Synthesis of and structure–property relationships in zinc complexes of bis-metaphenylene semiquinone biradical species

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The design of novel, functionalized bis-metaphenylene semiquinone (SQ) ligands and their corresponding metal complexes which combine conformational flexibility and electron-withdrawing, electron-donating, and conjugating substituents enable investigation of multiple structure–property relationships. Along these lines, we report the synthesis of three new bis($Zn^{II}(SQ)Tp^{Cum,Me}$) complexes containing the bis-metaphenylene coupling fragment. Using electron paramagnetic resonance spectroscopy, *ab initio* computations and superconducting quantum interference device magnetometry, we show how spin-density is affected by the bis-metaphenylene system substituents. Copyright © 2011 John Wiley & Sons, Ltd.
Supporting information may be found in the online version of this paper.

Keywords: bis(metaphenylene) semiquinone biradicals; electron paramagnetic resonance; SQUID magnetometry; substituent effects

INTRODUCTION

New paramagnetic ligands are of general interest in both organic and inorganic chemistry as components of sensors, switches, and molecular spintronics.[1–8] Previous research in our group has shown that both conformation and substituents can modulate spin density and exchange coupling in Bis($Zn^{II}(SQ)Tp^{Cum,Me}$) biradical ligand complexes.[9–11] The design of novel, functionalized semiquinone (SQ) ligands containing electron-withdrawing, electron-donating, and conjugating substituents enables investigation of multiple structure–property relationships and building blocks for new materials. In an effort to analyze the nature of the substituent effects observed in the bis($Zn^{II}(SQ)Tp^{Cum,Me}$) complexes, a broader range of substituents was required to round out the series initially studied by us, where X=t-Bu, N($CH_3)_2$, and NO_2.[1] Therefore, the unsubstituted case (X=H) was prepared as a reference, a conjugating substituent (X=Ph) was selected, as well as the π-electron donor/σ-acceptor substituent (X=OCH_3) (Fig. 1).

RESULTS AND DISCUSSION

Synthesis

To acquire these new ligand species and zinc complexes, the synthetic strategy shown in Scheme 1 was employed. Yields at each step are provided. The bis($Zn^{II}(SQ)Tp^{Cum,Me}$) complexes were prepared using proven synthetic methodology:[1] (1) Suzuki coupling to form compounds **3a–c**, (2) deprotection to the catechols **4a–c** and (3) complexation to form compounds **5a–c**. Full

details of the experimental procedures are found in the supplemental material.

Characterization of the Bis($Zn^{II}(SQ)Tp^{Cum,Me}$) complexes

The bis($Zn^{II}(SQ)Tp^{Cum,Me}$) complexes **5a–c** were characterized by several means. Absorptions in the infrared (IR) spectra readily identify the $Tp^{Cum,Me}$ ligand (~2540 cm^{-1}, ν_{B-H}) and the SQ (~1450 cm^{-1}, $\nu_{C=O}$) functionality. Also, observation of an $n \rightarrow \pi^*$ transition from 10,000–15,000 cm^{-1} in the UV–Vis spectra verifies the SQ moiety.[1] The triplet biradical complexes were readily identified by electron paramagnetic resonance (EPR), and X-ray

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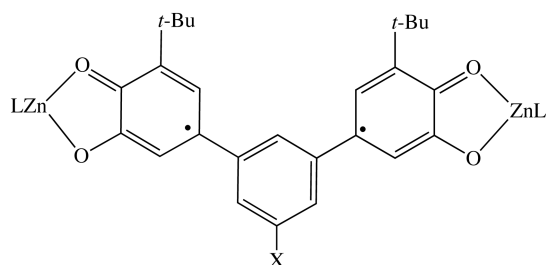
Figure 1. Substituted bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes

crystallographic data confirm the structures of the complexes. Finally, superconducting quantum interference device (SQUID) magnetometry measured the magnetic susceptibility of the complexes, from which values for *J* were calculated.

Spectroscopy

Infrared and UV–Vis absorptions of the bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes prepared in Scheme 1 were found to be consistent with those reported earlier.[1] Critical absorption energies are shown below in Table 1.
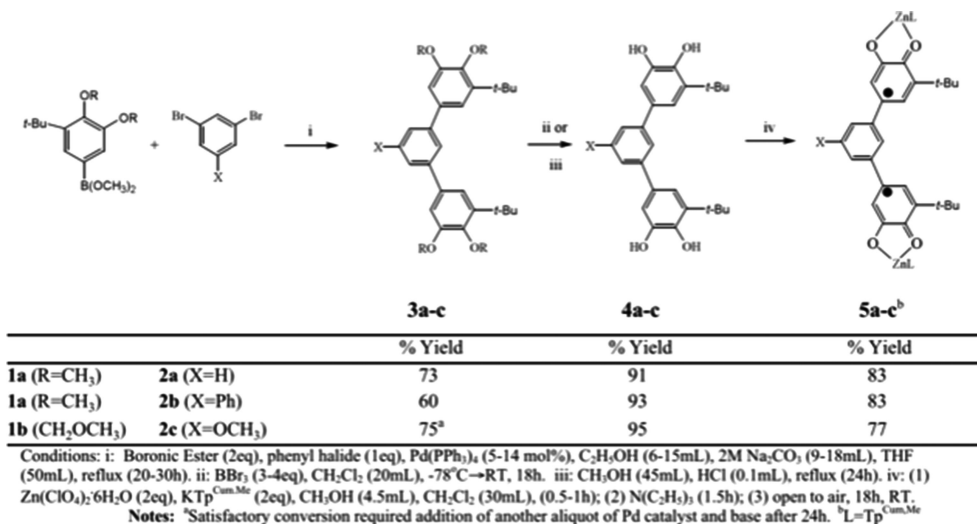
Electron paramagnetic resonance spectroscopic measurements of the bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes as both frozen matrices (77 K) and as solutions at room temperature (298 K) yield two important but different pieces of information. Because molecular tumbling is minimized in frozen matrices, electron–electron (i.e., dipole–dipole) interactions dominate the EPR spectra and are manifested as the $\Delta m_s = 1$ transition.[4] In contrast, the random tumbling of molecules in a fluid zeros out dipolar interactions, allowing hyperfine coupling interactions to dominate the EPR

