

# The Reason of the Significant Differences in Antiferromagnetic Interactions between Homologous $\mu$ -Acetato-Bridged Dicopper(II) Complexes: A Theoretical Study

E. Kavlakoglu, A. Elmali\*, and Y. Elerman\*

Department of Engineering Physics, Faculty of Engineering, Ankara University,  
06100 Besevler-Ankara, Turkey

\* Alexander von Humboldt Fellow

Reprint requests to Dr. A. E.; E-mail: elmali@science.ankara.edu.tr

Z. Naturforsch. **57 a**, 209–214 (2002); received January 14, 2002

The influence of the overlap interactions between the bridging ligands and the metal d orbitals on the super-exchange coupling constant has been studied by ab-initio Restricted Hartree-Fock molecular orbital calculations. The interaction between the magnetic d orbitals and the HOMOs of the acetate oxygens has been investigated in homologous  $\mu$ -acetato-bridged dicopper(II) complexes which have significantly different  $-2J$  values (the energy separation between the spin – triplet and spin – singlet states).

**Key words:** Dinuclear Copper(II) Complex; Antiferromagnetic Coupling; Overlap Interaction; Countercomplementary Effect; Ab-initio Restricted Hartree-Fock Molecular Orbital Calculation.

## 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 the dicopper(II) complexes have shown some interesting magnetostructural correlations. In bis ( $\mu$ -hydroxo) and bis ( $\mu$ -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 compound 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]. 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 [16]. 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, Meenakumari et al. [15] reported the crystal structures, spectral and magnetic properties of ( $\mu$ -hydroxo) ( $\mu$ -acetato) dicopper(II) complexes, [Cu<sub>2</sub>(OH)(O<sub>2</sub>CMe)(tmen)<sub>2</sub>] [ClO<sub>4</sub>]<sub>2</sub> (**1**), [Cu<sub>2</sub>(OH)(O<sub>2</sub>CMe)(dmen)<sub>2</sub>] [ClO<sub>4</sub>]<sub>2</sub> (**2a**) and [Cu<sub>2</sub>(OH)(O<sub>2</sub>CMe)(H<sub>2</sub>O)<sub>2</sub>(dmen)<sub>2</sub>] [ClO<sub>4</sub>]<sub>2</sub> (**2b**) [tmen = N,N,N',N'-tetramethylethane-1,2-diamine and dmen = N,N-dimethylethane-1,2-diamine]. Very recently, we also studied the crystal structures and magnetic properties of ( $\mu$ -alkoxo)( $\mu$ -acetato) dicopper(II) complexes, [Cu<sub>2</sub>(L1)(O<sub>2</sub>CMe)]·H<sub>2</sub>O (**3**) and [Cu<sub>2</sub>(L2)(O<sub>2</sub>CMe)]·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O (**4**) where H<sub>3</sub>L1 and H<sub>3</sub>L2 are Schiff bases derived from 1,3-diamino-2-propanol and 2-hydroxy-1-naphthaldehyde or 2-hydroxy-5-chlorosalicylaldehyde [8, 17]. Antiferromagnetic interactions which were observed for these complexes show significant differences, although they have

