Article

Topology, Distance, and Orbital Symmetry Effects on Electronic Spin−Spin Couplings in Rigid Molecular Systems: Implications for Long-Distance Spin−Spin Interactions

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ABSTRACT: Understanding factors that underpin the signs and magnitudes of electron spin−spin couplings in biradicaloids, especially those that are integrated into highly delocalized electronic structures, promises to inform the design of molecular spintronic systems. Using steady-state and variable temperature electron paramagnetic resonance (EPR) spectroscopy, we examine spin dynamics in symmetric, strongly π-conjugated bis[(porphinato)copper] (bis[PCu]) systems and probe the roles played by atom-specific macrocycle spin density, porphyrin-to-porphyrin linkage topology, and orbital symmetry on the magnitudes of electronic spin−spin couplings over substantial Cu−Cu distances. These studies examine the following: (i) *meso*-to-*meso*-linked bis[PCu] systems having oligoyne spacers, (ii) *meso*-to-*meso*-bridged bis[PCu] arrays in which the PCu centers are separated by a single ethynyl unit or multiple 5,15-diethynyl(porphinato)zinc(II) units, and (iii) the corresponding β-to-β-bridged bis[PCu] structures. EPR data show that, for β-to-β-bridged systems and *meso*-to-*meso*-linked bis[PCu] structures having oligoyne spacers, a through σ-bond coupling mechanism controls the average exchange interaction (J_{avg}). In contrast, PCu centers separated by a single ethynyl or multiple 5,15-diethynyl(porphinato)-zinc(II) units display a phenomenological decay of $\ln[J_{avg}]$ versus Cu−Cu σ-bond separation number of ∼0.115 per bond, half as large as for these other compositions, congruent with the importance of π-mediated spin−spin coupling. These disparities derive from effects that trace their origin to the nature of the macrocycle−macrocycle linkage topology and the relative energy of the Cu $d_{x^2-y^2}$ singly occupied molecular orbital within the frontier orbital manifold of these electronically delocalized structures. This work provides insight into approaches to tune the extent of spin exchange interactions and distance-dependent electronic spin−spin coupling magnitudes in rigid, highly conjugated biradicaloids.
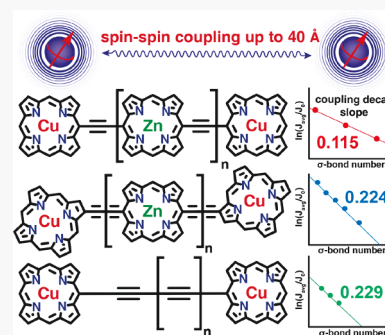
INTRODUCTION

Central to the field of molecular magnetism is the design and synthesis of polynuclear complexes containing paramagnetic transition metal ions with predetermined structures and predictable electronic, optical, and magnetic properties.[1] In addition to their use as models for fundamental research on electron exchange and electron transfer phenomena between distant metal centers through extended bridges, homo- and heterovalent polynuclear complexes are of great importance in the "bottom-up" approach to molecular spintronic devices.[2,3] In this regard, the distance dependence of the magnitude of the electronic spin exchange coupling *J* can provide important information regarding spin distributions, spin densities, and pathways for facilitating the electron exchange process.[4−6]

Understanding factors that determine electron spin−spin coupling magnitudes in biradical and biradicaloid systems[7] promises to inform the design of molecular spintronic systems. In contrast to work investigating exchange coupling in metal−metal dimers and organic radicals,[8−12] little experimental data

