Long-Range Magnetic Coupling through Extended π-Conjugated Aromatic Bridges in Dinuclear Copper(II) Metallacyclophanes

Emilio Pardo,[1a] Juan Faus,[1a] Miguel Julve,[1a] Francesc Lloret,*[1a] M. Carmen Muñoz,[1b] Joan Cano,*[1c] Xavier Ottenwaelder,[1c] Yves Journaux,*[1c] Rosa Carrasco,[1d] Gonzalo Blay,[1e] Isabel Fernández,[1e] and Rafael Ruiz-García*[1e]

Departament de Química Inorgànica, Instituto de Ciencia Molecular, and Departament de Química Orgànica, Facultat de Química, Universitat de València, 46100 Burjassot, València, Spain, Departamento de Física Aplicada, Universidad Politécnica de València, 46071 València, Spain, and Laboratoire de Chimie Inorganique and Laboratoire de Chimie Bioorganique et Bioinorganique, Université Paris-Sud, 91405 Orsay, France

Received January 28, 2003; E-mail: rafael.ruiz@uv.es

Polymetallic complexes with strong magnetic exchange interactions between distant metal centers across extended bridges are a major topic in the field of magnetochemistry.[2] In particular, dinuclear copper(II) complexes with aromatic bridging ligands have been actively investigated for the study of long-distance electron exchange, termed "long-range magnetic coupling".[3] With some notable exceptions,[4−6] weak intramolecular antiferromagnetic couplings ($-J < 32$ cm^{-1}) have been reported for dicopper(II) complexes with long intermetal distances ($r > 6$ Å) (Table S1). In most cases, the exchange interaction between the Cu(II) centers is mainly transmitted through the σ-bonds of the aromatic bridge, with little or no contribution from the π-bond system.

Here we report on two new anionic dinuclear copper(II) complexes with the ligands *N,N′*-1,4-phenylenebis(oxamate) (ppba) and *N,N′*-4,4′-biphenylenebis(oxamate) (bpba) (**1** and **2**, Chart 1). This type of rigid dinucleating ligands leads to discrete, self-assembled dicopper(II) metallamacrocycles of the [3,3]*p*-cyclophane type, with a π-stacked arrangement of the aromatic rings connected by two N−Cu−N linkages. Hence, the metal basal planes are coplanar and disposed almost perpendicularly to the two parallel aromatic spacers. As shown earlier for the meta derivative,[7] this particular geometry ensures a unusual π-type pathway for the exchange interaction between the unpaired electrons of the two Cu-(II) ions through the double aromatic diamide bridges. The complexes described herein can be considered as the first members of a novel series of dinuclear copper(II) metalla-amidocyclophanes with linear π-conjugated oligo-*p*-phenylene spacers $-(C_6H_4)_n-$ ($n = 1-5$) of various lengths (**1−5**, Chart 1). Electronic structure calculations on this series offer a unique opportunity to examine the effect of intermetal distance on magnetic coupling in dicopper systems with Cu−Cu distances in the range 8−25 Å.

Complexes **1** and **2** were isolated as a variety of salts with different countercations, both coordinating like Li$^+$ or Na$^+$, and noncoordinating like Ph$_4$P$^+$ or Bu$_4$N$^+$ (Supporting Information). Single-crystal X-ray diffraction analyses of the sodium salts **1B** and **2B** confirmed the anionic dimeric molecular structures (Figures 1 and 2, respectively).

The copper environment is essentially square-planar for **1B** and distorted square-pyramidal for **2B**, with two amide nitrogen and two carboxylate oxygen atoms in the basal plane and an apical water molecule for the latter [metal deviations from the mean basal planes of 0.15 (**1B**) and 0.19 Å (**2B**)]. The copper basal planes are not exactly oriented perpendicular to the phenylene planes [dihedral angles (φ) of 60.6 (**1B**) and in the range 51.9−69.5° (**2B**)]. In addition, the phenylene rings are slightly tilted around the C−C single bond for **2B** [dihedral angle (ψ) of 19.7°]. Overall, these
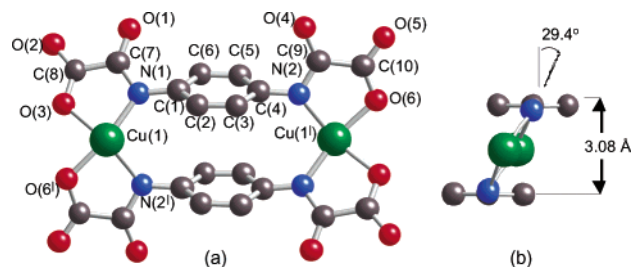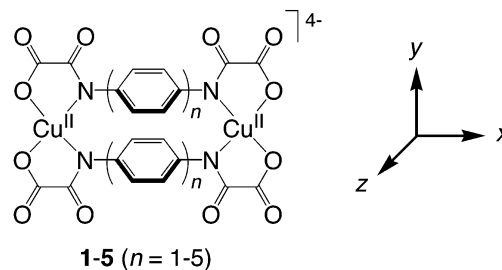