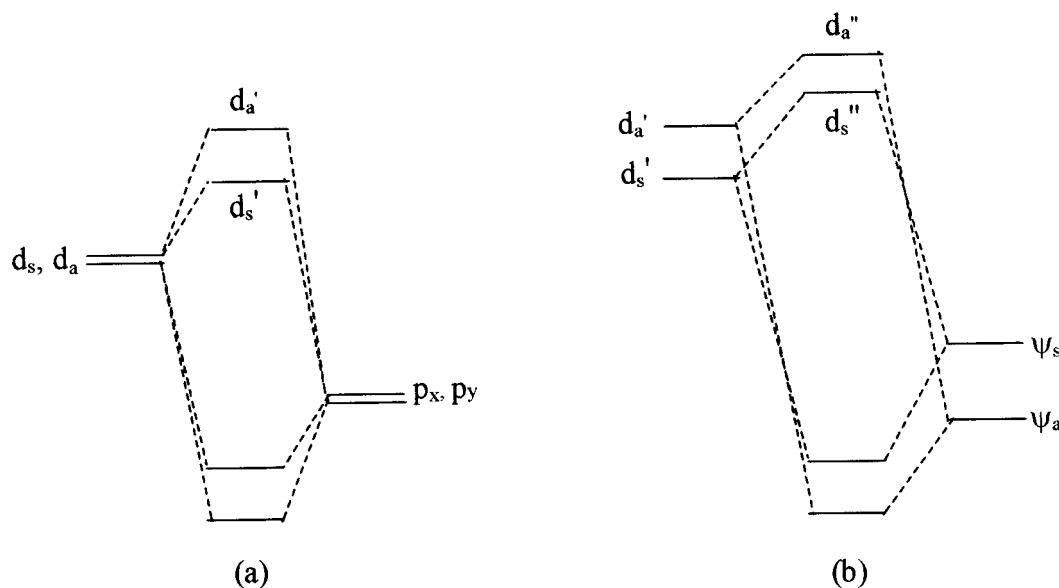


Fig. 1. The orbital energy level diagrams showing the interaction between the magnetic orbitals and bridging group orbitals, (a) for a single alkoxide- or hydroxide-bridged system; (b) for an additional bridging ligand.

almost the same bridging ligands. In this paper, we have studied the magnetostructural correlations for these compounds by ab-initio restricted Hartree-Fock molecular orbital calculations to explain the significant differences in antiferromagnetic interactions between homologous  $\mu$ -acetato-bridged dicopper(II) complexes.

### Molecular Orbital Calculations

Ab-initio restricted Hartree-Fock (RHF) calculations for the acetate ion were carried out by using the GAUSSIAN-98 program [18]. STO-3G [19] minimal bases sets were adopted for the carbon and oxygen atoms. The structural parameters were obtained from x-ray analysis [15].

### Theoretical Model

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 ( $\mu$ -alkoxo)- or ( $\mu$ -hydroxo)-bridged dinuclear copper complexes, when the Cu-O-Cu angle is larger than  $90^\circ$  ( $120 - 135.5^\circ$ ), the  $d_a$  overlap with  $p_x$  is larger than the  $d_s$  overlap with  $p_y$ . Consequently,  $d_a$  and  $d_s$  split, as illustrated in Fig. 1a. Thus,  $d'_a$  and  $d'_s$  molecular orbitals are formed. The larger energy separation of  $d'_a$  and  $d'_s$  gives a strong antiferromagnetic interaction. In the presence of a second bridging ligand, according to the orbital symmetries,  $d'_a$  and  $d'_s$  interact with antisymmetric ( $\psi_a$ ) and symmetric ( $\psi_s$ ) combinations of the 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 the ( $\mu$ -alkoxo) ( $\mu$ -acetato) or ( $\mu$ -hydroxo) ( $\mu$ -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.

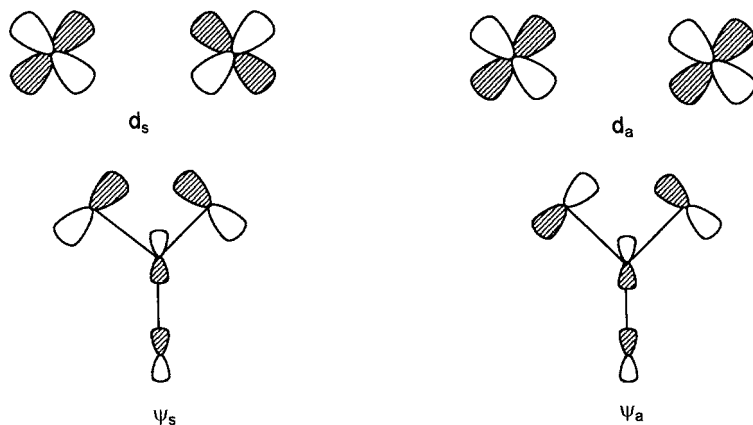


Fig. 2. Orbital symmetry combinations of metal d orbitals and acetate HOMO's.