exist that probe metal−metal spin−spin couplings in molecular wire frameworks that support highly delocalized electronic structures. Mechanistic studies of such biradicaloids, as well as the delineation of key structure−function relationships, are aided by structural rigidity, which helps illuminate how factors such as metal−ligand d−π mixing, metal orbital spin density, and spin−spin coupling pathways through the spacer (Sp) linking the two biradicaloid centers impact properties that include spin delocalization, magnetism, and magnitudes of electronic spin−spin couplings.
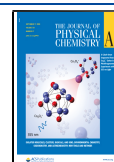
*Meso*-to-*meso* alkyne-bridged (porphinato)metal oligomers define a family of experimentally well-investigated structures that display exceptional electronic properties, ripe for exploitation in molecular electronic and spintronic devices.[13−24] A recent study on *meso*-to-*meso* ethyne-bridged bis[(porphinato)copper(II)] systems[25] reveals that this highly conjugated structure facilitates an electronic exchange interaction between the unpaired electron spins on each Cu ion. In order to more fully assess molecular wire motifs capable of supporting the long-range transmission of spin information, we have examined topological, distance, and orbital symmetry effects on electronic spin−spin couplings in a broader family of highly conjugated, rigidly linked bis[PCu] structures described in Chart 1.

Chart 1. Chemical Structures of *Meso*-to-*Meso*-Bridged Bis[(porphinato)Cu(II)] Arrays[a] and Their Corresponding β-to-β-Bridged Analogues,[b] Linked by Ethynyl, Oligoynyl, 5,15-Diethynyl(porphinato)zinc(II), and 5,15-Butadiynyl(porphinato)zinc(II) Spacer Units[c]
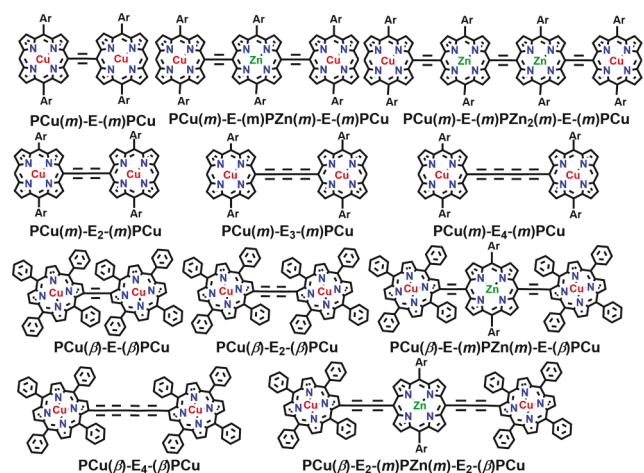
[a]*mm*-Bis[PCu]; top two rows. [b]*ββ*-Bis[PCu]; bottom two rows. [c]Ar = 2′,6′-bis(3,3-dimethyl-l-butyloxy)phenyl.

METHODS

Synthesis and Characterization. A full account of the syntheses and characterization data for all new compounds, complete with detailed reaction schemes, is provided in the Supporting Information.

Steady-State Electron Paramagnetic Resonance Spectroscopy. All electron paramagnetic resonance (EPR) spectra were acquired on either a JEOL JES FA-100 or JEOL JES X310 spectrometer operating at X-band (9.5 GHz) using a TE_{011} cylindrical microwave resonator with 100 kHz field modulation. Samples were rigorously degassed with three consecutive freeze−pump−thaw cycles on a vacuum line. Experimental conditions: scan time = 8 min, output time constant = 0.3 s, sweep width = 2000 G (centered at 3140 G); 100 kHz field modulation amplitudes were typically 8 G. For variable temperature studies (258−363 K) the microwave resonator was equipped with a quartz Dewar with flowing nitrogen gas for low temperatures and warm compressed air for high temperatures. All temperature readings are ±1 K.

