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Very Long-Distance Magnetic Coupling in a Dicopper(II) Metallacyclophane with Extended π-Conjugated Diphenylethyne Bridges

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Supporting Information

ABSTRACT: Self-assembly of the rigid rodlike ligand *N,N′*-4,4′-diphenylethynebis(oxamate) (dpeba) and Cu^{2+} ions affords a novel dinuclear copper(II) metallacyclophane $(nBu_4N)_4[Cu_2(dpeba)_2]\cdot 4MeOH\cdot 2Et_2O$ (**1**) featuring a very long intermetallic distance (r = 15.0 Å). Magnetic susceptibility measurements for **1** reveal a moderately weak but nonnegligible intramolecular antiferromagnetic coupling between the two metal centers across the double para-substituted diphenylethynediamidate bridge ($J = -3.9$ cm^{-1}; $H = -JS_1S_2$, where $S_1 = S_2 = S_{Cu} = {}^1/_2$). Density functional electronic structure calculations on **1** support the occurrence of a spin polarization mechanism.

Polymetallic complexes with strong intramolecular electronic interactions between distant metal centers across extended bridges are a common topic in molecular magnetism and molecular electronics.[1−3] Besides the interest in them as models for the fundamental research on long-distance electron exchange (EE) and electron transfer (ET) phenomena,[1,2] they are also of great importance in the “bottom-up” approach to nanometer-scale electronic devices such as molecular wires and switches.[3] The examples of long-range magnetic coupling in exchange-coupled polynuclear complexes are relatively scarce in comparison with the more abundant examples of long-distance electron transport in mixed-valent polynuclear complexes.[4,5]

Dinuclear copper(II) metallacyclophanes with one unpaired electron per metal center have emerged as ideal model systems for the study of EE interactions through extended π-conjugated aromatic bridges in a discrete metallacyclic entity, from both experimental and theoretical points of view.[6,7] In fact, the design and synthesis of novel coordinating group-substituted aromatic bridging ligands that can transmit spin coupling effects between metal centers over long distances require both a skillful organic synthesis and a deep understanding of the EE mechanism. In this Communication, we report on the synthesis, crystal structure, and magnetic properties of a new example of dicopper(II) metallacyclophane $(nBu_4N)_4[Cu_2(dpeba)_2]\cdot 4MeOH\cdot 2Et_2O$ (**1**), where dpeba is the rigid rodlike bridging ligand *N,N′*-4,4′-diphenylethynebis(oxamate). Density functional (DF) calculations have been conducted to elucidate the mechanism of the long-range magnetic coupling in **1**.

The structure of **1** consists of centrosymmetric dinuclear copper(II) complex anions and tetra-*n*-butylammonium cations, together with methanol and diethyl eter as crystallization solvent molecules (Figure 1). The anionic dicopper(II) complex, $[Cu^{II}_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-dpeba})_2]^{4-}$, is a novel metallamacrocycle of the dicopper tetraaza[3.3]-4,4′-diphenylethynophane type, in which the two 4,4′-diphenylethyne spacers of the bridging bis(bidentate) dpeba ligands are connected by two N−Cu−N linkages (Figure 1a). The coordination environment of the two centrosymmetrically related Cu(1) and $Cu(1)^I$ atoms is essentially square-planar, CuN_2O_2, formed by two amidate nitrogen and two carboxylate oxygen atoms from the

