathbf{2})$$

The our calculations for the compound **(1)** shows that the value of $S(a-s)$ correlate very well with the J values of **(2)**, **(3)**, **(4)**, **(5)**.

An energy difference $\Delta\varepsilon = [E(d_a'') - E(d_s'')]$ of 0.615 eV is also obtained between the d_a'' and d_s'' orbitals by extended Hückel molecular orbital (EHMO) calculations for the compound **(1)**. 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):

$$-J(\mathbf{2}) > -J(\mathbf{1}) > -J(\mathbf{3})$$

$$-\Delta\varepsilon(\mathbf{2}) > -\Delta\varepsilon(\mathbf{1}) > \Delta\varepsilon > -\Delta\varepsilon(\mathbf{3})$$

These results also indicate that a large energy separation of d_a'' and d_s'' orbitals leads to a strong antiferromagnetic interaction.

3.3. 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 -acetato-bridged dinuclear copper(II) complexes **(1)**, **(2)**, **(3)**, **(4)**, **(5)** is explained by the countercomplementary fashion of the acetate bridge. In addition, our calculations show that because of the significant difference in the values of $S(a-s)$ and $\Delta\varepsilon$, there is a significant difference in J values of those complexes.

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Table 1 Structural and magnetic data for a series of related μ -acetato-bridged dinuclear copper(II) complexes **(1)**, **(2)**, **(3)**, **(4)**, **(5)**

Compound	Cu $\cdots$ Cu [$\text{\AA}$]	Cu – O – Cu	$-2J$ [cm^{-1}]
(1)	3.491(2)	132.0(1)	174.4
(2)	3.495(2)	133.3(2)	179.2
(3)	3.492(2)	133.5(1)	163.6
(4)	3.395(7)	123.6(2)	20.2
(5)	3.339(2)	120.1(2)	55.6
(6)	3.642	143.7(2)	1000
(7)	3.331	129.1	586
(8)	3.401	121.3	595

¹ $[\text{Cu}_2(\text{L}^1)(\text{O}_2\text{CMe})]1/2.\text{H}_2\text{O}$ (Zeyrek, Elmali, Elerman, Svoboda and Fuess [12])

² $[\text{Cu}_2(\text{L}^2)(\text{O}_2\text{CMe})]1/2.\text{H}_2\text{O}$ (Kavlakoglu, Elmali, and Elerman [13])

³ $[\text{Cu}_2(\text{L}^3)(\text{O}_2\text{CMe}).\text{H}_2\text{O}$ (Kavlakoglu, Elmali, Elerman, and Fuess [14])

⁴ $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})(\text{dmen}_2)(\text{ClO}_4)_2]$ (Meenakumari, Tiwari, Chakravarty [29]; Kavlakoglu, Elmali, and Elerman [30])

⁵ $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})(\text{tmen}_2)(\text{ClO}_4)_2]$ (Meenakumari, Tiwari, Chakravarty [29]; Kavlakoglu, Elmali, and Elerman [30])

⁶ $[\text{Cu}_2(\text{OH})(\text{ClO}_4)\text{A}](\text{ClO}_4)_2.\text{CHCl}_3$ [A:Binucleating macrocycle] (Coughlin and Lippard [31])

⁷ $[\text{Cu}_2(\text{L}_1)(\text{pyd})]\text{BF}_4.\text{H}_2\text{O}$ (Li et al. [32])

⁸ $[\text{Cu}_2(\text{L}^2)(\text{prz})]$ (Nishida, Y. and Kida [20])

Table 2 The comparison of the values of $S(a-s)$, $\Delta\varepsilon$ and J for compounds

Compound	$-J [\text{cm}^{-1}]$	$-S(a-s)$	$\Delta\varepsilon [\text{eV}]$
(1)	87.2	0.0163	0.615
(2)	89.6	0.0161	0.645
(3)	81.8	0.0169	0.605
(4)	10.1	0.0343	–
(5)	27.8	0.0172	–

Figure Captions

Fig. 1 The 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. 2 Symmetric (ψ_s), and antisymmetric (ψ_a) combinations of metal and ligand orbitals.

Fig. 3 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)**.