Figure 1. (a) Perspective view of the centrosymmetric anionic dicopper unit of **1B** with the atom-numbering scheme ($I = 1 - x, -y, 1 - z$). (b) Side view of the metallacyclophane core of **1B**.
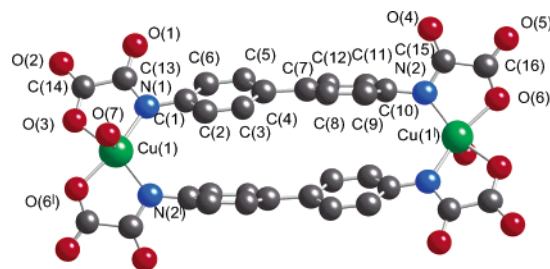
Figure 2. Perspective view of the centrosymmetric anionic dicopper unit of **2B** with the atom-numbering scheme ($I = 1 - x, -y, -z$).

Chart 1

1-5 (n = 1-5)

deviations from ideal D_{2h} symmetry may originate from the favorable π−π interactions in the parallel-displaced configuration of the phenylene dimers and the forced *o*−*o*′ repulsive interactions between the aromatic hydrogen atoms in the biphenylene spacers (intramolecular contributions), or from severe steric constraints in the crystal packing (intermolecular contribution). Actually, oxygen atoms from the oxamate groups bind sodium atoms leading to corrugated sheetlike solid-state structures (Figure S1). The intramolecular Cu−Cu distances (r) are 7.91 (**1B**) and 12.19 Å (**2B**), while the shortest intermolecular Cu−Cu distances are 6.84 (**1B**) and 6.87 Å (**2B**).
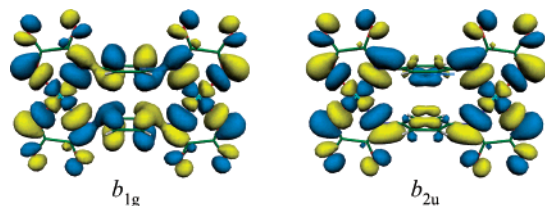
Figure 3. Perspective view of the calculated SOMOs for **1**.
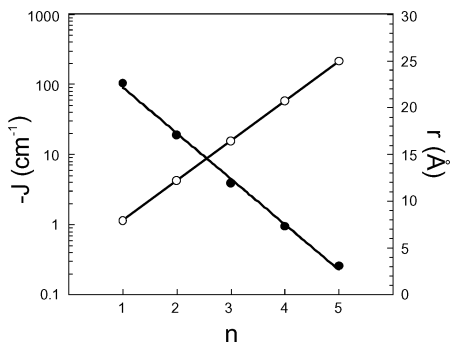
b_{1g} b_{2u}

Figure 4. Plot of the calculated singlet–triplet splitting (on a log scale) (●) and the intermetal distance (○) with the number of repeat units for **1–5**.

Variable-temperature magnetic susceptibility measurements (1.8–300 K) on complexes **1** and **2** revealed a magnetic behavior typical of antiferromagnetically coupled dicopper(II) pairs (Figure S2). The least-squares fit of the experimental data through the Bleaney–Bowers equation gave $-J$ values in the range 81–95 cm^{-1} for **1**, and 8.7–11.5 cm^{-1} for **2** ($H = -J\, S_1\cdot S_2$) (Table S2). Overall, the similar magnetic behavior with variation of the counterion within each family unambiguously indicates that the magnetic coupling is intramolecular in origin. Moreover, the significant antiferromagnetic couplings despite the relatively large intramolecular Cu–Cu separations are quite remarkable.[8] This suggests that the available π orbitals of the aromatic diamide bridges, made up of p_y carbon and nitrogen orbitals, are really effective in propagating the exchange interaction between the two unpaired electrons occupying the d_{xy} metal orbitals. For instance, this is reflected in the high covalency and strongly delocalized character of the two singly occupied molecular orbitals (SOMOs) of **1** depicted in Figure 3.