EPR Spectral Simulation. Details regarding the simulation of EPR spectra for bis[(porphinato)copper(II)] complexes have been described previously.[25]

RESULTS AND DISCUSSION

The compositions in Chart 1 provide many advantages over common biradicaloid systems for precise investigation of electronic spin−spin communication: (1) they are studied in their electronic ground states; (2) the molecules are highly rigid, with only the rotations and librations of the porphyrin rings contributing to dynamic spin−spin coupling effects; (3) the coupling is dominated by through-bond interactions; and (4) the magnetic properties of monomeric PCu complexes have previously been investigated in great depth, thus providing a solid platform for evaluating the dependences of average isotropic exchange interaction (J_{avg}) magnitudes in bis[PCu] systems upon the nature and topology of the conjugated Sp structure that bridges the two spin centers. We briefly note that we are using the Dirac formalism for J_{avg}, i.e., the term in the Hamiltonian is written as $-J_{avg}(1/2 + 2\ S_1 \cdot S_2)$. This leads to an equivalence of the singlet−triplet energy gap (also a conformationally averaged term) and $-2J_{avg}$, with a singlet ground state when the sign of J_{avg} is negative.[11,26]

Experiments that determine the magnitude of J_{avg} as a function of temperature demonstrate an augmented (porphinato)Cu−(porphinato)Cu electronic coupling made possible by ethyne bridges relative to butadiyne ones; analyses of these data indicate that, in addition to the coupling provided by the carbon σ-bond framework, the magnitude of J_{avg} in PCu(*m*)-E-(*m*)PCu (Chart 1) derives markedly from π-mediated spin−spin coupling.[25] Contrasting PCu(*m*)-E$_2$-(*m*)PCu (Chart 1), PCu(*m*)-E-(*m*)PCu possesses a reduced energy gap separating the $d_{x^2-y^2}$ orbitals of the two (porphinato)Cu units from the globally delocalized π-conjugated highest occupied molecular orbital (HOMO) characteristic of the *meso*-to-*meso* ethyne-bridged (porphinato)metal framework;[17,19,22] as this molecular orbital features a significant metal d_π contribution, it plays an important role in driving the larger magnitude Cu−Cu exchange interaction evident in PCu(*m*)-E-(*m*)PCu relative to PCu(*m*)-E$_2$-(*m*)PCu.[25] From a more global perspective, little is known about how topological effects impact spin−spin coupling magnitudes; for example, it is known for monomeric PCu complexes that the spin density stemming from the Cu $d_{x^2-y^2}$ orbital develops dominantly at the porphyrin β position.[27] While it is well established that electronic and excitonic coupling in *meso*-to-*meso* (*mm*) ethyne-bridged porphyrins exceeds that for their β-to-β (ββ) linked analogues,[13,14,28] it is unknown how the magnitude of the isotropic exchange interaction between two PCu biradicaloids depends on linkage topology within these highly conjugated structures; likewise, given the disparate buildup of the spin density at PCu β and *meso* positions, it is an open question as to how the nature of PCu-to-PCu connectivity impacts the electronic distance dependence of spin−spin coupling (Chart 1).

Figure 1 shows steady-state X-band EPR spectra of five β-to-β-bridged bis[(porphinato)copper(II)] structures obtained in a toluene solution at 298 K for the following: (a) PCu(β)-E-(β)PCu, (b) PCu(β)-E$_2$-(β)PCu, (c) PCu(β)-E$_4$-(β)PCu, (d) PCu(β)-E-(*m*)PZn(*m*)-E-(β)PCu, and (e) PCu(β)-E$_2$-(*m*)-PZn(*m*)-E$_2$-(β)PCu. In line with previous studies of a subset of *meso*-to-*meso*-linked bis[PCu] complexes,[25] the EPR spectra of these ββ-bridged bis[PCu] structures in fluid solution evince similar hyperfine coupling constants and g-factors to benchmark monomeric (porphinato)copper(II) complexes in which
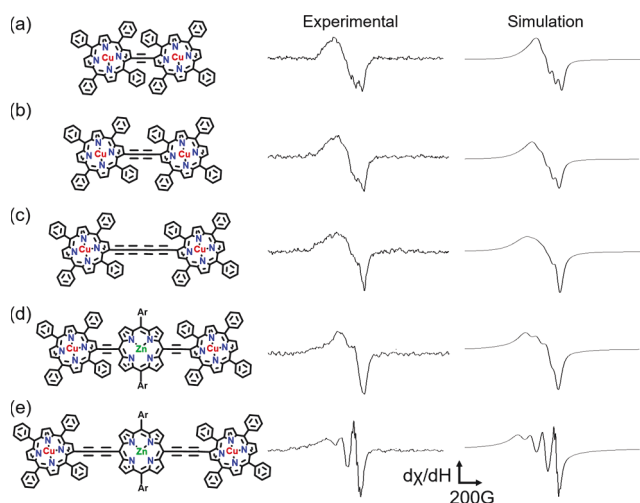
Figure 1. Steady-state X-band EPR spectra of β-to-β ($\beta\beta$)-bridged bis[(porphinato)copper(II)] structures obtained in toluene solution at 300 K for the following: (a) PCu(β)-E-(β)PCu, (b) PCu(β)-E$_2$-(β)PCu, (c) PCu(β)-E$_4$-(β)PCu, (d) PCu(β)-E-(m)PZn(m)-E-(β)PCu, and (e) PCu(β)-E$_2$-(m)PZn(m)-E$_2$-(β)PCu. The beta (β) and meso (m) labels that precede or follow the ethyne (E) or oligoyne (E$_n$) symbol denote the nature of the connectivity of this unit to the porphyrin macrocycle.