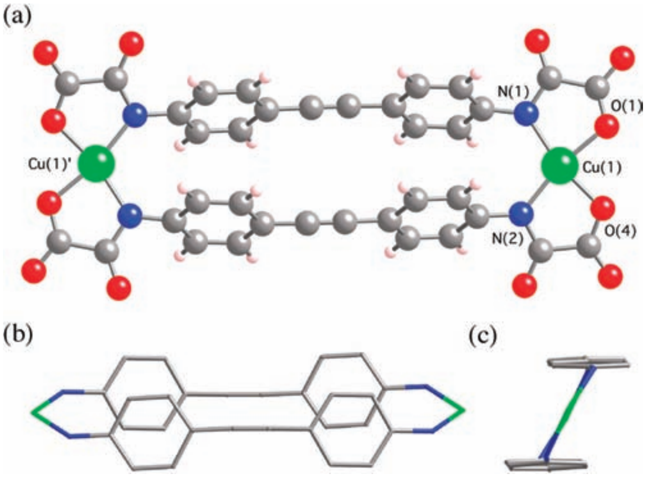

Figure 1. (a) Perspective view of the centrosymmetric anionic dicopper unit of **1** with the atom numbering scheme of the metal environment [symmetry code (I) = 2 − *x*, 1 − *y*, 2 − *z*]. (b) Front and (c) top projection views of the dicopper tetraaza[3.3]-4,4′-diphenylethynophane metallacyclic core (hydrogen atoms have been omitted for the sake of clarity).

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oxamato donor groups [tetrahedral twist angle (τ) of 8.7(1)°]. The average values of the Cu−N and Cu−O distances are 1.994(3) and 1.961(3) Å, respectively. The intramolecular Cu(1)−Cu(1)^{I} distance (r) across the double para-substituted diphenylethynediamidate bridge is 14.95(1) Å. The shortest intermolecular Cu(1)−Cu(1)^{II} separation is 8.09(1) Å, showing thus that the dicopper(II) complex anions are well separated from each other by the bulky tetrabutylammonium cations and the crystallization solvent molecules in the crystal lattice (Figure S1 of the Supporting Information).

Within the dinuclear metallacyclic core, $Cu^{II}_2(4,4'\text{-}N_2C_{14}H_8)_2$, each of the two 4,4′-diphenylethyne spacers is almost planar, reflecting thus potential extended π-conjugation for the dpeba bridging ligands. The torsion angle (ψ) between the terminal benzene rings around the central carbon−carbon triple bond is 7.8(1)°. Indeed, the short C−C distance of 1.212(6) Å between the central sp-type carbon atoms is typical of a C(sp)−C(sp) triple bond (1.20 Å), while the long C−C distance of 1.452(5) Å with the sp^2-type carbon atoms of the terminal benzene rings to which they are directly attached is characteristic of a C(sp)−C(sp^2) single bond (1.43 Å). The two diphenylethyne spacers show an offset (noneclipsed) disposition because of the parallel-displaced π-stacked arrangement of the two pairs of facing benzene rings (Figure 1b). The average inter-ring C−C distance is 3.60(1) Å, a value that is slightly longer than the van der Waals contact (3.40 Å). The angle between the centroid−centroid vector from the facing benzene rings and their normal (θ) is 23.9(1)°. Hence, the molecule has an approximate C_{2h} symmetry, whereby the copper basal planes are not exactly oriented perpendicular to the benzene planes [dihedral angles (ϕ) of 56.4(1) and 58.4(1) °] (Figure 1c).

The magnetic properties of **1** in the form of the χ_M and $\chi_M T$ versus T plots (χ_M being the molar magnetic susceptibility per dinuclear unit and T the temperature), both in the solid state and in a methanol solution, are typical of antiferromagnetically coupled Cu^{II}_2 pairs (Figure 2). At room temperature, the $\chi_M T$ value of 0.84 cm^3 mol^{-1} K is close to that expected for two magnetically isolated Cu^{II} ions [$\chi_M T = 2(N\beta^2 g_{Cu}{}^2/3k_B)S_{Cu}(S_{Cu} + 1) = 0.83$ cm^3 mol^{-1} K when $S_{Cu} = {}^1/_2$ and $g_{Cu} = 2.1$]. Once the sample has cooled, $\chi_M T$ remains constant until ~30 K and then decreases abruptly. The presence of a maximum of χ_M at 3.3 and 3.5 K, in the solid state and in a methanol solution, respectively, unambiguously supports the occurrence of a ground singlet ($S = 0$) spin state resulting from the antiferromagnetic intramolecular coupling between the two Cu^{II} ions through the 4,4′-diphenylethynediamidate bridges (inset of Figure 2). The least-squares fit of the experimental data of **1** through the Bleaney−Bowers equation for a dinuclear copper(II) complex [$H = -JS_1S_2 + g\beta H(S_1 + S_2)$, where $S_1 = S_2 = S_{Cu} = {}^1/_2$ and $g = g_{Cu}$] gave a J of −3.87(3) cm^{-1} and a g of 2.124(3) in the solid state and a J of −4.05(3) cm^{-1} and a g of 2.105(3) in a methanol solution, with R values of 1.5 × 10^{-5} and 1.8 × 10^{-5}, respectively {$R = \sum[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{exp}]^2$}.