According to the theoretical analysis of Hoffmann and co-workers [16], the coupling constant is expressed as

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

where  $K_{ab}$ ,  $J_{aa}$  and  $J_{ab}$  are the exchange integral and one-center and two-center 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 slowly 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. 1) is the determining factor for the magnitude of the coupling constant.

Nishida et al. [20] show for  $\psi_s$  higher in energy than  $\psi_a$ , 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  $\psi_s$  overlaps more effectively with  $d_s$  than  $\psi_a$  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.

### Magnetostructural Correlations

Magnetostructural correlations have been established for dinuclear copper(II) complexes in the last two decades [21 - 23]. It is instructive to compare the magnetic and structural properties of compounds **1**,

Table 1. Structural and magnetic data of reference compounds.

Compound	Cu...Cu [Å]	Cu-O-Cu[°]	$-2J$ [cm <sup>-1</sup> ]
<b>1</b>	3.339(2)	120.1(2)	55.6
<b>2</b>	3.395(7)	123.6(2)	20.2
<b>3</b>	3.492(2)	133.5(1)	163.6
<b>4</b>	3.495(2)	133.3(2)	179.2
<b>a</b>	3.384(9)	132.2(4)	820
<b>b</b>	3.642	143.7(2)	1000
<b>c</b>	3.331	129.1	586
<b>d</b>	3.401	121.3	595
<b>e</b>	3.360	121.8	540

<sup>a</sup> [ $\langle \text{Cu(II)} \dots (\text{OH}) \dots \text{Cu(II)} \rangle (\text{BF}_4)_3$  (Burk, Osborn, and Youinou [12]); <sup>b</sup> [ $\text{Cu}_2(\text{OH})(\text{ClO}_4)_2 \cdot \text{A}](\text{ClO}_4)_2 \cdot \text{CHCl}_3$  [A: Binucleating macrocycle] (Coughlin and Lippard [11]); <sup>c</sup> [ $\text{Cu}_2(\text{L}_1)(\text{pyd})\text{BF}_4 \cdot \text{H}_2\text{O}$  (Li et al. [23]); <sup>d</sup> [ $\text{Cu}_2(\text{L}^2)(\text{prz})$ ] (Nishida and Kida [20]); <sup>e</sup> [ $\text{LCu}_2(\text{prz})$ ] (Doman et al. [6]).

**2**, **3**, and **4** with those of dinuclear copper(II) complexes [6, 11, 12, 20, 23]. When we consider dinuclear copper(II) complexes in which single hydroxide bridged and double hetero bridged (pyrazolate or pyridazine instead of acetato bridge), we notice that, although the structural properties of the compounds **1**, **2**, **3**, and **4** are almost identical with those of other complexes, their antiferromagnetic superexchange interactions are weaker (Table 1). This may show that the presence of the second bridging ligand affects the strength of the antiferromagnetic superexchange interaction differently. In addition, although the second bridging ligands of **1** and **2** are the same as those of **3** and **4**, there is a significant difference in  $-2J$  values for these complexes. Since it is difficult to explain this fact in terms of structural factors, we consider overlap interactions between the metal d orbitals and HOMO's of the acetate ion.

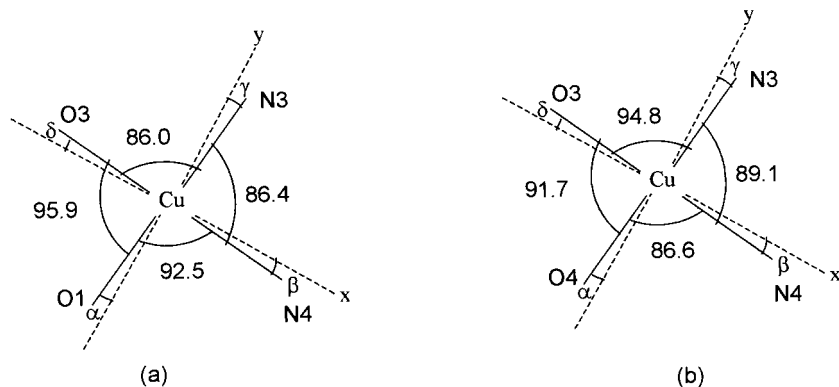


Fig. 3. Projection of Cu2 and donor atoms onto the best plane formed by these atoms (The broken lines are the axes of the magnetic d orbital) for **1** (a) and **2** (b).