g = 2.09, and the hyperfine interactions for the nitrogen nuclei and copper nucleus are A_N = 16 and A_{Cu} = 92 G, respectively. Table 1 lists the values for J_{avg}, the average exchange

Table 1. J_{avg} Values Obtained from Simulations of Figure 1 Experimental Data[a]

complex	J_{avg} (Gauss)
PCu(β)-E-(β)PCu	600
PCu(β)-E$_2$-(β)PCu	400
PCu(β)-E$_4$-(β)PCu	150
PCu(β)-E-(m)PZn(m)-E-(β)PCu	100
PCu(β)-E$_2$-(m)PZn(m)-E$_2$-(β)PCu	30
PCu(m)-E-(m)PCu[25]	80
PCu(m)-E$_2$-(m)PCu[25]	25
PCu(m)-E-(m)PZn(m)-E-(m)PCu[25]	24
PCu(m)-E$_3$-(m)PCu	15
PCu(m)-E$_4$-(m)PCu	10
PCu(m)-E-(m)PZn$_2$(m)-E-(m)PCu	10

[a]Solvent = toluene; T = 298 K. The error limits of J_{avg} and J_{mod} are ±10%.

interaction for these bis[PCu] complexes at 298 K. An additional fitting parameter, J_{mod}, which scales with the librational correlation time constant corresponding to the torsional motion of the porphyrin planes about the molecular axis defined by the E or E$_n$ linkages, has been described previously: the nature of J_{mod} and the methodology for including it in the simulation procedures have been discussed in detail in earlier publications.[25,26] EPR spectra and corresponding simulation data for PCu(m)-E$_3$-(m)PCu, PCu-(m)-E$_4$-(m)PCu, and PCu(m)-E-(m)PZn$_2$(m)-E-(m)PCu may be found in the Supporting Information.

The J_{avg} values for the $\beta\beta$-bridged bis[PCu] structures are several times larger than those of their mm-linked analogues, a consequence of the more expansive spin density at the PCu β-carbon atoms relative to the $meso$ carbons: this effect traces its