spectra at room temperature and gives rise to the $\Delta m_s = 2$ transition.

Shown in Fig. 2 are the results of EPR experiments. Immediately above each experimental spectrum is the simulated spectrum obtained via the WINEPR S$_{IM}$F$_{ONIA}$ fitting program.[3] The experimental spectra and zero-field splitting (ZFS) parameters recorded in Table 1 are in agreement with the simulations and are also consistent with spectra obtained from bis(Zn^{II}(SQ) Tp^{Cum,Me}) complexes reported earlier.[1,12] These findings, when taken together, suggest successful formation of triplet bis(semiquinone) biradical species. In the case of **5b**, it was unclear as to why the transition was broadened relative to those of other species.

Magnetometry

Superconducting quantum interference device magnetometry measurements were carried out to ascertain both the maximum spin (saturation) values (M_{sat}) and the dependence of the complexes' molar magnetic susceptibility (χ_M) on temperature as a function of substituent. For these biradicals, we observed M_{sat} to approach a maximum value of 2.0 Bohr magnetons (Fig. 3), corresponding to two unpaired electrons, as the magnetic field strength was increased at ~4K. Likewise, $\chi_M \cdot T$ values were observed to approach their maximum value of 1.0 emu·K/mol at low temperature, where population of the higher energy singlet state does not occur to a large extent. As the temperature was raised during the experiment, increasing population of the higher lying singlet state reduced the triplet contribution to χ_M, causing $\chi_M \cdot T$ values to approach 0.75 emu·K/mol. These findings are consistent with earlier SQUID magnetometry data

		3a-c	4a-c	5a-c^b
		% Yield	% Yield	% Yield
1a (R=CH$_3$)	2a (X=H)	73	91	83
1a (R=CH$_3$)	2b (X=Ph)	60	93	83
1b (CH$_2$OCH$_3$)	2c (X=OCH$_3$)	75^a	95	77

Conditions: i: Boronic Ester (2eq), phenyl halide (1eq), Pd(PPh$_3$)$_4$ (5-14 mol%), C$_2$H$_5$OH (6-15mL), 2M Na$_2$CO$_3$ (9-18mL), THF (50mL), reflux (20-30h). ii: BBr$_3$ (3-4eq), CH$_2$Cl$_2$ (20mL), -78°C→RT, 18h. iii: CH$_3$OH (45mL), HCl (0.1mL), reflux (24h). iv: (1) Zn(ClO$_4$)$_2$·6H$_2$O (2eq), KTp^{Cum,Me} (2eq), CH$_3$OH (4.5mL), CH$_2$Cl$_2$ (30mL), (0.5-1h); (2) N(C$_2$H$_5$)$_3$ (1.5h); (3) open to air, 18h, RT.
Notes: ^{a}Satisfactory conversion required addition of another aliquot of Pd catalyst and base after 24h. ^{b}L=Tp^{Cum,Me}

Scheme 1. Bis(Zn^{II}(SQ)Tp^{Cum,Me}) complex synthetic sequence

Table 1. Spectroscopic frequencies for bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes

	IR frequencies		UV–Vis transitions		EPR ZFS parameters	
Compound	B–H (cm^{-1})	SQ (cm^{-1})	n→π* (cm^{-1})	Δv_{n}→π* (cm^{-1})	D/hc (cm^{-1})	E/hc (cm^{-1})
5a	2536	1440	13,086	0	0.00399	0.000017
5b	2547	1440	13,080	−6	0.00372	0.000042
5c	2547	1439	14,060	974	0.00398	0.000076

collected on analogous compounds.[1] Strength of exchange coupling can be determined by fitting the magnetic data to a field-independent van Vleck expression (using H=−2*J*Ŝ₁·Ŝ₂), Eqn 1,[4,5]

$$\chi T = \frac{2Ng^2\beta^2}{k[3 + e^{-2J/kT}]} \quad (1)$$

where *g* is the isotropic Landé constant (*g*=2.0023), β is the Bohr magneton, *T* is the temperature in Kelvin, *k* is Boltzmann's constant, ***J*** is the intramolecular exchange coupling parameter (2***J***=Δ*E*$_{ST}$), and Ŝ₁ and Ŝ₂ are the spin operators for the semiquinones. The decrease of the χ*T* data at very low temperatures (below 5 K) was accounted for with a Weiss correction, using the expression χ$_{eff}$=χ/(1− ϑχ), where ϑ=2*zJ*′/(*Ng²*β²).[6] The origin of *J*′ can be ZFS, intermolecular interactions, saturation effects, or some combination of these.[7] The curve fit results are seen in Table 2. For comparison, values for complexes prepared by Shultz *et al.* are also included.

