Inorg. Chem. **2007**, *46*, 5134–5136

Inorganic Chemistry
Communication

Ferromagnetic vs Antiferromagnetic Coupling in Bis(*μ*-phenoxo)dicopper(II) Complexes. Tuning of the Nature of Exchange Coupling by Remote Ligand Substituents†

Phalguni Chaudhuri,* Rita Wagner, and Thomas Weyhermüller

Max-Planck-Institute for Bioinorganic Chemistry, Stiftstrasse 34−36, D-45470 Mülheim an der Ruhr, Germany

Received February 7, 2007

Two bis(μ-phenoxo)dicopper(II) complexes, $[(L^{CH_3})_2Cu_2]$ (**1**) and $[(L^{t-Bu})_2Cu_2]$ (**2**), where L^{CH_3} and L^{t-Bu} represent the dianions of (methylamino)-*N*,*N*-bis(2-methylene-4,6-dimethylphenol) and of (methylamino)-*N*,*N*-bis(2-methylene-4,6-di-*tert*-butylphenol), respectively, are reported to demonstrate the effect of remote substituents on the nature of exchange coupling interactions between the copper(II) centers. In contrast to **1**, which is as usual antiferromagnetically coupled, complex **2** is a rare example of a ferromagnetically coupled diphenoxodicopper(II) complex.

Hydroxo-, alkoxo-, and phenoxo-bridged dicopper(II) complexes involving a Cu_2O_2-bridging moiety are numerous in the literature, primarily because of their relevance to copper enzymes[1] and to molecular magnetism.[2] A considerable body of experimental results has been accumulated to elucidate the magnetostructural relationship. The major factor controlling the exchange coupling is observed to be the bridging Cu−O−Cu angle, and a linear variation of $2J$ with θ (the Cu−O−Cu angle) was observed for the hydroxo-bridged complexes.[3] A similar correlation has also been reported,[4,5] both theoretically and experimentally, for the alkoxo-bridged dicopper(II) complexes. Analogous attempts for bis(μ-phenoxo)dicopper(II) macrocyclic complexes[6] predicted an angle of ~77° for the Cu−O(Ph)−Cu crossover point with $-2J = 0$ cm^{-1}. This angle is well below that expected for an oxygen bridge; the corresponding Cu−OH−Cu angle of 97.5° is the crossover point, below which the magnetic behavior changes from antiferromagnetic to ferromagnetic coupling. Interestingly, structurally characterized bis(μ-phenoxo)dicopper(II) complexes (349 hits in Cambridge Crystal Structure Data Base) exhibit almost exclusively antiferromagnetic spin coupling;[7] weak ferromagnetic behavior[8] is observed only for four compounds in which the Cu−O(Ph)−Cu angle lies in the range of 90.8−96.1°. Irrespective of the bridging angle, bis(μ-phenoxide)dicopper(II) complexes can be arbitrarily divided into four groups according to the nature and strength of the exchange coupling observed between the copper(II) centers: (i) $J > 0$ cm^{-1}; (ii) $-J \leq 50$ cm^{-1}; (iii) $-J \leq 50-150$ cm^{-1}; (iv) $-J \leq 150$ and above. Most of the diphenoxide complexes of copper(II) are moderate to strongly antiferromagnetically coupled, thus belonging to the groups iii and iv and with the Cu−O(Ph)−Cu angle greater than ~97°.[6] Only for a few members of this class of compounds is the magnitude of the exchange coupling weak antiferromagnetic (for group ii, $-J \leq 50$ cm^{-1}),[7e] which was rationalized on the basis of structural parameters other than the bridging angle. In this Communication, we report two such dicopper(II) compounds with the ligands[9] $H_2L^{CH_3}$ and H_2L^{t-Bu}, in which the ligands

---

† This work was supported by the DFG Priority Program “Molecular Magnetism (SPP 1137)” Ch 111/3-3.

* To whom correspondence should be addressed. E-mail: Chaudh@mpi-muelheim.mpg.de.

(1) Reed, C. A.; Orosz, R. D. Spin Coupling Concepts in Bioinorganic Chemistry. In *Research Frontiers in Magnetochemistry*; O’Connor, C. J., Ed.; World Scientific: Singapore, 1993; p 351.

(2) Kahn, O. *Molecular Magnetism*; Wiley-VCH, Weinheim, Germany, 1993.

(3) (a) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107. (b) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.

(4) (a) Handa, M.; Koga, N.; Kida, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3853. (b) Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, 875.

(5) (a) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997,** *119*, 1297. (b) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683.