Density functional theory (DFT) calculations on complexes **1** and **2**, with ideal D_{2h} symmetry,[9] showed a singlet spin ground-state lying well below the triplet excited state. For these model molecules, the calculated value of the singlet–triplet energy gap ($\Delta E_{\mathrm{ST}} = -J$) decreases from 104 for **1** to 18.8 cm^{-1} for **2**. The experimental values for **1** are close to the calculated one, the slight deviations being due to the loss of orthogonality between the copper and phenylene planes ($\phi \neq 90°$). In addition, the somewhat reduced experimental values for **2** compared to the calculated one also reflect a partial loss of π-conjugation in the biphenylene spacer ($\psi \neq 0°$).[10] The results of DFT calculations on the D_{2h}-symmetric model complexes **1–5** are summarized in Figure 4 (Table S3). Together with a perfect linear increase in the estimated intermetal distances (r), the calculated singlet–triplet energy gap ($-J$) decreases in an approximately exponential manner with the number of phenylene repeat units ($n = 1-5$) along this series.

The fit of the calculated data for **1–5** gave a decay law of exchange interaction with intermetal distance as $-J = 1.47 \times 10^3 \exp(-0.35r)$. The relation obtained by Coffman and Buettner,[3b] and the more recent ones based on experimental magnetostructural data on dicopper(II) complexes, predict a faster decay of magnetic coupling with an exponential factor varying in the range 1.5–1.8 Å^{-1} (Figure S3). Once again, this reflects the relative efficiency of

π- versus σ-type exchange pathways. For instance, our results estimate a weak but nonnegligible antiferromagnetic coupling ($J = -3.9$ cm^{-1}) between two Cu(II) ions separated by up to 16.5 Å through triphenylenediamide bridges in **3**, which contrasts with that of -0.0002 cm^{-1} derived from the Coffman–Buettner relation. Nevertheless, two nanometers appears to be the upper limit for the observation of magnetic coupling ($-J < 1.0$ cm^{-1}) in the longer homologues of this series, **4** and **5**, including several C–C single bonds in the aromatic spacers.

In conclusion, we have experimentally observed a strong to moderately strong intramolecular magnetic coupling between two Cu(II) centers in **1** and **2**. This has been supported by theoretical calculations which identify the predominantly π-type orbital pathways through the aromatic diamide bridges as the origin of the exchange interaction. Moreover, a slow rate of decay of magnetic coupling with distance through oligo-p-phenylenediamide bridges is theoretically predicted in **1–5**. This leads our current research toward other dicopper(II) metalla-amidocyclophanes with better π-conjugated oligoacene spacers, so as to get further insights on long-range magnetic coupling through extended aromatic bridges.

Supporting Information Available: Experimental preparation, analytical, spectral, and magnetic susceptibility data for **1** and **2**, X-ray crystallographic data of **1B** and **2B**, and computational details on **1–5** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(1) (a) Departament de Química Inorgànica. (b) Departamento de Física Aplicada. (c) Laboratoire de Chimie Inorganique. (d) Laboratoire de Chimie Bioorganique et Bioinorganique. (e) Departament de Química Orgànica.

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(8) Hendrickson et al. have reported comparable antiferromagnetic couplings in related dicopper(II) complexes with phenylene- and biphenylenediamine bridges ($-J$ values up to 70 and 9 cm^{-1}, respectively) (Table S1). In light of our results, it appears that the exchange interaction in these compounds also involves predominantly π-orbital pathways.

(9) Molecular geometries for **1–5** were not optimized, but their structural dimensions were taken from the crystal structure of **1B** ($\phi = 90°$). For **2–5**, the phenylene rings connected by the C–C single bond were coplanar ($\psi = 0°$) and the C–C inter-ring distance was taken as 1.49 Å.

(10) Preliminary DFT energy calculations show that the calculated singlet–triplet energy gap is sensitive to the dihedral angle between the copper and phenylene planes (ϕ) in **1** and that between the phenylene planes (ψ) in **2**. Thus, the $-J$ value becomes smaller as the more different from 90° is ϕ and from 0° is ψ, as a result of these global torsions around the C–N and C–C single bonds of the aromatic diamide bridges (data reported elsewhere).