genesis to the 1/2-filled $d_{x^2-y^2}$ orbitals of the terminal PCu units in these conjugated arrays.[27] In addition to this increase in the overall magnitude of the exchange interaction of $\beta\beta$-bridged bis[PCu] structures relative to corresponding mm-linked systems having identical Sp structures, the data in Table 1 underscore that these biradicaloid structural motifs manifest different dependences of the magnitude of J_{avg} upon the PCu–PCu distance. Figure 2 plots the logarithm of each of the Table
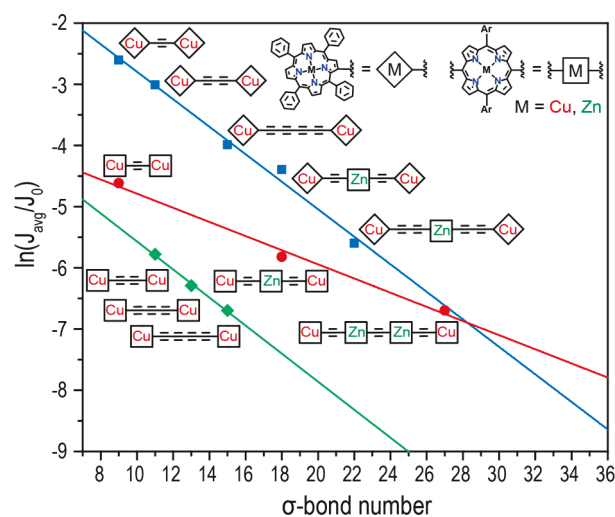

Figure 2. Natural log plots of the measured value of the average exchange interaction (J_{avg}) versus the number of σ bonds between the two Cu ions in the Chart 1 bis[(porphinato)copper(II)] biradicaloid structures. Green line: $meso$-to-$meso$-bridged bis[PCu] systems having oligoyne spacers. Blue line: β-to-β-connected bis[PCu] structures. Red line: $meso$-to-$meso$-linked systems in which the PCu centers are separated by a single ethynyl or multiple 5,15-diethynyl(porphinato)-zinc(II) (E-(m)PZn(m)-E) units. J_0 = 6000 G, taken from the J value measured for a bis[PCu] structure in which the two PCu complexes are directly β-to-β-linked via a single bond.[27]

1 J_{avg} values against the number of σ bonds between the two Cu ions and segregates the Chart 1 biradicaloids into three distinct classes: (i) $\beta\beta$-bridged bis[PCu] structures, (ii) mm-linked systems having oligoyne spacers, and (iii) mm-linked systems in which the PCu centers are separated by a single ethynyl or multiple 5,15-diethynyl(porphinato)zinc(II) (E-(m)PZn(m)-E) units.

A number of striking trends are evident from the Figure 2 data. First, note that the distance-dependence of ln[J_{avg}] versus the Cu–Cu σ-bond separation number for mm-linked systems having oligoyne spacers mirrors that for $\beta\beta$-bridged bis[PCu] structures, displaying a phenomenological decay parameter of ~0.226 per bond. Given that temperature-dependent EPR data indicate that the PCu–PCu exchange interaction magnitude for $meso$-to-$meso$ butadiyne-bridged bis[PCu] (PCu(m)-E$_2$-(m)PCu) is dominated by a through σ-bond electronic coupling mechanism,[25] the identical dependence of the PCu–PCu exchange interaction magnitude with distance for $\beta\beta$-bridged bis[PCu] structures and mm-linked systems having oligoyne spacers indicates that a through σ-bond coupling mechanism controls the exchange interaction for bis[PCu] biradicaloids that are connected via a β carbon-to-β carbon linkage topology. Note in this regard that earlier work underscores that the electronic structures of ethyne- and butadiyne-bridged mm and $\beta\beta$ bis(porphyrin) systems are dramatically different,[13,14,25,28] with the $meso$-to-$meso$ single

ethyne bridge providing the largest porphyrin-to-porphyrin electronic coupling. Congruent with optical and potentiometric methods that probe the extent of electronic coupling for these linkage motifs,[13,14,28] the Figure 2 data emphasize that the Sp π system plays a minimal role in regulating the exchange interaction in β-to-β-bridged bis[PCu] structures. Temperature-dependent EPR data reinforce this picture (Supporting Information).