(6) Thompson, L. K.; Mandal, S. K.; Tandon, S. S.; Bridson, J. N.; Park, M. K. *Inorg. Chem.* **1996**, *35*, 3117.

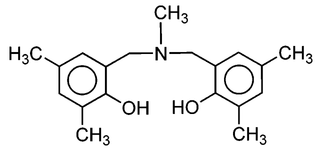
(7) Selected recent examples: (a) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1988**, *27*, 4149. (b) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J.; Nag, K. *Inorg. Chem.* **1990**, *29*, 1324. (c) Berti, E.; Caneschi, A.; Daiguebonne, C.; Dapporto, P.; Formica, M.; Fusi, V.; Giorni, L.; Guerri, A.; Micheloni, M.; Paoli, P.; Pontellini, R.; Rossi, P. *Inorg. Chem.* **2003**, *42*, 348. (d) Paschke, R.; Liebsch, S.; Tschierske, C.; Dakley, A.; Sinn, E. *Inorg. Chem.* **2003**, *42*, 8230. (e) Saimiya, H.; Sunatsuki, Y.; Kojima, M.; Kashino, S.; Kambe, T.; Hirotsu, M.; Akashi, H.; Nakajima, K.; Tokii, T. *J. Chem. Soc., Dalton Trans.* **2002**, 3737 and references cited therein.

(8) (a) Shyu, H. L.; Wie, H. H.; Lee, G. H.; Wang, Y. *Inorg. Chem.* **1996**, *35*, 5396. (b) Kruse, T.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chim. Acta* **2002**, *331*, 81. (c) Mukhopadhyay, S.; Mandal, D.; Chatterjee, P. B.; Desplanches, C.; Sutter, J.-P.; Butcher, R. J.; Chaudhury, M. *Inorg. Chem.* **2004**, *43*, 8501.

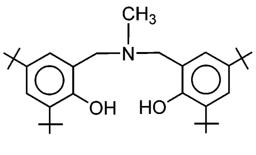
(9) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 4945.

10.1021/ic070238p CCC: $37.00

contain the same [O,N,O]-donor atoms but with different remote substituents on the involved phenol rings.



$H_2L^{CH_3}$



$H_2L^{t\text{-}Bu}$

Complex **1**,[10] $[Cu_2(L^{CH_3})_2]$, with the bridging angles at 97.0(2)° and 99.4(2)°, exhibits as expected antiferromagnetic exchange coupling ($J = -136$ cm^{-1}); on the contrary, in complex **2**,[10] $[Cu_2(L^{t-Bu})_2]$ with the Cu−O(Ph)−Cu angles at 86.34(2)° and 85.92(3)°, the copper(II) centers are ferromagnetically coupled ($J = +26$ cm^{-1}).

Preparation of complex **1** involves an intermolecular redox reaction, $2Cu^I \rightarrow Cu^0 + Cu^{II}$, in which presumably a semiquinone radical is an intermediate. Complex **1** (Figure 1) has a noncentrosymmetric structure[11] with a binuclear $Cu_2(\mu\text{-}OPh)_2$ asymmetric rectangular core. Each copper center is four-coordinate with two bridging μ_2-phenoxide oxygen atoms, an amine nitrogen, and a phenolate monodentate oxygen. The trans angles at the copper centers lying in the range of 164.5−172.3° indicate the distorted square-planar nature of the metal geometry. A weak interaction between an acetonitrile molecule with Cu(2), N(50)−Cu(2) at 2.528 Å, exists (not shown). Two angles, O(1)−Cu(2)−O(3) and O(1)−Cu(1)−O(3) with 74.8° and 76.8°, deviate largely from the ideal 90°. The bridging phenoxo oxygen atoms, O(3) and O(1), for **1** adopt almost planar geometry, with the sum of the bond angles around the oxygen atoms being 359.8° and 357°, respectively. The Cu(1) and Cu(2) atoms are displaced by 0.225 and 0.217 Å, respectively, from the mean plane Cu(1)−O(3)−Cu(2)−O(1). As expected, Cu(1)−O(bridging) with an avearge of 1.94 Å is appreciably longer than Cu(1)−O(nonbridging) at 1.87 Å; similarly, Cu(2)−O(bridging) at an average of 1.98 Å is longer than Cu(2)−O(4) at 1.89 Å. The bridging angles with Cu(1)−O(1)−Cu(2) at 97.0(2)° and Cu(1)−O(3)−Cu(2) at 99.4° and the Cu(1)···Cu(2) separation of 2.967 Å fall in the ranges as observed for similar complexes with antiferromagnetic spin coupling.[6,7]