Figure 2. Bis(Zn^{II}(SQ)Tp^{Cum,Me}) EPR Δm_s=1 and Δm_s=2 transitions

X-ray crystallography

The structures of complexes **5a–c** were verified by X-ray crystallography. Crystal structures are shown in Fig. 4 and the crystallographic parameters are provided in Table 3. Complete crystallographic files may be found in the supporting information and the crystallographic data files have been deposited with the Cambridge Crystallographic Data Center.

Substituent effects study

Spectroscopic, magnetometric, and crystallographic properties of these complexes may permit elucidation of substituent effects. These new compounds allow expansion of our investigation of substituent effects on exchange coupling between SQ moieties,[9] to include substituted-SQ-paramagnetic metal ion exchange coupled species.

Hancock and Clague showed that shifts in the *n*→π* transitions in the electronic absorption spectra of monoradical species are linearly related to σ values.[13] Variation in the ZFS parameters *D* and *E* measured by EPR can also provide information on changes in spin density distribution. *Ab initio* computations can yield additional insights on the changes in SQ spin density distribution brought about by substituents. Changes in ***J*** values obtained through SQUID magnetometry as a function of the substituent may also correlate to Hammett parameters. Finally, examination of the SQ ring torsion angles obtained through X-ray
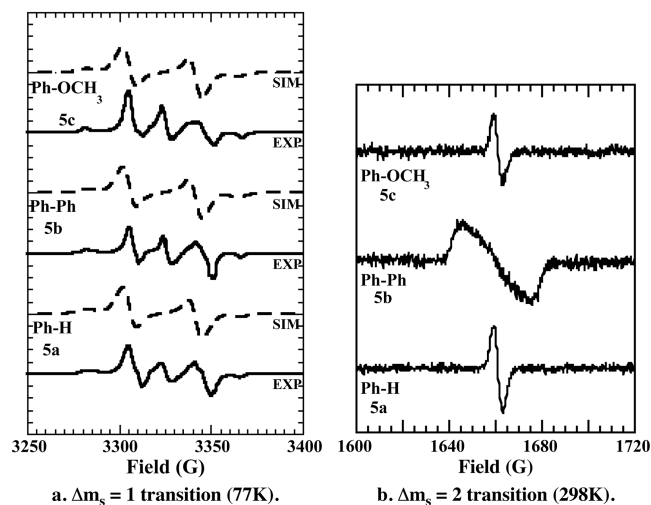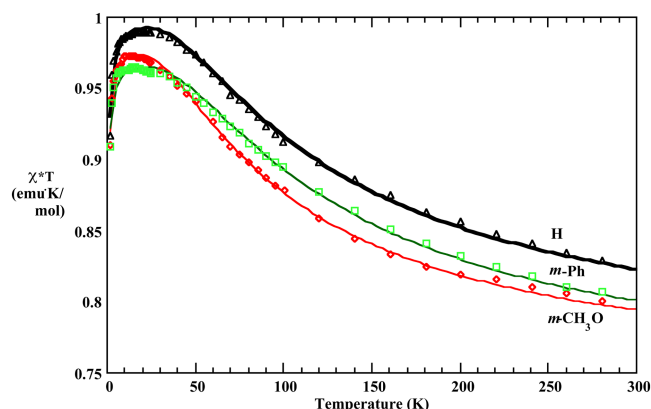

Figure 3. Bis(Zn^{II}(SQ)Tp^{Cum,Me}) complex χ*T* versus *T*

Table 2. Bis(Zn^{II}(SQ)Tp^{Cum,Me}) complex and bis(SQ) biradical parameters

Compound (Substituent)	Torsion angles		Exchange parameters			Bis(SQ)[b] spin density	
	φ_1 (°)	φ_2 (°)	*J* (cm^{-1})	*zJ*′ (cm^{-1})	C₇, C₈[c]	Σ[C$_{1-6}$][d]	Σ[substituent][d]
5a[b] (H)	38.3	27.2	46.0	−0.25	0.072, 0.089	0.197	NA
5b[b] (Ph)	37.6	41.9	47.4	−0.005	0.096, 0.093	0.222	0.0257
5c[b] (CH₃O)	33.3	30.8	35.9	−0.07	0.104, 0.092	0.222	0.0016
5d[a] (NO₂)	33.3	33.5	31.0	−0.07	0.085, 0.091	0.221	0.0096
5e[a] (N(CH₃)₂)	36.0	31.0	34.9	−0.11	0.089, 0.098	0.214	0.0040
5f[a] (*t*-Bu)	30.2	30.8	59.3	−0.11	0.080, 0.095	0.204	0.0019