## Results

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

In compounds **1** and **2**, since the orbital energy of  $\psi_s$  is higher than that of  $\psi_a$  by 0.201 eV and 0.204 eV, respectively, the energies of the interacting orbitals cause the acetate bridge to work in a countercomplementary fashion with the hydroxide bridge in both compounds.

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  $S(d_s, \psi_s)$  and calculated the difference between  $S(d_a, \psi_a)$  and  $S(d_s, \psi_s)$  for compounds **1** and **2**.

For this calculation, we obtained the HOMO's of the acetate ions of compounds **1** and **2** by using the GAUSSIAN-98 program [18]. The HOMO's are expressed in terms of LCAO's in (1) and (2) for compound **1**:

$$\begin{aligned} \psi_s = & 0.0018 [s(O1) + s(O2)] \\ & + 0.7090 [p_x(O1) - p_x(O2)] \\ & + 0.0202 [p_y(O1) + p_y(O2)] \\ & + (\text{terms of carbon orbitals}), \end{aligned} \quad (1)$$

$$\begin{aligned} \psi_a = & 0.0005 [s(O1) - s(O2)] \\ & + 0.2923 [p_x(O1) + p_x(O2)] \\ & + 0.0229 [p_y(O1) - p_y(O2)] \\ & + (\text{terms of carbon orbitals}), \end{aligned} \quad (2)$$

and in (3) and (4) for compound **2**:

$$\begin{aligned} \psi_s = & 0.0394 [s(O1) + s(O2)] \\ & + 0.4008 [p_x(O1) - p_x(O2)] \\ & + 0.5531 [p_y(O1) + p_y(O2)] \\ & + (\text{terms of carbon orbitals}), \end{aligned} \quad (3)$$

$$\begin{aligned} \psi_a = & 0.0064 [s(O1) - s(O2)] \\ & + 0.3021 [p_x(O1) + p_x(O2)] \\ & + 0.1693 [p_y(O1) - p_y(O2)] \\ & + (\text{terms of carbon orbitals}). \end{aligned} \quad (4)$$

The overlap integrals are given as functions of  $\alpha$  [20], where  $\alpha$  is the angle between the Cu-acetate O bond vector and the nearest lobe of the local magnetic d orbital (see Fig. 3). Figure 3 shows the projection of Cu2 and donor atoms onto the coordination plane together with the axes of the magnetic d orbital (broken lines).

We determined the orientation of magnetic d orbitals. In order to fulfill the requirement of maximum overlapping, the function

$$F(\alpha) = \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \quad (5)$$

was minimized, where  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are the angles formed by the coordination bonds and the axes of the d orbitals (Fig. 3).

For compound **1**, when the values

$$\begin{aligned} \beta &= \alpha + 90 - 92.5, \\ \gamma &= \alpha + 180 - 92.5 - 86.4, \\ \delta &= \alpha + 270 - 92.5 - 86.4 - 86.0 \end{aligned}$$

are used in (5),  $\alpha$  is obtained as

$$\alpha = -0.9^\circ$$

For compound **2**, in a similar way the value of  $\alpha$  is obtained as

$$\alpha = -1.8^\circ.$$

Finally, we determined the overlap integrals between  $d_s$  and  $\psi_s$ , and between  $d_a$  and  $\psi_a$ . When the  $x$  and  $y$  axes in Fig. 3 are rotated by  $\alpha$ , the  $d_1$  orbital is expressed in terms of the new coordinate system as