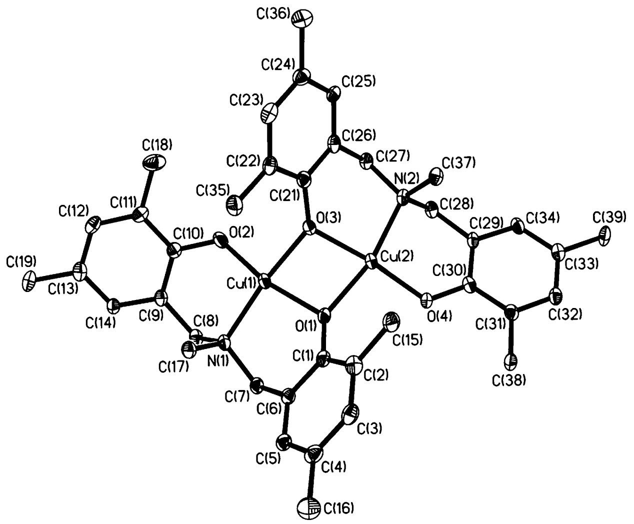


Figure 1. ORTEP drawing of **1**. Selected bond lengths (Å) and angles (deg): Cu(1)−O(1) 1.946(4), Cu(1)−O(3) 1.936(3), Cu(1)−O(2) 1.865(4), Cu(1)−N(1) 2.010(3), Cu(2)−O(1) 2.014(3), Cu(2)−O(3) 1.954(4), Cu(2)−N(2) 2.025(4), Cu(2)−O(4) 1.889(4); O(2)−Cu(1)−O(3) 93.4(2), O(2)−Cu(1)−O(1) 164.52(14), O(3)−Cu(1)−O(1) 76.81(14), O(2)−Cu(1)−N(1) 96.5(2), O(3)−Cu(1)−N(1) 169.0(2), O(1)−Cu(1)−N(1) 94.4(2), O(4)−Cu(2)−O(3) 172.25(14), O(4)−Cu(2)−O(1) 97.85(14), O(3)−Cu(2)−O(1) 74.84(13), O(4)−Cu(2)−N(2) 96.0(2), O(3)−Cu(2)−N(2) 91.3(2), O(1)−Cu(2)−N(2) 166.1(2).

The noncentrosymmetric structure of complex **2**,[11] displayed in Figure 2, reveals that the rectangular core $Cu_2(OPh)_2$ is more symmetrical but folded than that in **1**. Additionally, the copper geometry in **2** deviates more from square planar than that in **1**. The geometry around the bridging phenoxide oxygen atoms is closer to a pyramid for **2**, with the angles 337.9° and 339.2°. The two copper centers comprising the planes Cu(2)−N(48)−O(15)−O(41)−O(55) and Cu(1)−N(8)−O(1)−O(41)−O(15) form a folded structure with the dihedral angle between the mean planes at 75.4°. As expected, the Cu(1) and Cu(2) atoms are displaced from the best planes by 0.131 and 0.125 Å, respectively. Thus, deviation of the copper coordination geometry from square planarity for **2** is more severe than that for complex **1**. The bridging angles Cu(1)−O(15)−Cu(2) at 86.34(3)° and Cu(1)−O(41)−Cu(2) at 85.92(3)° are very similar and unprecedently short reported so far in the literature. The Cu(1)···Cu(2) separation with 2.697 Å is also the shortest known so far for similar complexes.[6−8]

Magnetic data (SQUID) for polycrystalline samples of **1** and **2** are displayed in Figure 3 as μ_{eff} per molecule vs T. Upon a decrease in the temperature, the effective magnetic