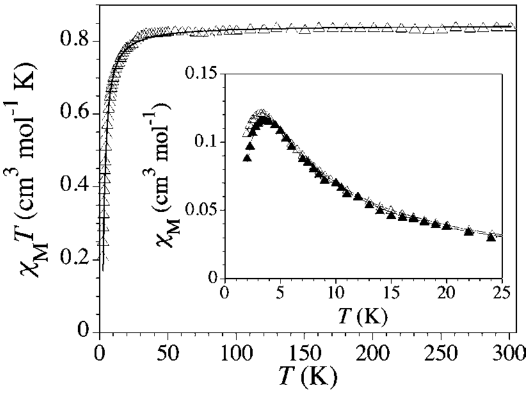

Figure 2. Temperature dependence of $\chi_M T$ for **1** (△) under an applied field of 10 kOe ($T \geq 25$ K) and 100 Oe ($T < 25$ K). The inset shows the maximum of χ_M in the low-temperature region for **1** in the solid state (△) and in a methanol solution (▲). The solid lines are the best-fit curves (see the text).

Variable-field (H = 0.1−50 kOe) magnetic susceptibility measurements for **1** at low temperatures (<25 K) reveal that no appreciable saturation effects are observed when $H \leq 10$ kOe above 2 K (inset of Figure S2 of the Supporting Information), which determines the limit of applicability of the Bleaney−Bowers equation in this case. The least-squares fits by full-matrix diagonalization techniques (without depending on the van Vleck approximation) of the experimental data of **1** in the form of the M versus T/H plots (M being the molar magnetization per dinuclear unit and H the applied field) gave the following: $J = -3.84(4)$ cm^{-1}, $g = 2.124(3)$, and R = 1.8 × 10^{-5} (solid lines in Figure S2). As expected, the calculated J and g values are equivalent to those obtained by using the Bleaney−Bowers equation under low fields (H = 100 Oe). This moderately weak antiferromagnetic intramolecular coupling in **1** is quite remarkable given the very large Cu−Cu separation across the 4,4′-diphenylethynediamidate bridges (r = 15.0 Å).[8] By comparison, the $-J$ value for **1** is intermediate between those reported earlier for related dicopper(II) metallacyclophanes with 4,4′-diphenylenimine or 4,4′-diphenylene spacers (2.2 or 8.7 cm^{-1}, respectively), which possess rather shorter intermetallic distances (r = 10.8 or 12.2 Å, respectively).[6b,7b] This situation clearly contrasts with that predicted by Coffman and Buettner ($-J < 1.0$ cm^{-1} at $r > 9.0$ Å),[1a] showing thus that 1 nm was definitely not the upper limit for the observation of magnetic coupling in dinuclear copper(II) complexes.

