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Two Cu_2 and Zn_2 Metallamacrocycles Featuring a Novel Extended π-Conjugated Carbazole Bridge

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Two neutral dinuclear metallamacrocycles, $[Cu_2(hbca)_2]\cdot 2CHCl_3\cdot 2H_2O$ (**1**) and $[Zn_2(hbca)_2]\cdot 7H_2O$ (**2**), have been assembled from reactions of the new rigid carbazole-based ligand H_2hbca [*N*,*N*′-bis(2-hydroxobenzylidene)-9*H*-carbazole-3,6-diamine] with copper(II) or zinc(II) acetate. The extended aromatic ligand spacer is responsible for intermetallic antiferromagnetic exchange, which is rationalized using the spin-polarization formalism with the help of density functional theory calculations.

One of the research lines that has erupted since the advent of molecular magnetism is aimed at understanding and controlling the phenomenon of magnetic exchange. This is a highly interdisciplinary enterprise that has gathered efforts from synthetic chemists, physicists, or theoreticians that have produced many important fruits. Remarkable achievements are, for example, the magnetostructural correlations established, both theoretically[1,2] and experimentally,[3−9] for the magnetic superexchange between transition metals, as mediated by a variety of bridges. One of the identified mechanisms of magnetic superexchange is the spin polarization of the electronic cloud of species linking paramagnetic centers. If the link is aromatic, an alternation of the spin sign occurs, which leads to ferro- or antiferromagnetic coupling, depending on the number of atoms located in between the interacting ions.[10,11] We recently studied the spin polarization experienced by *m*-phenylene linkers and provided evidence of their condition as tuneable ferrocouplers of Cu^{II} centers.[12] The strength of the coupling was proven theoretically and experimentally to depend on the substituents accompanying the phenylene group, and predictions for very strong couplings (up to $+325\ cm^{-1}$ in the $H = -JS_1S_2$ convention) were made. This has also been studied by others and exploited to deliberately synthesize aggregates with high-spin ground states.[13,14] The coupling through other types of π-conjugated systems has equally been studied following a combination of theoretical and experimental approaches.[15,16] In this context, we have now prepared a new bridging ligand containing a rigid carbazole-based aromatic ligand, H_2hbca [*N*,*N*′-bis(2-hydroxobenzylidene)-9*H*-carbazole-3,6-diamine; Chart 1], and studied the spin-polarization exchange interaction mediated by it between Cu^{II} ions, both through magnetic measurements and by density functional theory (DFT) calculations.

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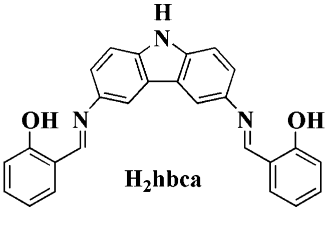
Chart 1



Carbazole derivatives have been studied in a very large variety of contexts. However, their involvement in coordination chemistry is scarce and has been recently reported to take place through the deprotonated carbazole N atom.[17,18] Ligand H_2hbca (Chart 1) was prepared in high yield through a multistep reaction sequence involving nitration, reduction, and Schiff base condensation (Scheme S1 in the Supporting Information). It contains two imine/phenol chelating arms separated by a carbazole unit, to which they are attached through positions 3 and 6. The intended comparison of the magnetic coupling potential through aromatic carbazole, with respect to benzene in *m*-phenylenes, was subject to the condition that the reactivity toward transition metals be analogous for both types of ligands. We have thus investigated the products from the reaction of H_2hbca with stoichiometric amounts of $Cu_2(OAc)_4{\cdot}2H_2O$ or $Zn(OAc)_2{\cdot}2H_2O$, in 1:1 chloroform/methanol solvent mixtures. In both cases, dinuclear compounds were isolated with the formulas $[Cu_2(hbca)_2]{\cdot}2CHCl_3{\cdot}2H_2O$ (**1**) and $[Zn_2(hbca)_2]{\cdot}7H_2O$ (**2**), as is consistent with elemental analysis and solution electrical conductivity (in DMF; see the Supporting Information for details). Complexes **1** and **2** were also characterized by IR and UV−vis spectroscopic studies (see the Supporting Information for details). The structures of **1** and **2** were confirmed by single-crystal X-ray crystallography (see the Supporting Information for details), which also revealed their content in solvent molecules, as described by the formulas $[Cu_2(hbca)_2]{\cdot}2CHCl_3{\cdot}2H_2O$ and $[Zn_2(hbca)_2]{\cdot}7H_2O$ for **1** and **2**, respectively. Both compounds respond to the same description and consist of dinuclear complexes of tetracoordinated M^{II} ions (M = Cu, **1**; Zn, **2**; see Figures 1 and S1 and S2 in the Supporting Information) bridged and chelated centrosymmetrically by two deprotonated H_2hbca ligands, the rigidity of which seems to preclude the establishment of a helical arrangement (Scheme S2 in the Supporting Information). The structure can be viewed as metallamacrocycle of two composite aromatic rings connected by two N−M−N fragments (M = Cu, Zn).

