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One-Electron Reduction of an Antiferromagnetically Coupled Triradical Yields a Mixed-Valent Biradical with Enhanced Ferromagnetic Coupling

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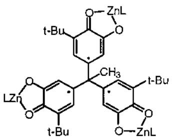
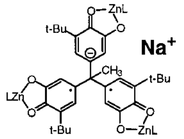
A variety of molecule-based magnetic materials[1,2] has been prepared in which the primary structural element is a high-spin ($S \geq 1$) organic molecule.[3−7] The most common high-spin molecule design is to attach paramagnetic functional groups to a π-system[8,9] (a **Coupler**) to form a cross-conjugated, nondisjoint[10] spin system. For example, the structural features of trimethylenemethane and *m*-xylylene form the basis of a multitude of high-spin molecules.[6,9,11] However, since the beginning of high-spin organic molecule research no new molecular design paradigm has been proposed.

Certain mixed-valent metal complexes exhibit a spin−spin coupling mechanism for which there is no organic counterpart: double exchange, also called spin-dependent delocalization (SDD).[2] The salient feature of SDD is that the highest spin-multiplicity state is lowest energy. An organic system that exhibits true SDD may be difficult to design, but exchange-coupled, mixed-valent organic species are not difficult to design. Despite this fact, only a few examples of such species have been reported, none of which relate either new coupling pathways or enhanced ferromagnetic coupling.[12−14] From these reports it appears that mixed valency does not offer new possibilities for designing high-spin organic molecules.

Nevertheless, we believe that there are opportunities, and to begin our search for new design principles based on mixed valency, we desired a three-spin system featuring an inherently weak antiferromagnetic **Coupler**. We suspected that the effects of mixed valency might be modest and difficult to observe in a strongly coupled system. Moreover, we wanted to discover enhanced ferromagnetic coupling as a consequence of mixed valency. Herein we report the first example of enhanced ferromagnetic coupling in a mixed-valent molecule that lacks an effective π-type ferromagnetic **Coupler** (**$[Na^+][(LZn)_3(SQ_2Cat)]^-$**), formed from one-electron reduction of an antiferromagnetically coupled triradical, **$(LZn)_3(SQ_3)$**.[15]



$(LZn)_3(SQ_3)$



$Na^+[(LZn)_3(SQ_2Cat)]^-$

Complex **$(LZn)_3(SQ_3)$** was prepared from the corresponding tris(catechol) using methodology first reported by Pierpont.[16,17]

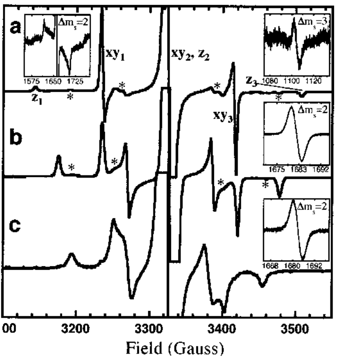


Figure 1. 77 K EPR spectra (inserts show $\Delta m_s \geq 2$ transitions) for (a) **$(LZn)_3(SQ_3)$**, (b) incompletely oxidized reaction mixture containing a large mole fraction of **$(LZn)_3(SQ_2HCat)$**, (c) **$[Na^+][(LZn)_3(SQ_2Cat)]^-$**. Asterisks (*) denote biradical species. All samples were ca. 10 mM solutions in 2-MTHF. See Table 1 for zero-field splitting parameters.

Table 1. Zero-Field Splitting Parameters for Triradical and Biradicals[a]

complex	$\lvert D/hc\rvert/\mathrm{cm}^{-1}$	$\lvert E/hc\rvert/\mathrm{cm}^{-1}$
$(LZn)_3(SQ_3)$	0.00854	0
$(LZn)_3(SQ_2HCat)$	0.01417	0.00108
$[Na^+][(LZn)_3(SQ_2Cat)]^-$	0.01215	0.00058

[a] ZFS parameters determined by spectral simulation.[17,20]

As shown in Figure 1a, the triradical exhibits an axial quartet powder EPR spectrum[18,19] at 77 K in 2-methyltetrahydrofuran (2-MTHF). Also visible are $\Delta m_s = 2$ (with fine structure), and $\Delta m_s = 3$ transitions, confirming the existence of the quartet state. The $\Delta m_s = 1$ region was simulated[17,20] to provide zero-field splitting parameters, $|D/hc| = 0.00854\ \mathrm{cm}^{-1}$, and $|E/hc| = 0\ \mathrm{cm}^{-1}$ (see also Table 1).