[a]See Ref. [1].
[b]This work.
[c]α spin density.
[d]α+β spin density.
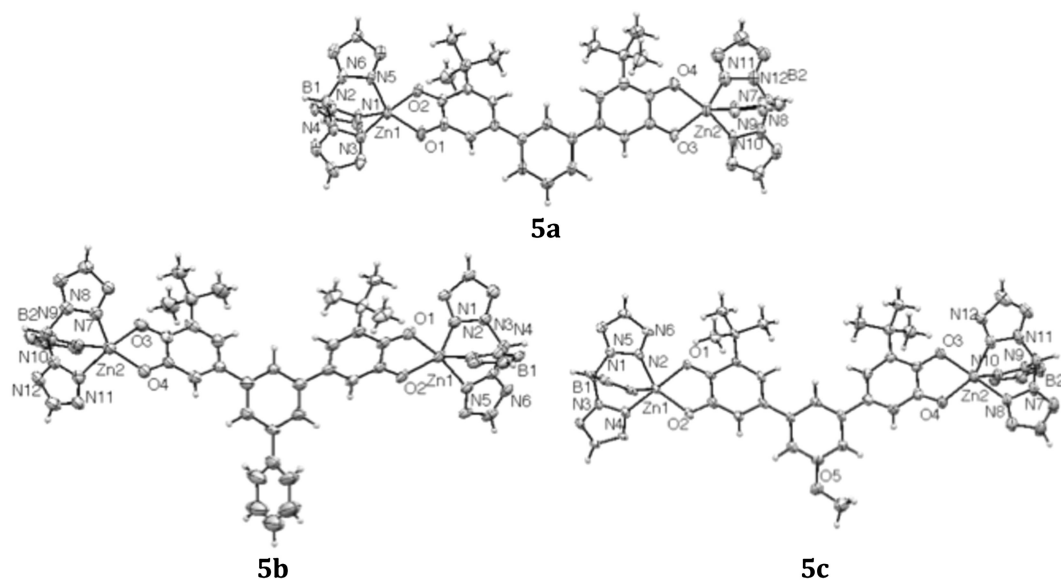
5a

5b   **5c**

Figure 4. Bis(Zn^{II}(SQ)Tp^{Cum,Me}) complex χT ORTEP drawings (ellipsoids are at the 50% probability level and selected atoms were omitted for clarity)

Table 3. Bis(Zn^{II}(SQ)Tp^{Cum,Me}) complex crystallography parameters			
Compound	**5a**	**5b**	**5c**
Empirical formula	$C_{104}H_{117}B_2N_{12}O_4Zn_2\cdot C_6H_{14}$	$C_{110}H_{122}B_2N_{12}O_4Zn_2\cdot(C_6H_{14})_{1.5}$	$C_{105}H_{118}B_2N_{12}O_5Zn_2$
Formula weight	1837.74	1957.94	1780.58
Temperature (K)	123(2)	108(2)	110
Wavelength	0.71073 A	0.71073	0.71070
Crystal system, space group	Monoclinic, $P2(1)/c$	Triclinic, $P1$	Triclinic, $P1$
Unit cell (Å)	$a=11.1192(12)$ Å	$a=11.6009(10)$ Å	$a=12.3136(5)$Å
	$\alpha=90°$;	$\alpha=76.390°(5)$;	$\alpha=98.021°(3)$;
	$b=21.822(2)$ Å	$b=18.5966(16)$Å	$b=13.0048(6)$Å
	$\beta=94.885°$ (7);	$\beta=85.934°(6)$;	$\beta=95.060°(3)$;
	$c=44.040(5)$ Å	$c=29.423(3)$ Å	$c=33.3571(15)$Å
	$\gamma=90°$	$\gamma=89.359°(6)$.	$\gamma=97.950°(2)$.
Volume (A^3)	10647(2)	6154(9)	5207(4)
Z, Calc density (Mg/m^3)	4, 1.146	2, 1.057	2, 1.137
F(000)	3908	2086	1888
Crystal size (mm)	$0.34\times0.24\times0.12$	$0.34\times0.18\times0.16$	$0.28\times0.20\times0.06$
θ range for data	1.84° to 22.10°	1.85° to 22.16°	4.34° to 44.12°
Reflections collected/unique	127468/13121	80150/15210	18080/18080
Completeness to θ	99.3 %	98.5 %	99.3 %
Absorption Correction	Semi-emp from equiv	Semi-emp from equiv	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/param	13121 / 0 / 1121	15210 / 45 / 1196	18080 / 0 / 1160
Final R indices [I > 2σ(I)]	$R1=0.0858,$	$R1=0.0605,$	$R1=0.0614,$
	$wR2=0.1777$	$wR2=0.1545$	$wR2=0.1612$
GOF	1.092	0.993	1.064
R indices (all data)	$R1=0.1057, wR2=0.1865$	$R1=0.1021, wR2=0.1704$	$R1=0.0976, wR2=0.1726$
Largest difference peak and hole	0.970 and -0.700 e.A^{-3}	0.491 and -0.365 e.A^{-3}	0.656 and -0.556 e.A^{-3}

crystallography within this series of complexes may be informative of substituent effects.

UV–Vis spectroscopy

To ascertain whether the change in the $n\rightarrow\pi^*$ transition correlates with σ_x for bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes **5a–5c**, we

calculated $\Delta\nu_n\rightarrow\pi_*$ for the complexes where $\Delta\nu_n\rightarrow\pi_*=\nu_n\rightarrow\pi_*$ $_{(5x)}-\nu_n\rightarrow\pi_{*(5a)}$ (Table 1).