---

(10) Complex **1**: To the pale-yellow solution containing $H_2L^{CH_3}$ (0.3 g, 1 mmol) and Et_3N (0.5 mL) in dry acetonitrile (50 mL) was added $[Cu^I(CH_3CN)_4]ClO_4$ (0.33 g, 1 mmol), and the solution was refluxed under argon for 0.5 h, upon which the solution turned to red-brown with a copper mirror on the surface of the round-bottomed flask. The solution was cooled and brought to air with stirring for 0.5 h. The precipitated dark-green microcrystalline solid was isolated by filtration and air-dried. Yield: 0.14 g (39%). Anal. Calcd for $C_{38}H_{46}N_2O_4Cu_2$: C, 63.22; H, 6.42; N, 3.88; Cu, 17.61. Found: C, 62.9; H, 6.4; N, 3.9; Cu, 18.0. MS-EI: *m/z* 721 (M^+), 360 ($M^+/2$). UV−vis in CH_2Cl_2 (λ, nm; ϵ, M^{-1} cm^{-1}): 423 (5600), 620 (8200), 760sh (~350). IR (KBr, cm^{-1}): 2914, 1634, 1476, 1306, 1255, 1161, 806. X-ray-quality crystals were grown from a solvent mixture (1:1) of dichloromethane and acetonitrile. Complex **2**: A solution of the ligand H_2L^{t-Bu} (0.8 mmol) and Et_3N (0.5 mL) in distilled methanol (50 mL) was degassed and charged with solid CuCl (0.1 g, 1 mmol). The solution was refluxed for 40 min under argon and exposed to air, upon which a gold-brown crystalline solid precipitated out. Yield: 0.2 g (~47%). Anal. Calcd for $C_{62}H_{94}N_2O_4Cu_2$: C, 70.35; H, 8.95; N, 2.65; Cu, 12.01. Found: C, 69.2; H, 9.1; N, 2.7; Cu, 12.1. MS-EI positive in CH_2Cl_2: *m/z* 1059 (M^+). UV−vis in CH_2Cl_2 (λ, nm; ϵ, M^{-1} cm^{-1}): 430 (5500), 325 (10 500), 302 (17 000), 650 (980), 830 (230). IR (KBr, cm^{-1}): 2959, 2904, 2868, 2678, 1604, 1474, 1442, 1413, 1360, 1305, 1284, 1236, 1166, 1095, 836, 827.

(11) Crystal data for **1**: $C_{38}H_{46}Cu_2N_2O_4 \cdot CH_3CN \cdot 0.5H_2O$, $M_f = 771.91$, $T = 100(2)$ K, triclinic, $a = 11.6777(9)$ Å, $b = 12.908(2)$ Å, $c = 13.519(2)$ Å, $\alpha = 79.69(2)°$, $\beta = 77.03(2)°$, $\gamma = 67.96(2)°$, $V = 1830.3(4)$ Å^3, space group $P1$, $Z = 2$. A total of 5111 independent reflections was used for solution and refinement (*SHELX97*) by full-matrix least squares on F^2; absorption correction, Gaussian, face-indexed. Final R indices: R1 = 0.0522, R1(all data) = 0.0855. Crystal data for **2**: $C_{62}H_{94}Cu_2N_2O_4$, $M_f = 1058.47$, $T = 100(2)$ K, triclinic, $a = 10.0842(6)$ Å, $b = 10.7271(6)$ Å, $c = 27.6144(14)$, $\alpha = 93.97(1)°$, $\beta = 94.92(1)°$, $\gamma = 90.00(1)°$, $V = 2969.0(3)$ Å^3, space group $P1$, $Z = 2$. A total of 22 513 independent reflections was used for solution and refinement (*SHELX97*) by full-matrix least squares on F^2. Final R indices: R1 = 0.0351, R1(all data) = 0.0417.

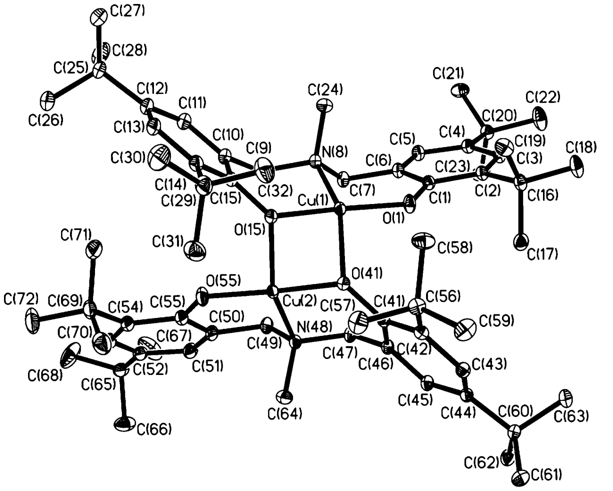


Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Cu(1)−O(1) 1.8439(8), Cu(1)−O(15) 1.9195(8), Cu(1)−N(8) 2.0077(10), Cu(1)−O(41) 2.0267(8), Cu(2)−O(55) 1.8496(9), Cu(2)−O(41) 1.9302(8), Cu(2)−N(48) 2.0025(9), Cu(2)−O(15) 2.0217(8); O(1)−Cu(1)−O(15) 167.01(4), O(1)−Cu(1)−N(8) 95.94(4), O(15)−Cu(1)−N(8) 95.22(4), O(1)−Cu(1)−O(41) 96.65(4), O(15)−Cu(1)−O(41) 76.56(3), N(8)−Cu(1)−O(41) 150.57(4), O(55)−Cu(2)−O(41) 168.06(4), O(55)−Cu(2)−N(48) 95.84(4), O(41)−Cu(2)−N(48) 94.38(4), O(55)−Cu(2)−O(15) 97.11(4), O(41)−Cu(2)−O(15) 76.45(3), N(48)−Cu(2)−O(15) 151.70(4).