$$d_1 = (\cos(2\alpha))d_{x^2-y^2} + (\sin(2\alpha))d_{xy}. \quad (6)$$

The  $\psi_s$  and  $\psi_a$  orbitals of the acetate ion can be expressed as the sum of the orbitals on O1 and O2 and the neighboring carbon atoms:

$$\psi_s = \phi_{s1} + \phi_{s2} + \phi_{sC}, \quad (7)$$

$$\psi_a = \phi_{a1} + \phi_{a2} + \phi_{aC}. \quad (8)$$

These orbitals can be expressed in terms of the new coordinate system in which the  $y$  axis is on the Cu2-O1 bond (for compound **1**):

$$\begin{aligned} \phi_{s1} &= 0.0018 s + 0.7090 [(\cos 30) p_x + (\sin 30) p_y] \\ &\quad + 0.0202 [-(\cos 60) p_x + (\sin 60) p_y] \\ \phi_{s1} &= 0.0018 s + 0.6039 p_x + 0.3720 p_y. \end{aligned} \quad (9)$$

From (6) and (9) follows

$$\begin{aligned} S(d_1, \phi_{s1}) &= 0.0018 (\cos(2\alpha)) \cdot S(3d, 2s) \\ &\quad + 0.6039 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ &\quad + 0.3720 (\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma). \end{aligned} \quad (10)$$

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

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

$$\begin{aligned} S(d_s, \psi_s) &= 0.0026 (\cos(2\alpha)) \cdot S(3d, 2s) \\ &\quad + 0.8541 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ &\quad + 0.5261 (\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma). \end{aligned} \quad (12)$$

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

$$\begin{aligned} S(d_a, \psi_a) &= 0.0008 (\cos(2\alpha)) \cdot S(3d, 2s) \\ &\quad + 0.3418 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ &\quad + 0.2347 (\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma). \end{aligned} \quad (13)$$

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

$$\begin{aligned} S(d_s, \psi_s) &= 0.0558 (\cos(2\alpha)) \cdot S(3d, 2s) \\ &\quad + 0.0998 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ &\quad + 0.9608 (\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma) \end{aligned} \quad (12)$$

$$\begin{aligned} S(d_a, \psi_a) &= 0.0090 (\cos(2\alpha)) \cdot S(3d, 2s) \\ &\quad + 0.2503 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ &\quad + 0.4210 (\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma). \end{aligned} \quad (13)$$

The difference between  $S(d_a, \psi_a)$  and  $S(d_s, \psi_s)$  was calculated for compound **1** and **2**. The rough overlap integrals are evaluated by using data from Jaffe and Kuroda [24, 25]:  $S(3d, 2s) \approx 0.04$ ,  $S(3d_\pi, 2p_\pi) \approx 0.02$ ,  $S(3d_\sigma, 2p_\sigma) \approx 0.06$ . The difference between  $S(d_a, \psi_a)$  and  $S(d_s, \psi_s)$  is denoted as  $S(a-s)$ . In the

Table 2. The comparison of the values of  $S(a-s)$  and  $J$  for compounds **1**, **2**, **3**, and **4**.

Compound	$-J$ (cm $^{-1}$ )	$-S(a-s)$
<b>2</b>	10.1	0.0343
<b>1</b>	28	0.0172
<b>4</b>	81.8	0.0169
<b>3</b>	89.6	0.0161

case of **1**

$$S(a-s) = S(d_a, \psi_a) - S(d_s, \psi_s) = -0.0172,$$

and in the case of **2**

$$S(a-s) = -0.0343.$$

## Discussion

The  $S(a-s)$  values of **1**, **2**, **3**, and **4** are given in Table 2. We notice that in all cases  $S(a-s)$  is negative, i. e.

$$S(d_s, \psi_s) > S(d_a, \psi_a).$$

This shows that  $\psi_s$  overlaps more effectively with  $d_s$  than  $\psi_a$  overlaps with  $d_a$ . 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 **2** has been found to be the biggest. This indicates that the  $S(d_s, \psi_s)$  overlap for **2** is the most effective one, and the energy separation between  $d_a$  and  $d_s$  is the smallest. Consequently, the weakest antiferromagnetic coupling is observed for compound **2**. 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.

$$-S(a-s)(2) > -S(a-s)(1) > -S(a-s)(4) > -S(a-s)(3),$$

$$-J(2) < -J(1) < -J(4) < -J(3).$$

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

## 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  $\mu$ -acetato-bridged dicopper(II) complexes 1, 2, 3, and 4 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  $S(a-s)$ , there is a significant difference in  $J$  values of those complexes.