Correlations with a number of different σ_x parameters with $\Delta\nu_n\rightarrow\pi_*$ values for the bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes were explored. Neither σ., $\sigma-$, σ_{para}, σ_{meta} nor the dual parameter $\sigma_{JJ}+\sigma_x$ system provided satisfactory correlations. This is not surprising because the gap between the two lowest states is a

function of interactions amongst at least four different states – the triplet state and the three lowest singlet states. Hence, substituents can alter the energies of the four lowest energy states and the singlet states can mix through both configuration interaction and second-order Jahn–Teller effects.[14]

Electron paramagnetic resonance spectroscopy

Exchange coupled biradical complexes have unique magnetic characteristics that manifest as anomalous absorbances in EPR spectrum.[15] Most notable among these for the bis(Zn^{II}(SQ) $Tp^{Cum,Me}$) complexes ($S=1$ systems) is a triplet spin degeneracy arising from the dipole–dipole interaction of the unpaired electrons. In the absence of an applied magnetic field, all three sublevels of the triplet state are isoenergetic. However, infinitesimally small magnetic fields generated by the unpaired electrons lift the degeneracy in the triplet manifold. These intrinsic magnetic fields are operative regardless of the presence or absence of an applied field. Because no external field is necessary, the degeneracy lifting has been termed ZFS and is described using the parameters D and E (Fig. 5).

The ZFS parameter D is an e^-/e^- repulsion energy and describes the deviation from cubic symmetry. E is commonly referred to as the rhombic parameter and is a measure of the molecule's deviation from axial symmetry.[16] Both D and E are anisotropic; therefore, the molecule must be restricted from freely tumbling to observe absorbances corresponding to the ZFS parameters.[4] The bis(Zn^{II}(SQ)$Tp^{Cum,Me}$) complexes we report give D/hc and E/hc values (Table 1) consistent with our previously published results.[1,12] Values for the ZFS parameter D obtained for compounds **5a–c** do not vary significantly in magnitude within this series ($D/hc_{avg}=0.00389\pm0.00017$). Thus, we can discern no substituent effect from this data.

Ab initio computations

Figure 6 depicts the spin density distributions for bis(semiquinone) [bis(SQ)] precursors to complexes **5a–f** obtained by *ab initio* methods.[17–21] In Table 2, we record the gas-phase *ab initio* spin densities at selected carbon centers and substituents for our bis(SQ) series. As the data show, calculated values for $\rho_{[C7,C8]}$ and $\Sigma\rho_{[C1–C6]}$ re larger than the spin densities for the bis(SQ) precursor to **5a**, implying a substituent effect. Furthermore, a significant proportion of the available spin density is retained in the *meta*-phenylene linker group. On average, over 20% of the spin density resides in this ring. Conversely, and somewhat unexpectedly, we see that substituents attached to the *meta*-phenylene ring retain spin densities ranging from <0.2 – 2.5%, a minimal proportion of that available.

We then investigated whether a correlation was present between spin densities at the bis(SQ) radical sites C_7 and C_8, $C_{1–6}$ and various Hammett σ-parameters, but no linear relationship was found.
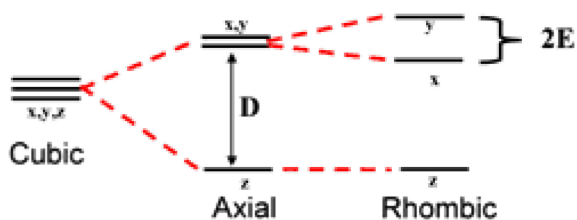
Reasons for the lack of a correlation include both structural and electronic considerations. In the crystal structures of the complexes, C_2 symmetry is evident, whereas gas-phase *ab initio* results show bis(SQ) radical anion structures with the lower C_S symmetry. Additionally, the computations do not account for interactions that the $Zn^{II}Tp^{Cum,Me}$ ligands may have on conformational changes or the electronic environment.

Magnetometry

A general trend consistent with earlier findings[1] is evident in the data presented in Table 2. The magnitude of the exchange parameter **J** is related to the magnitude of the exchange integral. The data, taken as a whole, clearly show a twofold change in **J**, as a function of substituent. We then used the method of Lahti[22] to determine whether a relationship exists between the spin density, ρ, and **J** for our series of radicals by Eqn 2

$$J_{calc} = J_0 \rho^A \rho^B \qquad (2)$$

Estimation of the exchange parameter, **J**, for the bis(semiquinone)s gives us a basis for comparison of our experimentally determined **J** values.

To determine J_{calc} for this series, the *ab initio*-computed spin densities for the bis(SQ) precursors to **5a–f** at C_7 and C_8 were substituted for ρ^A and ρ^B, respectively. Calculated values for **J** using Eqn 2 range from approximately $20\,cm^{-1}$–$34\,cm^{-1}$. As Table 2 shows, J_{exp} was within this range for complexes **5d** and **5e**. The remaining complexes' J_{exp} values were larger than J_{calc} by factors ranging from 1.06–1.74. These variations are addressed below.

To determine empirically the nature of a substituent effect in the bis(Zn^{II}(SQ)$Tp^{Cum,Me}$) complexes proposed earlier, we investigated the relationship between the exchange parameter, **J**, and various σ constants. Correlations between **J**, Δ**J**, log (**J/J_0**), and a variety of Hammett σ values including σ_I, σ_m, σ_-, σ_p, σ^+, and $\sigma_{\Delta\nu}$ were examined without success. Given this fact, it is difficult to deduce any empirical relationship between **J** and established σ systems.