Fig. 1

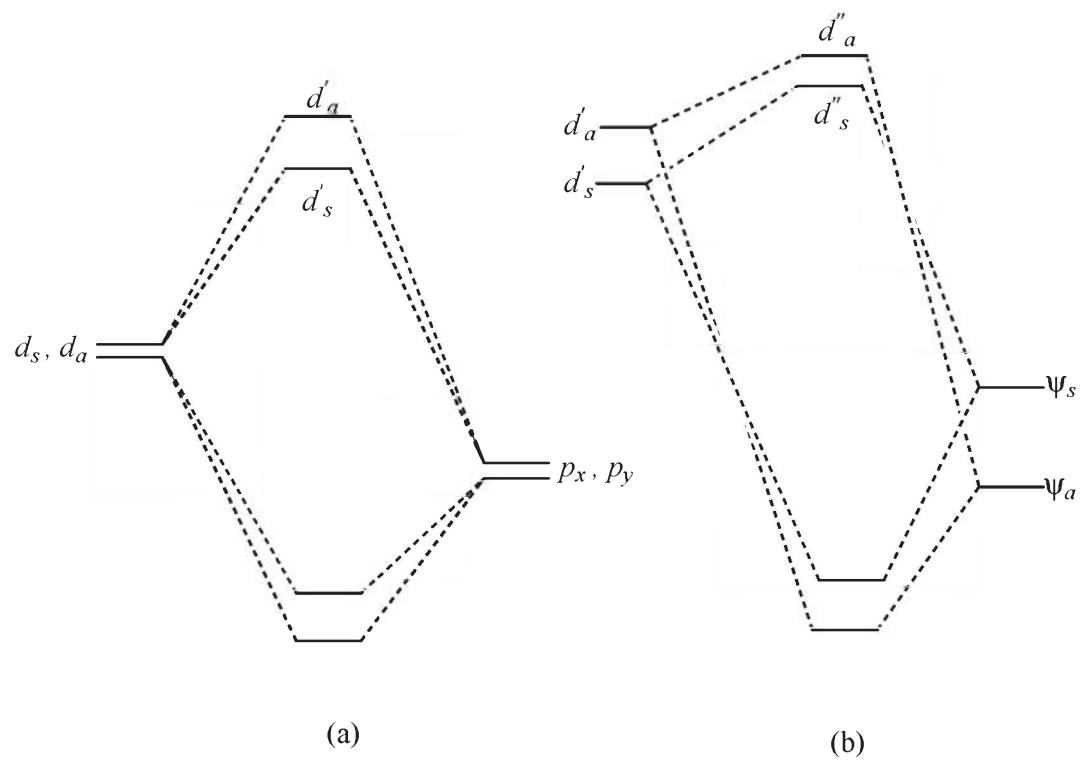


Fig. 2

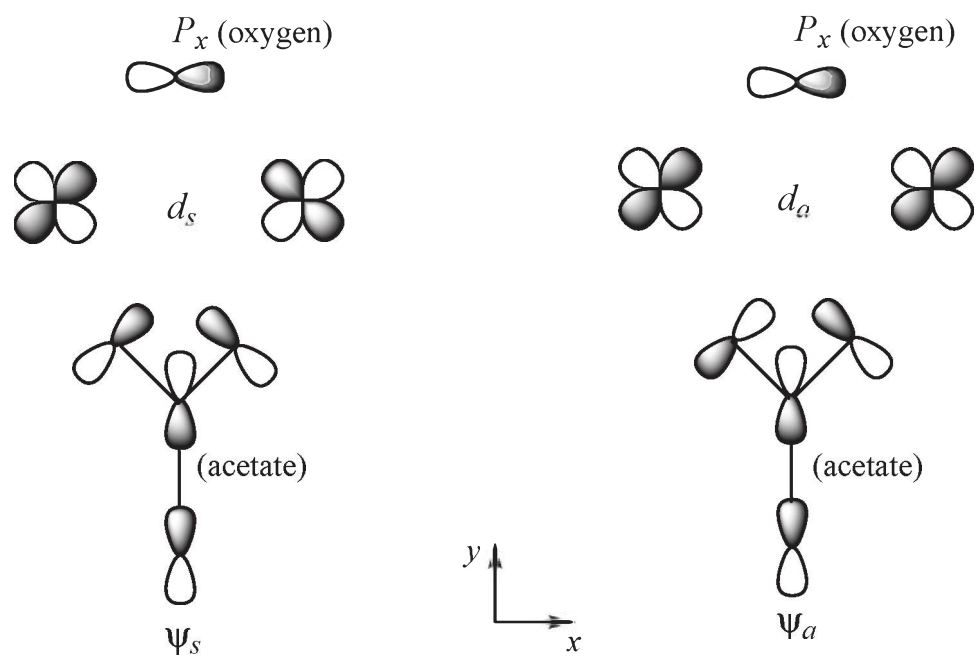


Fig. 3