Figure 2a shows the EPR Curie plot for the triradical. Assuming a Boltzmann distribution of spin states and regular-triangular[21] coupling, the data were fit according to the expression:

$$I_{\text{quartet}} = \frac{C}{T}\left[\frac{4\exp(3J/kT)}{4 + 4\exp(3J/kT)}\right]$$

The fit parameters give $J = -18\ \mathrm{cm}^{-1}$; that is, for **$(LZn)_3(SQ_3)$** the three spins are antiferromagnetically coupled. This was both desired and expected since **$(LZn)_3(SQ_3)$** lacks an effective ferromagnetic **Coupler**.[8,9]

To demonstrate *intrinsic* antiferromagnetic coupling within this molecular framework, we examined the spin−spin coupling in the localized biradical, **$(LZn)_3(SQ_2HCat)$**. If the oxidation

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(19) Signals marked with an * in the EPR spectrum are for two different $S = 1$ species: **$(LZn)_3(SQ_2HCat)$** and **$[M^+][(LZn)_3(SQ_2Cat)]^-$**, see text.

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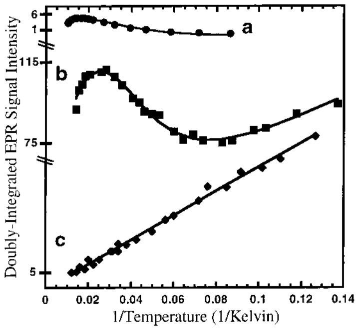
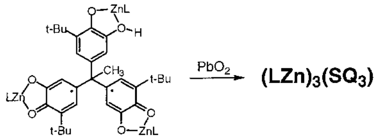


Figure 2. Curie plots and fits for (a) **$(LZn)_3(SQ_3)$** ($J = -18$ cm^{-1}), (b) **$(LZn)_3(SQ_2HCat)$** ($J = -24$ cm^{-1}), and (c) **$[Na^+][(LZn)_S(SQ_2Cat)]^-$**. ($J \geq 0$). All samples were ca. 10 mM solutions in 2-MTHF.

reaction that provides **$(LZn)_3(SQ_3)$** is halted prematurely, the majority of the reaction mixture is biradical **$(LZn)_3(SQ_2HCat)$**. Figure 1b shows the EPR spectrum of this biradical. Zero-field splitting parameters are given in Table 1. Addition of the oxidant PbO_2 to the EPR tube results in the disappearance of signals attributed to **$(LZn)_3(SQ_2HCat)$** and an increase in the quartet signals, supporting our assignment. A small amount of a second triplet, **$[M^+][(LZn)_3(SQ_2Cat)]^-$**, is also present, whose signals are marked with * (M^+ = pyrazole-H^+ or LZn^+) in Figure 1b.



$(LZn)_3(SQ_2HCat)$

When the temperature of the incompletely oxidized sample is lowered, $\Delta m_s = 1$ signals of **$(LZn)_3(SQ_2HCat)$** decrease in intensity, indicating a singlet ground state, while signals due to **$[M^+][(LZn)_3(SQ_2Cat)]^-$** increase in intensity.

The EPR Curie plot using double integration of the coincident $\Delta m_s = 2$ signals for these two biradicals is shown in Figure 2b and was fit according to the expression:[22]

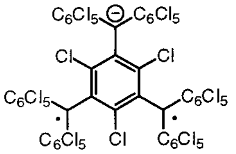
$$I_{\text{triplet}} = \frac{C}{T}\left[\frac{3\exp(2J/kT)}{1 + 3\exp(2J/kT)}\right] + \left(\frac{C}{T} + b\right)$$

The first right-hand term is for **$(LZn)_3(SQ_2HCat)$**, and the second is for **$[M^+][(LZn)_3(SQ_2Cat)]^-$** that was expected (see below) to exhibit a linear Curie plot. Fit parameters give $J = -24$ cm^{-1}; that is in **$(LZn)_3(SQ_2HCat)$** the two spins are antiferromagnetically coupled. The coupling in this localized biradical provides strong evidence that the molecular geometry imposed by the bulky, encapsulating **L** ligands enforces antiferromagnetic coupling in isovalent species *regardless of the number of unpaired electrons*.