Earlier work has shown that **J** can be modulated by torsion angle.[12] To determine whether this was the case for bis(Zn^{II}(SQ) $Tp^{Cum,Me}$) complexes, we investigated the possible correlation between **J** and the *m*-phenylene torsion angles φ_1 and φ_2 determined by X-ray crystallography (see Fig. 7 and Table 2). Correlations between $(\cos\varphi_1)^2(\cos\varphi_2)^2$ and **J** were examined, but were found to be unsatisfactory ($R<0.8$). With the exception of **5b**, $\varphi_{avg}=32°\pm2$, a small variation within the series. Given these facts, it is difficult to assess any definitive modulation of **J** by complex conformation in this series.

Even with the apparent lack of any simple empirical relationship between **J** and Δν, a_H, ρ (spin density), known σ parameters or conformational variations, the results from our study are consistent with previous work.[1]

The magnetic studies and *ab initio* computations show that neither electron withdrawing groups, electron donors nor conjugating groups facilitate delocalization of the semiquinone radical anions into the central coupling *meta*-phenylene ring to increase the ferromagnetic exchange. In addition, our *ab initio* results have revealed new information regarding the nature of spin density distribution in this system.

The simple Hückel molecular orbital theory argument posited in an earlier work by our group[1,8] that mesomeric substituents attenuate the exchange coupling by spin density dilution relative
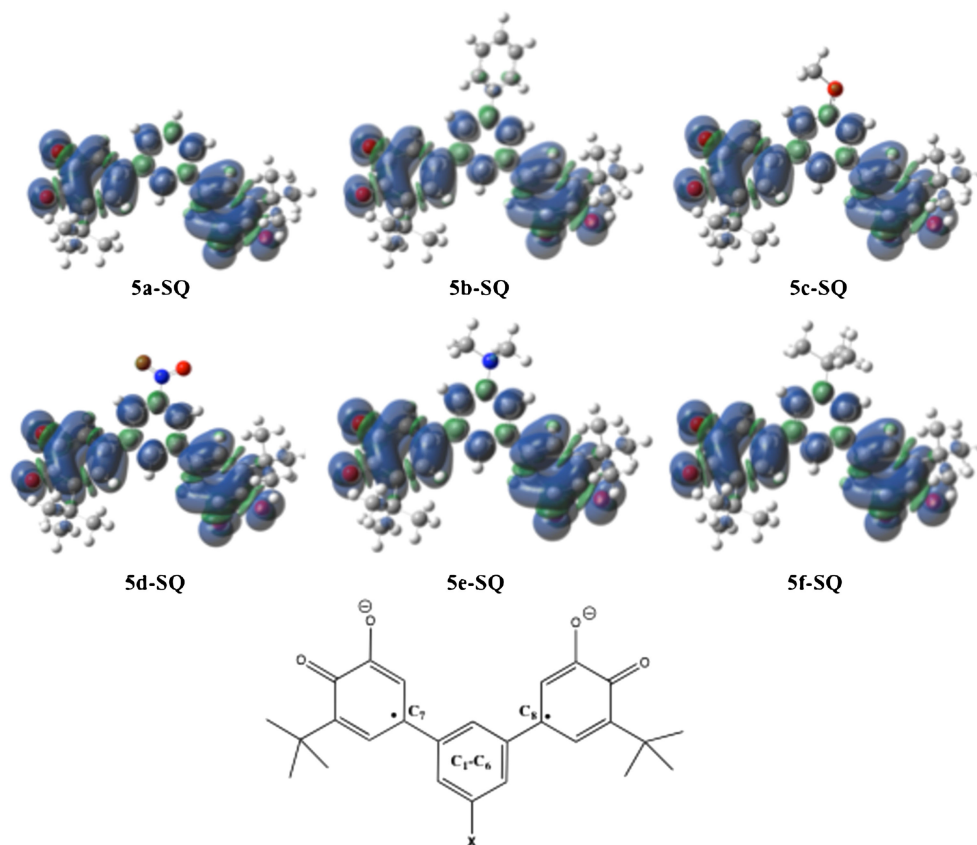

Figure 5. Splitting of formerly threefold degenerate triplet states

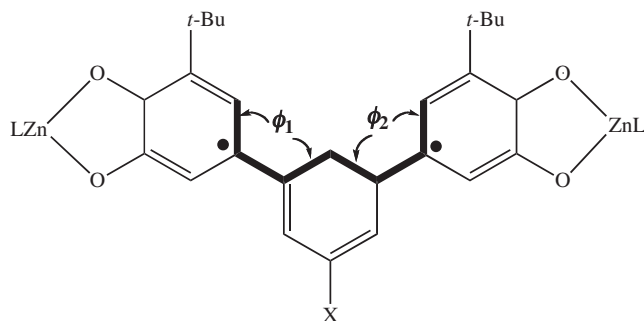**Figure 6.** Bis(SQ) spin density distributions and atoms of interest (Blue=α spin density, green=β spin density)

Figure 7. *m*-Phenylene torsion angles $\varnothing_1$ and $\varnothing_2$

to the unsubstituted *meta*-phenylene singly occupied molecular orbitals appears now to be incorrect, even though the correct trend was predicted. While this semi-empirical approach yielded serendipitous results, the more rigorous computations presented in this work show that the Hückel molecular orbit theory overestimates the delocalization of spin density into the 5-X-*meta*-phenylene substituents.