- [1] K. D. Karlin and Z. Tyeklar (Editors), *Bioinorganic Chemistry of Copper*, Chapman and Hall, New York 1993.
- [2] L. Q. Jun and A. E. True, *Prog. Inorg. Chem.* **38**, 97 (1990).
- [3] D. Gatteschi, O. Khan, and R. D. Willet, *Magnetostructural Correlations in Exchange Coupled Systems* Reidel, Dordrecht 1984.
- [4] O. Khan, *Angew. Chem. Int. Ed. Engl.* **24**, 834 (1985).
- [5] O. Khan, *Struct. Bonding (Berlin)*, **68**, 89 (1987).
- [6] T. N. Doman, D. E. Williams, J. F. Banks, R. M. Buchanan, H-R. Chang, R. J. Webb, and D. N. Hendrickson, *Inorg. Chem.* **29**, 1058 (1990).
- [7] T. Kawato, M. Yamanaka, S. Ohba, Y. Nishida, M. Nagamatsu, T. Tokii, M. Kato, and O. W. Steward, *Bull. Chem. Soc. Japan* **65**, 2739 (1992).
- [8] E. Kavlakoglu, A. Elmali, Y. Elerman, and H. Fuess, *Z. Naturforsch.* **55b**, 561 (2000).
- [9] V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.* **15**, 2107 (1976).
- [10] (a) W. E. Hatfield, *ACS Symp. Ser. No.5*, 108 (1974). (b) D. J. Hodgson *Prog. Inorg. Chem.* **19**, 173 (1975).
- [11] P. K. Coughlin and S. J. Lippard, *J. Amer. Chem. Soc.* **103**, 3228 (1981).
- [12] P. L. Burk, J. A. Osborn, and M-T. Youinou, *J. Amer. Chem. Soc.* **103**, 1273 (1981).
- [13] Y. Nishida, M. Takeuchi, K. Takahashi, and S. Kida, *Chem. Lett.* 1815 (1983).
- [14] Y. Nishida and S. Kida, *J. Chem. Soc. Dalton Trans.* 2633 (1986).
- [15] S. Meenakumari, S. K. Tiwari, and A. R. Chakravarty, *J. Chem. Soc. Dalton Trans.* 2175 (1993).
- [16] P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Amer. Chem. Soc.* **97**, 4884 (1975).
- [17] E. Kavlakoglu, A. Elmali, and Y. Elerman, will be published in *Z. Naturforsch.* (2002).
- [18] Gaussian 98, Revision A. 3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
- [19] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
- [20] Y. Nishida and S. Kida, *Inorg. Chem.* **27**, 447 (1988).
- [21] M. Handa, N. Koga, and S. Kida, *Bull. Chem. Soc. Japan* **61**, 3853 (1988).
- [22] L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson, and M. K. Park, *Inorg. Chem.* **35**, 3117 (1996).
- [23] C. Li, N. Kanehisa, Y. Miyagi, Y. Nakao, S. Takamizawa, W. Mori, and Y. Kai, *Bull. Chem. Soc. Japan* **70**, 2429 (1997).
- [24] (a) H. H. Jaffe and G. O. Doak, *J. Chem. Phys.* **21**, 196 (1953). (b) H. H. Jaffe, *J. Chem. Phys.* **21**, 258 (1953).
- [25] Y. Kuroda and K. Ito, *Nippon Kagaku Zasshi* **76**, 545 (1955).