A noteworthy aspect of the Figure 2 data is highlighted by the crossing point of the natural log plots of the measured J_{avg} value versus the number of σ bonds between the two Cu ions for β-to-β-connected bis[PCu] structures (blue line) and meso-to-meso-linked systems in which the PCu centers are separated by a single ethynyl or multiple 5,15-diethynyl(porphinato)-zinc(II) units (red line). These disparate distance dependences underscore the importance of the energy gap between the singly occupied molecular orbital (SOMO) (Cu $d_{x^2-y^2}$) and the globally delocalized, π-symmetric, highest energy filled molecular orbital that characterizes meso-to-meso-linked systems in which the PCu centers are separated by a single ethynyl or multiple 5,15-diethynyl(porphinato)zinc(II) units.[17,19,22] Because this nearby filled delocalized orbital has a significant metal d_π contribution and lies closer in energy to the SOMO than for linkage motifs that feature meso-to-meso oligoyne spacers or β-to-β bridges, π-mediated spin–spin coupling causes the distance dependence of the Cu–Cu exchange interaction magnitude to be softer for meso-to-meso-linked systems in which the PCu centers are separated by a single ethynyl or multiple 5,15-diethynyl(porphinato)zinc(II) (E-(m)PZn(m)-E) units. At σ-bond distances beyond the crossover point, these mm-linked structures, with their slower decay of J_{avg}, are poised to impact molecular spintronic designs where facilitating longer range electronic spin–spin couplings is important. Similar EPR measurements of any bis[PCu] complexes having longer 5,15-diethynyl(porphinato)zinc(II) or 5,15-butadiynyl(porphinato)zinc(II) Sp units are unlikely to add new information, as J_{avg} values beyond those measurable here would be much smaller than the expected natural line width of 8−10 G. These systems however offer the potential for spin polarization transfer experiments to create the well-known antiphase structure (APS) line shapes of spin-correlated radical pairs (or biradicals), which can be detected by time-resolved EPR experiments. When APS is observed in correlated systems, the lower limit of measurable couplings may be decreased below the natural line width, extending the minimal exchange interaction measurable by at least 1 order of magnitude.[29] Such experiments are outside the scope of this report but are planned for the near future.

CONCLUSIONS

In summary, this work examines molecular wire motifs capable of supporting the long-range transmission of spin information in a broad family of highly conjugated, rigidly linked bis[PCu] structures. These results highlight that a 3-orders-of-magnitude range of average electronic spin–spin exchange coupling values can be realized through modulation of the porphyrin-to-porphyrin linkage topology and the length and nature of the conjugated bridge linking the PCu centers. This work has important consequences for spintronics applications, demonstrating that (i) despite the large spin density at the PCu macrocycle β position relative to the meso carbon centers, because a σ-bond electronic coupling mechanism governs the exchange interaction, β-to-β-linkage topologies are inappro-

priate for engineering substantial spin–spin coupling at long PCu–PCu distances; (ii) in contrast to β-to-β-linked and meso-to-meso-bridged bis[PCu] systems having oligoyne spacers, which evince identical dependences of ln[J_{avg}] with distance, PCu centers separated by a single ethynyl unit or multiple 5,15-diethynyl(porphinato)zinc(II) units display a phenomenological decay of ln[J_{avg}] versus the Cu–Cu σ-bond separation number, which is congruent with π-mediated spin–spin coupling, demonstrating the importance of the magnitude of the energy gap between the Cu $d_{x^2-y^2}$ SOMO and the globally delocalized, π-symmetric highest energy filled molecular orbital that characterizes these meso-to-meso-linked bis[PCu] structures; (iii) oligoynes, perhaps the archetypal molecular wire motif, do not drive the largest electronic spin–spin couplings at long PCu–PCu distances; and (iv) orbital symmetry effects can play an important role in propagating long-range spin exchange couplings between unpaired electron spins (>40 Å). This study thus further illuminates strategies to manipulate the extent of spin exchange interactions in rigid, highly conjugated biradicaloids, which can be of great utility in the molecular level design of magneto-optical and spintronic materials that require precisely controlled and distance-dependent electronic spin–spin couplings.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c06112.

> Experimental methods, synthetic procedures, and additional EPR data (PDF)

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Notes

The authors declare no competing financial interest.

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