CONCLUSION

Several new bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes to supplement the earlier series have been prepared and fully characterized.[1] The results of the substituent study for these complexes indicate that there may be no straightforward empirical relationship between *J* and Δν, spin density, σ, or *m*-phenylene torsion. Our *ab initio* computations show that substituents do not modulate spin density in the *meta*-phenylene linker ring by more than 10%. Furthermore, calculations show negligible spin density on the phenylene substituents. This suggests that previous qualitative explanations of spin dilution by substituents that lead to exchange coupling attenuation were incidental.

Clearly, more effort is required to uncover the nature of the relationship between exchange coupling, spin density and substituents. Future work could include additional model systems that exhibit larger exchange couplings, so that comparisons might be made to the present work, and computations involving the bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes might hold even greater promise.

EXPERIMENTAL

Ab initio computations

Initial geometry optimizations and frequency calculations were carried out for each molecule using the hybrid density functional Becke, three-parameter, Lee–Yang–Parr (B3LYP)[17,18] and the 6-31G(d) basis set. After these initial optimizations, the structures were further refined using the EPR-II basis set of Barone *et al.*[19] The EPR-II basis sets were optimized for the computation of hyperfine coupling constants with density functional theory. It was at these B3LYP/EPR-II geometries that the spin densities were computed at the same level of theory. Z-matrices of the optimized B3LYP/EPR-II structures and the corresponding harmonic frequencies can be found in the Supplementary Information. All calculations were performed with the GAUSSIAN 03 suite of *ab initio* programs.[20] All figures were generated with GAUSSVIEW 3.0.[21]

Instrumentation

Nuclear magnetic resonance (NMR) data were collected on a Varian VXR-300 NMR (Agilent Technologies, Inc. 5301 Stevens Creek BLVD., Santa Clara, CA, USA 95051). All ^{1}H and ^{13}C-NMR chemical shifts reported are referenced to deuteriochloroform at the appropriate chemical shift unless specifically noted. Infrared data were collected using a Perkin–Elmer 1600 FT-IR spectrometer (Atlantic Microlab, Inc. 6180 Atlantic Blvd., Suitem, Noncross, GA 30071, USA). High resolution mass spectrometric analytical determinations were performed by the North Carolina State University Mass Spectral Facility. Elemental analyses were performed by Atlantic Microlab, Inc. Melting points were obtained on a Meltemp (Thermo Fisher Scientific, Inc. 81 Wyman Street, Waltham, MA 02454, USA) melting point apparatus and are uncorrected. X-band EPR spectra were recorded on an IBM-Bruker E200SRC spectrometer. Frozen solution EPR spectroscopy was performed on 1mM solutions of the bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes in methyl tetrahydrofuran (THF). Magnetometry data was collected using a Quantum Design MPMSXL SQUID magnetometer (Quantum Design, Inc., 6325 Lusk Blvd., San Diego, CA 92121, USA).

Chemicals

1,3-Dibromobenzene was purchased from Aldrich Chemical Company (Sigma-Aldrich Corp. 3050 Spruce Street, St. Louis, MO 63103) and were used without further purification. Compounds **1a**,[23] **1b**,[23] 3,5-dibromobiphenyl,[24] and 3,5-dibromoanisole[25] were prepared according to literature methods. All reactions, solvent distillations, and EPR sample preparation were conducted under nitrogen or argon atmosphere. Solvents were purchased from Fisher Scientific or Aldrich, and unless otherwise noted, were freshly distilled immediately prior to use. THF was distilled from sodium benzophenone-ketyl before use, while CH_2Cl_2 and CH_3OH were distilled from CaH_2.

General procedure for the synthesis of bis(metaphenylene)s (3)

To a Kjeldahl flask was added the 1,3-dibromoarene (1 eq), **1a** or **1b** (2 eq), Pd(PPh$_3$)$_4$ (5–10 mol %), dry THF (25–50mL), EtOH (5–15mL), 2 M Na$_2$CO$_3$ (7–22mL), and the reaction flask was purged three times with N$_2$. To this was added a reflux condenser, the flask covered with aluminum foil and refluxed for 18–36h. The crude product was taken up in CH_2Cl_2 and filtered through Celite (Celite Corp. 2500 San Miguelito Road, Lompoc, CA 93436). This solution was washed with saturated NaCl, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The resulting crude product was recrystallized or subjected to chromatography (Et$_2$O/CH$_2$Cl$_2$/P.E gradient elution), affording the bis (metaphenylene).

General procedures for the preparation of catechols (4)

Method A

A 100-mL round bottom flask equipped with a stir bar was charged with the *t*-butyl-bis(methoxymethyl)biphenyl (~1–3 mmol), concentrated HCl (2mL), and methanol (50–70mL). A reflux condenser was attached, and the mixture refluxed for 18 h with stirring under N$_2$, protected from light. The solvent was removed by evaporation under reduced pressure. The residue was taken up in CH_2Cl_2, extracted with saturated brine, and the bottom organic layer dried over Na$_2$SO$_4$. The solvent was evaporated to dryness to afford the catechol.

