Metal Porphyrins

DOI: 10.1002/ange.200501943

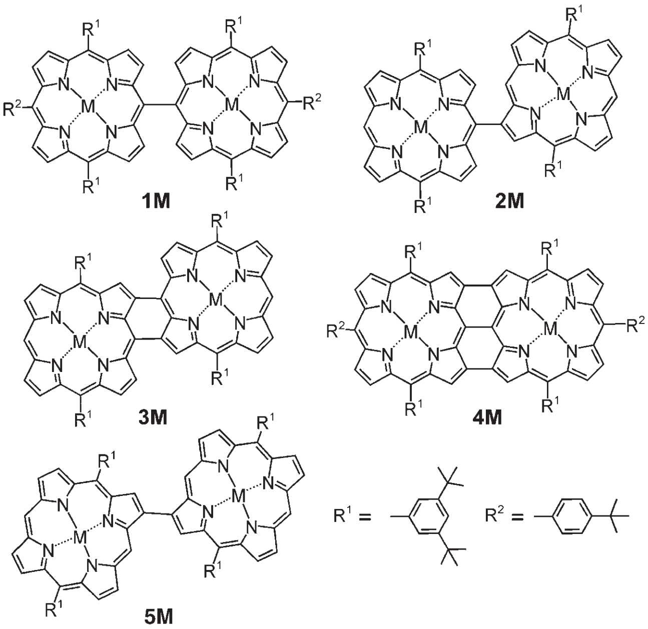
The Importance of a β–β Bond for Long-Range Antiferromagnetic Coupling in Directly Linked Copper(II) and Silver(II) Diporphyrins**

Takahisa Ikeue, Ko Furukawa, Hiroshi Hata, Naoki Aratani, Hiroshi Shinokubo, Tatsuhisa Kato, and Atsuhiro Osuka**

Magnetic exchange coupling between distant metal centers is a major topic in the field of magnetochemistry.[1] Although a great number of covalently linked oligomacrocycles (e.g. porphyrins or phthalocyanines) have so far been prepared, only a few such molecules have been tested for the exploitation of long-range magnetic coupling.[2,3] One difficulty in the use of these metalated macrocycles for magnetic coupling may be exemplified by the work of Eaton et al., in which a $-J$ value of only about 0.5 cm^{-1} was detected for a face-to-face coplanar bis-Cu^{II} diporphyrin with a short center-to-center distance of around 4.1 Å.[2a] However, suitably arranged intervening bridges may help magnetic communication between distant metal centers.[3]

In recent years, we have explored a series of directly linked diporphyrins, including the *meso–meso* singly linked diporphyrin **1**,[4a] the *meso*–β singly linked diporphyrin **2**,[4b,e] the *meso*–β, β–*meso* doubly linked diporphyrin **3**,[4c,e] and the *meso–meso*, β–β, β–β triply linked diporphyrin **4**.[4d,e,f] Because of their direct covalent linkages, these diporphyrins exhibit a large electronic interaction, which increases in the order $\mathbf{2} < \mathbf{1} \ll \mathbf{3} \ll \mathbf{4}$, as judged from the absorption spectra.[4] In these diporphyrins, two metal centers that are connected by various σ-bond networks are kept strictly apart due to the center-to-center distances of 8.34, 8.91, 8.60, and 8.42 Å for **1**, **2**, **3**, and **4**, respectively.[5] Herein we report antiferromagnetic coupling in bis-Cu^{II} and bis-Ag^{II} complexes of **1**–**4**. It is known that the unpaired spin of both Cu^{II} and Ag^{II} porphyrins is localized in the $d_{x^2-y^2}$ orbital, which leads to a situation where the unpaired electrons can be delocalized into the porphyrinic π-electronic network only through a σ-bond pathway.[6] In this context, the diporphyrins **1**–**4** constitute a nice set for systematic studies on the dependence of antiferromagnetic interactions on a direct linkage.

The free-base diporphyrins **1**–**4** were prepared by the reported methods[4] and metalated with $Cu(OAc)_2$ and AgOAc to afford **1Cu**–**4Cu** and **1Ag**–**4Ag**, respectively (Scheme 1). The effective magnetic moments (χT) at 300 K



Scheme 1. Directly linked porphyrins **1M**–**5M**. M: Cu^{II}, Ag^{II}.