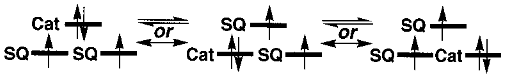
Having demonstrated intrinsic antiferromagnetic coupling in **$(LZn)_3(SQ_3)$** and **$(LZn)_3(SQ_2HCat)$**, we are now ready to examine coupling in the mixed-valent form. The 77 K EPR spectrum recorded after exposing triradical **$(LZn)_3(SQ_3)$** to sodium mirror in the presence of 18-crown-6[23] is shown in Figure 1c and is also characteristic of an $S = 1$ triplet.[24] A $\Delta m_s = 2$ transition confirms the existence of the triplet state. Simulation[17,20] of the $\Delta m_s = 1$ region gives zero-field splitting parameters, $|D/hc| = 0.01215$ cm^{-1}, and $|E/hc| = 0.00058$ cm^{-1} (Table 1). The *D*-value for **$[Na^+][(LZn)_3(SQ_2Cat)]^-$** is slightly less than that of **$(LZn)_3(SQ_2HCat)$**, suggesting *some* delocalization in mixed-valent **$[Na^+][(LZn)_3(SQ_2Cat)]^-$**.[25,26] Also, the *E*-value is much smaller than that of the localized biradical (0.00108 cm^{-1}), consistent with higher symmetry in the mixed-valent biradical. When ferrocenium tetrafluoroborate was added to the solution of **$[Na^+][(LZn)_3(SQ_2Cat)]^-$**, the triradical **$(LZn)_3(SQ_3)$** is slowly regenerated, confirming our assignment.

The Curie plot for the mixed-valent biradical is shown in Figure 2c and is linear, consistent with $J \geq 0$ cm^{-1}.[22] Thus, by virtue of being mixed-valent, the intrinsic antiferromagnetic coupling has been eclipsed by an increased ferromagnetic contribution.[27]

One possible explanation for the enhanced ferromagnetic coupling in **$[Na^+][(LZn)_3(SQ_2Cat)]^-$** could be that the transfer integral, $|\beta|$, that characterizes delocalization in the mixed-valent biradical anion[28] is greater than the intrinsic antiferromagnetic coupling constant, $|J|$. From spectral data Veciana et al. calculated an interaction parameter of 320 cm^{-1} for their mixed-valent biradical anion (shown below),[14] so a transfer integral $\geq$20 cm^{-1} might not be unreasonable for **$[Na^+][(LZn)_3(SQ_2Cat)]^-$**.[29]



Thus, like SDD, delocalization stabilizes the high-spin state:



The graphic above is not intended to relate relative orbital energies, only to suggest that delocalization favors a triplet spin-state.

We demonstrated a new paradigm for high-spin molecule design based on mixed-valency: delocalization enhances ferromagnetic coupling in a molecule that lacks an intrinsic ferromagnetic **Coupler**. Future work will focus on exploring the generality of this design, spectroscopic study of this and similar mixed-valent species with $S > {}^1/_2$, and experimentally determining the magnitude of the exchange parameter in such species.

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Supporting Information Available: Synthetic details, electrochemistry, and EPR simulations and spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] **$(LZn)_3(SQ_3)$** does not react with sodium mirror in the absence of the crown ether due to inherently slow heterogeneous electron transfer caused by the encapsulating ligands. The triradical also does not exhibit cyclic voltammetric waves in the potential region characteristic of other Zn(semiquinone) complexes prepared in our labs. Despite this, the mixed-valent biradical can also be formed by reacting **$(LZn)_3(SQ_2HCat)$** with potassium hydride, and **$(LZn)_3(SQ_3)$** can be prepared by oxidation of **$(LZn)_3(SQ_2HCat)$** with PbO_2.

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[27] The mixed-valent form was also prepared by $CoCp_2$ reduction of **$(LZn)_3(SQ_3)$**, and by KH deprotonation of **$(LZn)_3(SQ_2HCat)$**. In all cases, the mixed-valent form exhibits a linear Curie plot, suggesting that counterions do not play a significant role in the exchange coupling. See Supporting Information.

[28] We have shown that stabilization of mixed-valent semiquinone−catecholate species, as measured by redox splitting, is nearly identical to the stabilization of mixed-valent quinone−semiquinone species.[7] Redox splittings in the tris(quinone) derived from **$(H_2Cat)_3$** are ca. 215 mV.

[29] For now, the reactivity of **$[Na^+][(LZn)_3(SQ_2Cat)]^-$** precludes spectral analysis that would facilitate estimation of delocalization. Future efforts will include this area of study.