Method B

A 125-mL Kjeldahl flask equipped with a N$_2$ adapter and stir bar was charged with the *t*-butyl-dimethoxybiphenyl (1 equivalent, ~0.5–1.5mmol), distilled CH$_2$Cl$_2$ (~10mL), purged three times with N$_2$, and cooled to −78 °C. Then, a 1.0M solution of BBr$_3$ (3 equivalents, ~1.5–4.5mmol), was added dropwise slowly to the reaction mixture, which was then allowed to warm to room temperature and stir for 20h under N$_2$, protected from light. The reaction mixture was quenched with ice, washed with saturated brine and extracted with two 10mL portions of CH$_2$Cl$_2$. The organic layers were combined, dried over Na$_2$SO$_4$, and the solvent evaporated to dryness to afford the catechol.

General procedure for the synthesis of Bis(Zn^{II}(SQ)Tp^{Cum,Me}) complexes (5)

A 100-mL round bottom flask was charged with 1 equivalent KTp^{Cum,Me} (~0.2mmol), 30mL distilled CH$_2$Cl$_2$, 1 equivalent Zn (ClO$_4$)$_2$·6H$_2$O (~0.2mmol), and 4.5mL N$_2$ saturated methanol. The mixture was stirred until all reagents dissolved (15–30min). Then, 0.5 equivalents of the bis(catechol) (~0.1mmol) was added to the flask and the reaction mixture stirred under N$_2$ for an additional 1h. Finally, triethylamine (0.695mL of a 4% solution v:v with CH$_2$Cl$_2$) was delivered via syringe into the reaction flask and the mixture stirred for an additional 1.5h. The reaction flask was opened to air and stirred overnight. The greenish-brown solution was concentrated under reduced pressure. The resulting solid was washed with diethyl ether, filtered, and the solvent removed under reduced pressure. The resulting microcrystalline product was recrystallized, affording the complex.

SUPPORTING INFORMATION

Experimental methods, 1H and 13C spectral data, analytical data, ab initio parameters, and x-ray crystallographic parameters for reported compounds. This material is available free of charge via the online version of the paper. The crystal structural data have been deposited in the Cambridge Crystallographic Data Center and were assigned the following numbers: complex 5a: CCDC 817203, complex 5b: CCDC 817205, complex 5c: CCDC 817204.

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REFERENCES

[1] D. A. Shultz, S. H Bodnar, H. Lee, J. W. Kampf, C. D. Incarvito, A. L. Rheingold, *J. Am. Chem. Soc.* **2002a**, *124*, 10054.
[2] D. A. Shultz, S. H Bodnar, K. E. Vostrikova, H-J. Koo, M.-H. Whangbo, M. Kirk, E. Depperman, J. W. Kampf, *J. Chem. Soc.* **2003a**, *125*, 1607.
[3] Bruker WINEPR Simfonia, 1.25, Shareware Version, Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany, **1996**.
[4] O. Kahn, Molecular Magnetism, VCH Publishers, Inc, New York, **1993**.
[5] B. B. Bleaney, *Proc. R. Soc. Lond.* **1952**, *A214*, 451.
[6] C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, *29*, 203.
[7] A. D. Caneschi, C. P. Mussari, D. A. Shultz, L. Sorace, K. E. Vostrikova, *Inorg. Chem.* **2002**, *41*, 1086.

[8] W. T. Borden, R. R. Squires, C. R. Kemnitz, *J. Am. Chem. Soc.* **1997**, *119*, 6564.

[9] W. T. Borden, H. Iwamura, J. A. Berson, *Acc. Chem. Res.* **1994**, *27*, 109.

[10] E. R. Davidson, W. T. Borden, *J. Am. Chem. Soc.* **1977**, *99*, 4587.

[11] W. T. Borden, E. R. Davidson, *Acc. Chem. Res.* **1981**, *14*, 69.

[12] D. A. Shultz, R. M. Fico, S. H. Bodnar, R. K. Kumar, K. E. Vostrikova, J. W. Kampf, P. D. Boyle, *J. Am. Chem. Soc.* **2003b**, *125*, 11761–11771

[13] C. K. Hancock, D. Clague, *J. Am. Chem. Soc.* **1964**, *86*, 4942.

[14] D. A. Shultz, R. M. Fico, S. H. Bodnar, R. K. Kumar, K. E. Vostrikova, J. W. Kampf, P. D. Boyle, *J. Am. Chem. Soc.* **2002b**, *124*, 10054.

[15] J. E. Wertz, J. R. Bolton, Electron Spin Resonance, Chapman and Hall, **1986**.

[16] H. K. Kurreck, B. Kirste, W. Lubitz, Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution, VCH Publishers, Berlin, **1988**.

[17] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[18] P. J. Sephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[19] V. Barone, in: Recent Advances in Density Functional Methods, Part I, (Ed: D. P. Chong), World Scientific Publ. Co, Singapore, **1996**.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkarra, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision C.01, Gaussian, Inc., Wallingford, CT, **2004**.

[21] R. Dennington, II; T. Keith, J. Millam, K. Eppinnett, W. L. Hovell, R. Gilliland, GaussView, Version 3.0, Semichem, Inc, Shawnee Mission, KS, **2003**.

[22] P. Lahti ed., Magnetic Properties of Organic Materials, Marcel Dekker, Inc, New York, **1999**, p. 253.

[23] D. A. Shultz, A. K. Boal, D. J. Driscoll, G. T. Farmer, J. R. Kitchin, D. B. Miller, G. N. Tew, *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 303.

[24] T. Kelly, G. Bridger, C. Zhao, *J. Am. Chem. Soc.* **1990**, *112*, 8024.

[25] L. Dorman, *J. Org. Chem.* **1966**, *31*, 3666.

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