---

[*] Prof. Dr. T. Kato
Department of Chemistry
Graduate School of Science
Josai University
Sakado 350–0295 (Japan)
Fax: (+81) 49-271-7985
E-mail: rik@mail.josai.ac.jp

Dr. T. Ikeue, H. Hata, Dr. N. Aratani, Prof. Dr. H. Shinokubo, Prof. Dr. A. Osuka
Department of Chemistry
Graduate School of Science
Kyoto University
and
Core Research for Evolutional Science and Technology (CREST)
Japan Science and Technology Agency
Sakyo-ku, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp

Dr. K. Furukawa
Institute for Molecular Science
Myodaiji, Okazaki 444-8585 (Japan)

[**] This work was partly supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (no. 15350022 and 21st Century COE on Kyoto University Alliance for Chemistry) and by the International Innovation Center of Kyoto University.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

were determined to be 0.82–0.87 emu K mol^{-1} for **1Cu**–**4Cu**, thus indicating the presence of two magnetically uncoupled spin doublets (Figure 1 a; see also Supporting Information (SI)). Variable-temperature magnetic susceptibility measurements revealed that the χT values of **1Cu**, **2Cu**, and **3Cu** are nearly temperature-independent in the range 2–300 K, with essentially constant values of about 0.8 emu K mol^{-1}.

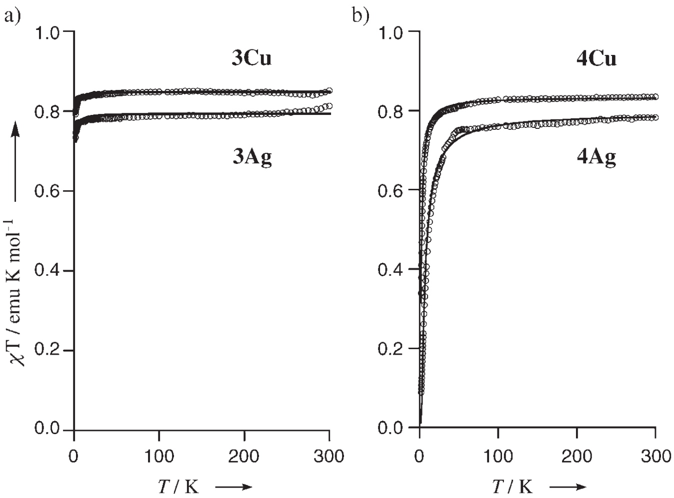


Figure 1. Variable-temperature magnetic susceptibility measurements in the range 2–300 K: a) **3Cu** and **3Ag**, b) **4Cu** and **4Ag**. The solid lines represent the fitting curves based on the Bleaney–Bowers equation.

The mean g values in the EPR spectra of **1Cu**, **2Cu**, and **3Cu** in frozen toluene at 4.0 K were 2.08, 2.13, and 2.13 (see SI), respectively, which were reproduced as a simple sum of an isolated Cu^{II} porphyrin. In contrast, the χT value of **4Cu** was found to drop sharply at temperatures below 20 K and to reach a value of 0.34 emu K mol^{-1} at 2.0 K (Figure 1 b). This temperature dependence is indicative of Curie law behavior with a weak antiferromagnetic coupling between the two copper(II) ions. A least-squares fit with the Bleaney–Bowers equation gave a $-J$ value of 1.43 cm^{-1} for **4Cu**. In line with the χT measurement, the EPR spectrum of **4Cu** at the mean g value of 2.11 could not be reproduced as a sum of isolated Cu^{II} porphyrins but as two magnetically interacting Cu^{II} porphyrins. This means that the spectrum of **4Cu** is due to the thermally populated $S = 1$ triplet state above the $S = 0$ ground state.

The magnetic properties of **1Ag**–**4Ag** were also examined. In the range 2–300 K, the χT values of **1Ag**–**3Ag** are temperature independent (ca. 0.8 emu K mol^{-1}; Figure 1 a), thus indicating the presence of two magnetically uncoupled spin doublets, while the χT values of **4Ag** exhibit a sharp drop below 20 K, reaching a value of 0.09 emu K mol^{-1} at 2.0 K (see SI and Figure 1 b). The mean g values in the EPR spectra of **1Ag**–**4Ag** in frozen toluene are 2.06, 2.07, 2.06, and 2.06, respectively. The spectra of **1Ag**–**3Ag** were reproduced as a simple sum of isolated Ag^{II} porphyrins, whereas that of **4Ag** could be reproduced as two magnetically interacting Ag^{II} porphyrins, similarly to the case of **4Cu** (see SI). The least-squares fit with the Bleaney–Bowers equation gave a $-J$ value of 3.64 cm^{-1} for **4Ag** (Figure 1 b).