By virtue of the mutual disposition of the aromatic fragments, which prevents $\pi-\pi$ interactions between them, the macrocycle is said to be in the anti form (Scheme S3 in the Supporting Information), as opposed to the syn form observed in related previously reported systems.[11] For complex **1**, this disposition keeps both planes 3.0 Å apart, whereas the distance between their centroids is 4.818 Å (Figure S3 in the Supporting Information). Interestingly, the planes of the carbazole are almost perpendicular to the plane defined by the metallamacrocycle atoms Cu1, N1, N3, Cu#1, N#1, and N#3, forming a dihedral angle of 99.56(10)°. The metals are at a distance of 10.779 Å, a separation that is intermediate between those observed for other $[Cu^{II}_2]$ complexes featuring similar aromatic spacers (Scheme S4 in the Supporting Information).[11,12,15,16] The coordination geometry exhibited by Cu is almost exactly half-way between tetrahedral and square planar, as revealed by continuous shape measures (CShMs; distances to the perfect tetrahedron, T, and the perfect square plane, SP, of 9.21 and 9.18, respectively).[19] This is also evident from the average dihedral angle of 49°, existing between both N−Cu−O planes of the six-membered chelate rings on each Cu ion. Such an intermediate geometry has been previously observed with other Cu^{II} ions, as caused by the geometric ligand strain.[20] It is not clear, however, whether this is the cause here (see below). Other metric parameters are summarized in Table S1 in the Supporting Information. The supramolecular organization of complex **1** within the crystal lattice is interesting. The molecules form a network of hydrogen bonds from the imine N−H group of their carbazole units to water molecules (OW). Every two such molecules form a diamond-shaped O_4 unit together with two phenolic O atoms from neighboring complex molecules (O2), with the ensemble disposed as an infinite sheetlike arrangement (Figure S4 in the Supporting Information). In between these sheets, and protected by the various aromatic moieties in this system, are accommodated a network of solvent $CHCl_3$ molecules (Figure S5 in the Supporting Information).

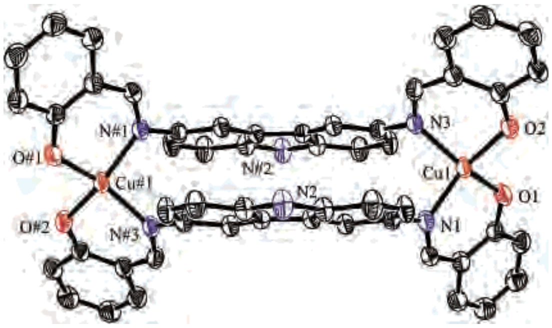


Figure 1. ORTEP representation of $[Cu_2(hbca)_2]$ (**1**) at the 50% probability level. H atoms are not shown for clarity. Only non-C atoms are labeled. Complex **2** has almost the same molecular structure as **1**.

The molecular structure of **2** is entirely analogous to that of **1** (Figure S1 in the Supporting Information), and therefore the above description remains valid for the Zn derivative, as well as the representation in Figure 1. Contrary to complex **1**, however, the metals here display a coordination geometry that is very close to tetrahedral, as indicated by CShMs of 19.96 (to SP) and 2.9 (to T) for Zn1 and of 20.57 (to SP) and 2.47 (to T) for Zn2. This underscores the fact that d^{10} metals prefer this geometry if not constrained by other factors.[21] The remaining metric parameters of complex **2** are

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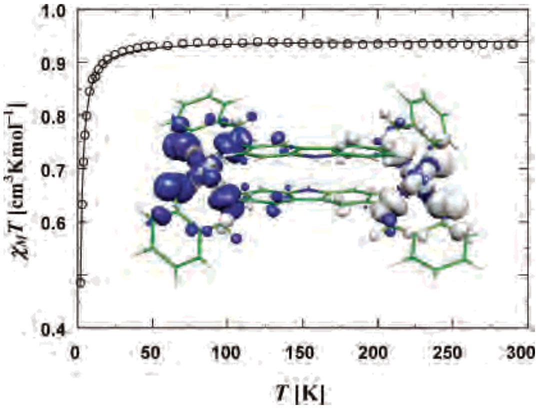
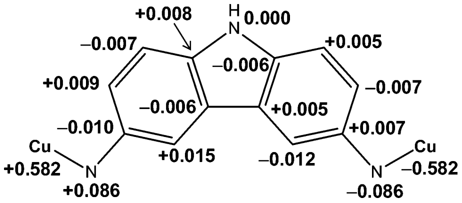


Figure 2. Plot of $\chi_M T$ vs T per molecule of $[Cu_2(hbca)_2]$ (**1**) and fit (solid line). Inset: Spin density representation of **1** as calculated through DFT methods.