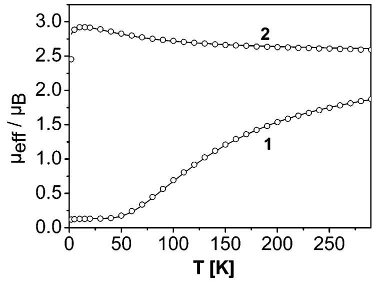


Figure 3. Simulated (solid lines) and experimental data (○) for the μ_{eff} vs T plots of complexes **1** and **2**.

moment for **1**, μ_{eff} of 1.872 μ at 290 K, decreases monotonically, reaching a value of 0.118 μ_{B} at 2 K. This arises from antiparallel spin coupling between two copper(II) centers with $S_{\mathrm{Cu}} = {}^{1}/_{2}$. Simulation ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$) of the data yields $J = -135.6$ cm^{-1}, $g = 1.988$, and PI = 0.6%, where PI represents the paramagnetic impurity of $S = {}^{1}/_{2}$. Considering that the simulated g value of 1.988 is small for copper(II), we have performed another simulation keeping g-fixed at 2.00. The simulation with $g = 2.00$ (fixed), shown in Figure 3 yields $J = -136.8$ cm^{-1} and PI = 0.6%. Thus, complex **1** belongs to the usual moderate to strong antiferromagnetically coupled diphenoxo-bridged copper(II) complexes (groups iii and iv). On the contrary, the μ_{eff} vs T plot for **2** shows a maximum at 10−20 K with $\mu_{\mathrm{eff}} = 2.918$ μ_{B}, indicating ferromagnetic coupling operating between the adjacent copper(II) centers. Simulation of the experimental data yields the following parameters: $J = +26.3$ cm^{-1} and $g = 2.068$.

A comparison of key structural parameters and exchange integrals for the bis(μ-phenoxo)dicopper(II) complexes reveals the dependence of J on (i) the Cu−O(phenolate)−Cu angle, (ii) the Cu···Cu distance, (iii) the pyramidal geometry around the phenolate oxygen atom, and (iv) the deviation of the copper coordination geometry from square pyramid. Ferromagnetically coupled complex **2** differs structurally from other similar compounds in the literature.[6−8]

Weak ferromagnetic coupling in such diphenoxo complexes (only four of them are known), which are exclusively five-coordinated, has been ascribed to the Cu−O−Cu angle (range of 90.8−96.1°), considered to be the main structural parameter responsible for the exchange coupling. Regrettably, none of the four said structural parameters alone can satisfactorily explain the trend of the exchange interactions in the present complex **2**. The parallel spin coupling in **2**, on the other hand, can be ascribed to the folded $\mathrm{Cu_2L_2}$ structure, in which two copper planes make an angle of 75.4°; thus, folding of the planes comprising the $\mathrm{Cu_2O_2}$ core in **2** lowers the magnitude of the antiferromagnetic interaction [which dominates exchange coupling between two copper(II) centers] due to loss of orbital overlap. Similar diminution of antiferromagnetic coupling due to a folded $\mathrm{Cr_2O_2}$ core has been observed earlier.[12] Moreover, although there are not many differences in the Cu−O distances for **1** and **2** (average 1.963 vs 1.975 Å, respectively), there is a remarkable reduction in the Cu···Cu separation for **2** with 2.697 vs 2.967 Å for **1**. This reduction favors the direct interaction, increasing also the ferromagnetic contribution.

The inductive (I) effects of the substituents for the methyl and *tert*-butyl groups are not very different and, therefore, do not provide a basis for an explanation of the different magnetic behaviors for **1** and **2**. Hence, the difference in the structural and magnetic data for **1** and **2** can be ascribed to the structural influence of steric bulk related to the *tert*-butyl groups in the ligand $\mathrm{H_2L}^{t\text{−Bu}}$.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070238P

---

(12) Paine, T. K.; Weyhermüller, T.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **2002**, *41*, 6538.