The marked differences observed between the magnetic coupling behaviors of **4M** and **1M**–**3M** led us to consider the importance of a β–β bond for effective long-range magnetic coupling, since such a linkage only exists in **4M**. We thus prepared a new β–β singly linked diporphyrin **5M** from a β-borylated porphyrin precursor.[7] Both bis-metalated complexes **5Cu** and **5Ag** exhibit long center-to-center distances of around 9.63 Å and the lowest excitonic coupling in the absorption spectra in the series. Nevertheless, as shown in Figure 2, both the χT values of **5Cu** and **5Ag** exhibit temperature-dependent behavior at low temperature, reaching values of 0.65 and 0.24 emu K mol^{-1} at 2.0 K, respectively. The least-squares fit of the χT values with the Bleaney–Bowers equation provided $-J$ values of 0.55 and 1.73 cm^{-1}, respectively. These results clearly indicate the critical role of a direct β–β bond in the long-range antiferromagnetic coupling.

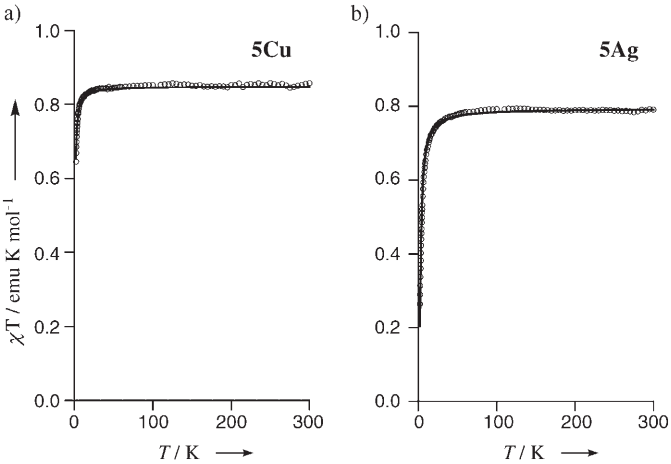


Figure 2. Variable-temperature magnetic susceptibility measurements in the range 2–300 K: a) **5Cu** and b) **5Ag**. The solid lines represent the fitting curves based on the Bleaney–Bowers equation.

Although excited triplet states are present in **4Cu**, **4Ag**, **5Cu**, and **5Cu**, no EPR signal was observed at the half field. This can be accounted for in terms of a small fine-structure interaction $|D|$ in the triplet states (see SI) of these diporphyrins.[8] The $|D|$ value should become smaller with increasing spin–spin distance. Actually, a simple estimation of $|D|$ for **4M** and **5M** led to a prediction that the "forbidden transition" at the half field is hardly observed in these cases (see SI); this seems to be a general feature of diporphyrins with a large center-to-center distance.

The critical importance of a direct β–β bond can be explained in terms of the spin densities of Cu^{II} and Ag^{II} porphyrin monomers, as calculated by the DFT method at the B3LYP level. The 6-31G* basis set was employed except for Cu and Ag, for which a basis set consisting of the Stuttgart effective core potential was used. In both cases, the calculations confirmed that the unpaired electron in the $d_{x^2-y^2}$

orbital develops only at the β position and not at the *meso* position (see SI), thus highlighting the importance of a direct β–β bond. In fact, the calculated singly occupied MOs (SOMOs; Figure 3) of a model compound for **4 Cu**, in which all *meso* substituents were replaced with hydrogen, indicate that the spin orbital of the copper porphyrin interacts only through the β–β bond in the $S=1$ state (Figure 3 a). In addition, the DFT calculations support our interpretation of the EPR measurements, namely that the $S=0$ ground state lies below the $S=1$ state.

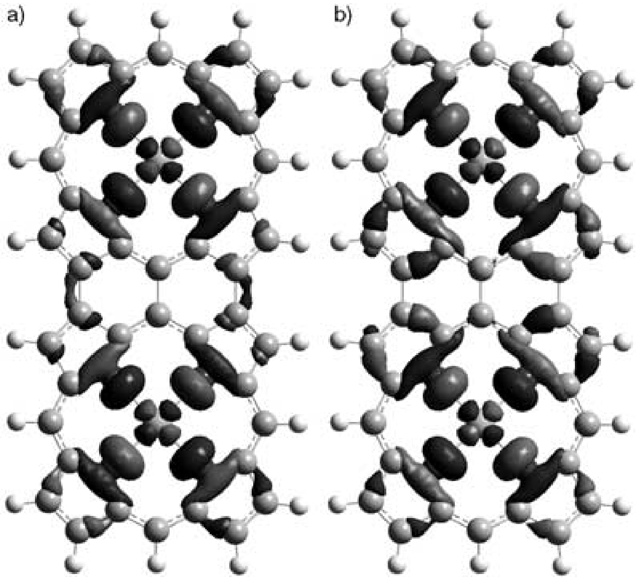


Figure 3. Two calculated SOMOs of a model for **4 Cu** in the $S=1$ state.