DF energy calculations with **1** show a ground broken-symmetry (BS) singlet spin state lying below the excited triplet spin state. The calculated singlet−triplet energy gap ($\Delta E_{ST} = -J$) is 6.1 cm^{-1}, a value that is quite close to the experimental one ($J = -3.9$ cm^{-1}). Natural molecular orbital calculations provide evidence that the exchange interaction between the two unpaired electrons occupying the σ-type $d_{x^2-y^2}$ orbitals of the square-planar Cu^{II} ions ("magnetic orbitals") and pointing toward the equatorial Cu−N and Cu−O bonds is mainly transmitted through the π-bond system of the dpeba bridging ligands. This is clearly reflected in the high metal−ligand covalency and strongly delocalized character of the two singly occupied molecular orbitals (SOMOs), noted b$_g$ and b$_u$, for the ground BS singlet spin state of **1** (Figure 3a). They are composed of the symmetric and antisymmetric combinations, respectively, of the $d_{x^2-y^2}$(Cu) orbitals mixed with the corresponding combinations of the two π-type orbitals of the p-diphenylethyne spacers of appropriate symmetry, which are made up of p$_z$(C) orbitals of the sp^2- and sp-type carbon atoms from the two terminal benzene rings and from the central triple bond, respectively.

Spin densities obtained by natural bond orbital (NBO) analysis on the ground BS singlet spin state of **1** conform to a

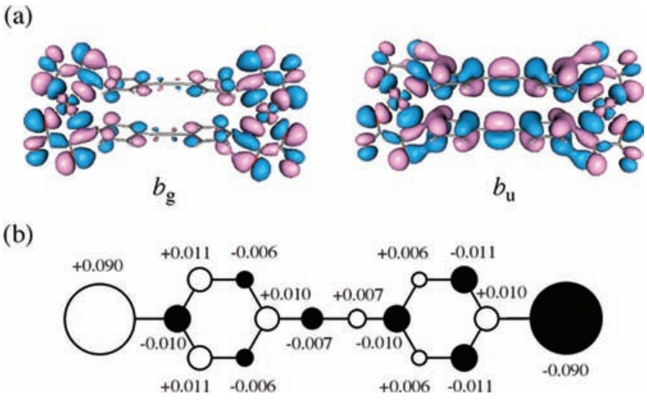

Figure 3. (a) Perspective view of the calculated SOMOs for the ground BS singlet spin state of **1**. (b) Projection view of the spin density distribution in the *p*-diphenylethynediamidate bridge with calculated atomic spin density values (*e*) for the ground BS singlet spin state of **1**. Empty and filled circles represent positive and negative spin densities, respectively, with scaled surface areas.

spin polarization mechanism for the propagation of the exchange interaction between the unpaired electrons of the two metal centers through the π-type orbital pathways of the *p*-diphenylethynediamidate bridges (Figure 3b). In fact, the alternation in sign of the spin density at the carbon atoms of the *p*-diphenylethyne spacers agrees with a spin polarization by the amidate nitrogen atoms.

In conclusion, we report on a new dinuclear copper(II) complex with the extended π-conjugated ligand *N,N′*-4,4′-diphenylethynebis(oxamate). This type of rigid rodlike dinucleating ligand leads to discrete, self-assembled dicopper(II) metallacyclophanes possessing two parallel diphenylethyne spacers disposed almost perpendicularly to the metal basal planes. This particular geometry ensures an unusual π-type pathway for the propagation of the exchange interaction between the unpaired electrons of the two metal centers through the double *p*-diphenylethynediamidate bridges. We are currently investigating other members of a novel series of dicopper(II) metallacyclophanes with extended π-conjugated oligo-*p*-phenylethyne (OPE) spacers of various lengths as potential candidates for magnetic molecular wires (MMWs).

■ ASSOCIATED CONTENT

Supporting Information

Experimental preparation and physical characterization data, X-ray crystallographic data and crystal packing view, variable-field magnetic susceptibility measurements, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The magnetic properties of the bulkier tetraphenylphosphonium derivative of formula $(Ph_4P)_4[Cu_2(dpeba)_2]\cdot 4H_2O$ (**2**) are similar to those of **1** (see the Supporting Information). The least-squares fits by full-matrix diagonalization techniques of the variable-field (H = 1−50 kOe) magnetic susceptibility data of **2** at low temperatures (<25 K) gave the following: $J = -4.23(4)$ cm^{-1}, $g = 2.127(3)$, and $R = 1.7 \times 10^{-5}$ (Figure S3 of the Supporting Information).