## Metal Porphyrins

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

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Magnetic exchange coupling between distant metal centers is a major topic in the field of magnetochemistry.<sup>[1]</sup> Although a

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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.<sup>[2,3]</sup> 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<sup>-1</sup> was detected for a face-to-face coplanar bis-Cu<sup>II</sup> diporphyrin with a short center-to-center distance of around 4.1 Å.<sup>[2a]</sup> However, suitably arranged intervening bridges may help magnetic communication between distant metal centers.<sup>[3]</sup>

In recent years, we have explored a series of directly linked diporphyrins, including the meso-meso singly linked diporphyrin 1,<sup>[4a]</sup> the *meso*- $\beta$  singly linked diporphyrin 2,<sup>[4b,e]</sup> the meso- $\beta$ ,  $\beta$ -meso doubly linked diporphyrin **3**,<sup>[4c,e]</sup> and the *meso-meso*,  $\beta$ - $\beta$ ,  $\beta$ - $\beta$  triply linked diporphyrin 4.<sup>[4d,e,f]</sup> Because of their direct covalent linkages, these diporphyrins exhibit a large electronic interaction, which increases in the order 2 < $1 \ll 3 \ll 4$ , as judged from the absorption spectra.<sup>[4]</sup> In these diporphyrins, two metal centers that are connected by various  $\sigma$ -bond networks are kept strictly apart due to the center-tocenter distances of 8.34, 8.91, 8.60, and 8.42 Å for 1, 2, 3, and 4, respectively.<sup>[5]</sup> 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<sup>II</sup> and Ag<sup>II</sup> 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  $\pi$ -electronic network only through a  $\sigma$ -bond pathway.<sup>[6]</sup> 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<sup>[4]</sup> and metalated with Cu(OAc)<sub>2</sub> and AgOAc to afford 1Cu–4Cu and 1Ag–4Ag, respectively (Scheme 1). The effective magnetic moments ( $\chi T$ ) at 300 K



Scheme 1. Directly linked porphyrins 1 M-5 M. M: Cu<sup>II</sup>, Ag<sup>II</sup>.

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were determined to be 0.82–0.87 emu K mol<sup>-1</sup> for **1Cu–4Cu**, thus indicating the presence of two magnetically uncoupled spin doublets (Figure 1a; see also Supporting Information (SI)). Variable-temperature magnetic susceptibility measurements revealed that the  $\chi T$  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<sup>-1</sup>.



*Figure 1.* Variable-temperature magnetic susceptibility measurements in the range 2–300 K: a) **3 Cu** and **3 Ag**, b) **4 Cu** and **4 Ag**. 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<sup>II</sup> porphyrin. In contrast, the  $\chi T$  value of **4Cu** was found to drop sharply at temperatures below 20 K and to reach a value of  $0.34 \text{ emu K mol}^{-1}$  at 2.0 K (Figure 1b). 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<sup>-1</sup> for **4Cu**. In line with the  $\chi T$  measurement, the EPR spectrum of 4Cu at the mean g value of 2.11 could not be reproduced as a sum of isolated Cu<sup>II</sup> porphyrins but as two magnetically interacting Cu<sup>II</sup> 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  $\chi T$  values of **1Ag-3Ag** are temperature independent (ca. 0.8 emu K mol<sup>-1</sup>; Figure 1 a), thus indicating the presence of two magnetically uncoupled spin doublets, while the  $\chi T$  values of **4Ag** exhibit a sharp drop below 20 K, reaching a value of 0.09 emu K mol<sup>-1</sup> 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<sup>II</sup> porphyrins, whereas that of **4Ag** could be reproduced as two magnetically interacting Ag<sup>II</sup> 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<sup>-1</sup> for 4Ag (Figure 1b).

The marked differences observed between the magnetic coupling behaviors of **4M** and **1M–3M** led us to consider the importance of a  $\beta$ – $\beta$  bond for effective long-range magnetic coupling, since such a linkage only exists in **4M**. We thus prepared a new  $\beta$ – $\beta$  singly linked diporphyrin **5M** from a  $\beta$ -borylated porphyrin precursor.<sup>[7]</sup> 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  $\chi T$  values of **5Cu** and **5Ag** exhibit



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

temperature-dependent behavior at low temperature, reaching values of 0.65 and 0.24 emu K mol<sup>-1</sup> at 2.0 K, respectively. The least-squares fit of the  $\chi T$  values with the Bleaney– Bowers equation provided -J values of 0.55 and 1.73 cm<sup>-1</sup>, respectively. These results clearly indicate the critical role of a direct  $\beta$ - $\beta$  bond in the long-range antiferromagnetic coupling.

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.<sup>[8]</sup> 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  $\beta$ - $\beta$  bond can be explained in terms of the spin densities of Cu<sup>II</sup> and Ag<sup>II</sup> 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<sub>x<sup>2</sup>-y<sup>2</sup></sub>

orbital develops only at the  $\beta$  position and not at the *meso* position (see SI), thus highlighting the importance of a direct  $\beta$ - $\beta$  bond. In fact, the calculated singly occupied MOs (SOMOs; Figure 3) of a model compound for **4Cu**, in which



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

all *meso* substituents were replaced with hydrogen, indicate that the spin orbital of the copper porphyrin interacts only through the  $\beta$ - $\beta$  bond in the S=1 state (Figure 3a). 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.

The antiferromagnetic couplings are larger in the Ag<sup>II</sup> complexes than in their Cu<sup>II</sup> counterparts. Since the spin distribution patterns are similar due to the spin location in the  $d_{y^2-y^2}$  orbital, the observed difference may be attributed to different spin densities. The spin density distribution via the σcontact contribution can be estimated by a <sup>2</sup>H NMR method. Typically, the <sup>2</sup>H NMR spectrum of Cu<sup>II</sup>(tpp) exhibits the pyrrole  $\beta^{-2}$ H signal at around  $\delta = 41$  ppm as a broad signal,<sup>[9]</sup> while the signals of Ag<sup>II</sup>(tpp) are too broad to be detected, thus indicating that the  $\sigma$ -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<sup>[10]</sup> suggests that the direct  $\beta$ - $\beta$  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 **4Cu**, **4Ag**, **5Cu**, and **5Ag**, thus underlining the crucial importance of a direct  $\beta$ - $\beta$  bond. However, even in the extensively  $\pi$ -conjugated diporphyrins **4Cu** and **4Ag**, the long-range antiferromagnetic interaction is considered to propagate via a  $\beta$ - $\beta$   $\sigma$ -bond pathway. These results will be quite useful for further molecular design of magnetically coupled molecules. The exploration of higher

Cu<sup>II</sup> and Ag<sup>II</sup> porphyrin arrays is an attractive subject that is actively being pursued in our laboratory.

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