Chart 2



similar to those of **1** (Table S2 in the Supporting Information). Complex **2** in the solid state features two independent $[Zn_2]$ clusters along with seven water molecules in the asymmetric unit. The Zn···Zn intramolecular distances are 10.75(1) and 10.76(1) Å, whereas the shortest intermolecular separation between metals is 6.219 Å. In the crystal lattice of **2**, there is a network of hydrogen bonds involving two molecules of water (OW1 and OW2) per cluster. The former are present as linear tetrameric centrosymmetric units, bound to a total of four $[Zn_2]$ clusters through hydrogen bonds with the phenolic O atoms or the carbazole N−H groups (Figure S6 in the Supporting Information).

The magnetic exchange through carbazole was studied for the first time through variable-temperature bulk magnetization measurements on complex **1**, under a constant magnetic field of 1 T in the 2−300 K temperature range. In Figure 2 is a $\chi_M T$ vs T plot (χ_M is the molar paramagnetic susceptibility) of **2**, revealing that indeed the magnetic interaction between the $S = {}^1/_2$ spins of Cu^{II} is very weak and antiferromagnetic. This exchange was evaluated quantitatively through fitting of the experimental data to the Bleany−Bowers equation (Figure 2), by considering the spin Hamiltonian $H = -JS_1S_2$. The parameters obtained from the fit are $J = -2.22$ cm^{-1} and $g = 2.24$. Inclusion of a term for possible intermolecular interactions did not result in a noticeable improvement of the fit. This coupling constant is almost of the same magnitude but of opposite sign to that calculated for the analogous compound with an *m*-phenylene bridge instead of carbazole.[12] It may be argued that, in the present case, the magnetic exchange can be described through the spin-polarization mechanism, as was done for the case of the *m*-phenylene spacer. This was investigated through DFT calculations by using the B3LYP functional[22] and Ahlrichs's pVDZ basis set.[23] For this calculation, the structural parameters of complex **1** obtained from the crystallographic analysis were used. The J value as calculated through the broken-symmetry procedure ($J = [E(\mathrm{Tr}) - E(\mathrm{BSS})]$, where Tr is the triplet and BSS is the broken-symmetry singlet) was found to be very close to the experimental one: $J_{\mathrm{calc}} = -2.3$ cm^{-1}.

Analysis of the Mulliken populations (Chart 2) shows indeed the alternative sign of the spin densities throughout the aromatic system, which suggests the operation of the spin-polarization mechanism in this system. Contrary to the case of the *m*-phenylene couplers, the nature of the interaction is found here to be antiferromagnetic because the number of aromatic atoms between both Cu^{II} centers is even. Indeed, the Mulliken population analysis shows that the path through the imine N atom is suppressed because it bears zero spin density. Presumably, this is related to the fact that when the resonance forms of the carbazole unit are added, the N atom retains the lone p electron pair most of the time. The calculation also reveals that the total spin population located on the spacer itself is comparatively small ($\sum|\rho_i| = 0.277$ on the carbazole unit), which is consistent with the weak character of the coupling.

This is also illustrated by the spin-density map shown in Figure 2 (inset). It is expected that the strength of the coupling can be tuned by chemically manipulating the nature of the remaining part of the bischelating ligand, as was demonstrated for the family of *m*-phenylene-bridged compounds. This is to be achieved by tuning the relative electronegativity of the donors to Cu^{II} in order to control the side of the chelate to which the majority of spin delocalization from the metal occurs. Experimental and theoretical work is now in progress to proof this hypothesis in the case of the antiferromagnetic coupling.

In summary, the synthetic and structural study of two new dinuclear metallomacrocycles involving Cu^{II} and Zn^{II}, respectively, gives insight into the factors favoring the dinucleating self-assembly process. This novel aromatic spacer has now offered the opportunity to investigate the phenomenon of magnetic exchange by the mechanism of spin polarization for the antiferromagnetic case, through both theory and experiment.

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Supporting Information Available: Crystallographic data, tables of selected bond lengths and angles, CIFs, Schemes S1−S4, Figures S1−S6, and syntheses and characterization of ligand H_2hbca and complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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