The antiferromagnetic couplings are larger in the Ag^{II} complexes than in their Cu^{II} counterparts. Since the spin distribution patterns are similar due to the spin location in the $d_{x^2-y^2}$ orbital, the observed difference may be attributed to different spin densities. The spin density distribution via the σ-contact contribution can be estimated by a ^{2}H NMR method. Typically, the ^{2}H NMR spectrum of Cu^{II}(tpp) exhibits the pyrrole β-^{2}H signal at around $\delta = 41$ ppm as a broad signal,[9] while the signals of Ag^{II}(tpp) are too broad to be detected, thus indicating that the σ-contact contribution is larger for Ag^{II} porphyrin than Cu^{II} porphyrin. The fact that **5 Ag** lies roughly on the long-range limit predicted by the Coffman–Buettner equation[10] suggests that the direct β–β bond allows an effective σ-bond pathway for long-range antiferromagnetic coupling between distal paramagnetic metal ions in porphyrins (see SI).

In conclusion, we have shown that antiferromagnetic coupling is only effective for **4 Cu**, **4 Ag**, **5 Cu**, and **5 Ag**, thus underlining the crucial importance of a direct β–β bond. However, even in the extensively π-conjugated diporphyrins **4 Cu** and **4 Ag**, the long-range antiferromagnetic interaction is considered to propagate via a β–β σ-bond pathway. These results will be quite useful for further molecular design of magnetically coupled molecules. The exploration of higher Cu^{II} and Ag^{II} porphyrin arrays is an attractive subject that is actively being pursued in our laboratory.

Received: June 6, 2005

Keywords: copper · magnetochemistry · metal–metal interactions · porphyrinoids · silver

---

[1] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.
[2] a) S. S. Eaton, G. R. Eaton, C. K. Chang, *J. Am. Chem. Soc.* **1985**, *107*, 3177; b) J. Wojacyznski, L. Latos-Grażyński, P. J. Chmielewski, P. V. Calcar, A. L. Balch, *Inorg. Chem.* **1999**, *38*, 3040; c) M. Zhao, C. Zhong, C. Stern, A. G. M. Barrett, B. M. Hoffman, *Inorg. Chem.* **2004**, *43*, 3377.
[3] Some directly linked oligoporphyrins have been used for spin alignment of π radicals; see: a) H. Segawa, D. Machida, Y. Senshu, J. Nakazaki, K. Hirakawa, F. Wu, *Chem. Commun.* **2002**, 3032; b) H. Segawa, Y. Senshu, J. Nakazaki, K. Susumu, *J. Am. Chem. Soc.* **2004**, *126*, 1354.
[4] a) A. Osuka, H. Shimidzu, *Angew. Chem.* **1997**, *109*, 93; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135; b) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Angew. Chem.* **1999**, *111*, 140; *Angew. Chem. Int. Ed.* **1999**, *38*, 176; c) A. Tsuda, A. Nakano, H. Furuta, H. Yamochi, A. Osuka, *Angew. Chem.* **2000**, *112*, 572; *Angew. Chem. Int. Ed.* **2000**, *39*, 558; d) A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem.* **2000**, *112*, 2649; *Angew. Chem. Int. Ed.* **2000**, *39*, 2549; e) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304; f) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79.
[5] The center-to-center distances were estimated from the X-ray crystal structures of the related diporphyrins given in reference [4e].
[6] G. N. La Mar, F. A. Walker in *The Porphyrins, Vol. IVB* (Ed.: D. Dolphin), Academic Press, New York, **1979**, p. 57.
[7] H. Hata, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 8264.
[8] A. Bencini, D. Gatteschi, *EPR of Exchange Coupled Systems*, Springer, Berlin, **1989**.
[9] G. M. Godziela, H. M. Goff, *J. Am. Chem. Soc.* **1986**, *108*, 2237.
[10] R. E. Coffman, G. R. Buettner, *J. Phys. Chem.* **1979**, *83*, 2387.