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Structure and exchange in silicon-linked tetraradicals†

Yi Liao,[a] Martha Baskett,[a] Paul M. Lahti*[a] and Fernando Palacio[b]
[a] *Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA. E-mail: lahti@chem.umass.edu*
[b] *Instituto de Ciencia de Materiales de Aragón, CSIC – Universidad de Zaragoza 50009. Zaragoza, Spain. E-mail: palacio@posta.unizar.es*

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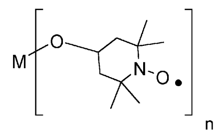
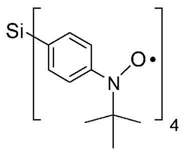
The EPR spectroscopy, crystallography, and magnetic susceptibility of tetrakis(*N*-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)silane and tetrakis(4-*N*-*tert*-butyl-*N*-aminoxylphenyl)silane show that silicon acts as a weak intramolecular exchange linker for polynitroxides, although both tetraradicals show onset of inter-spin exchange at reduced temperatures.

The availability of relatively low-lying, unoccupied d-orbitals in the second row elements gives them electronic properties that are not possible for the first row elements. The ability of silicon to exchange couple unpaired electrons in open-shell molecules is an intriguing property for possible use in molecular magnetic materials. There is limited information about the exchange linking capability of silicon. Iwamura and coworkers[1] found the intramolecular exchange in phenylnitrene units linked by one or two tetravalent silicon atoms to be weak in all connectivity isomers. Multiple workers[2] found nonconjugated tetraradical **1a** to exhibit a nine-line, tetraradical electron paramagnetic resonance (EPR) spectrum consistent with interaction of the nitroxide nitrogen nuclear spins with four unpaired electrons. Nakajima *et al.* have investigated the magnetic behavior of polycrystalline **1a**,**b** and interpreted their findings in terms of weak-exchange spin cluster formation at low temperatures.[2c]



1a M = Si, n = 4
1b M = P, n = 3



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In an effort to clarify the role of silicon as an exchange linker, we compared the known[2] properties of **1a** with those of a new tetraradical, tetrakis(4-*N*-*tert*-butyl-*N*-aminoxylphenyl)silane, **2**. We also investigated the crystallography of both tetraradicals. These systems could in principle be used to create 3-D networked magnetic materials by exchange through both the conjugated benzene rings and the silicon atom, if coordinated by transition metal cations.[3] Compound **1** was made by adaptation of known syntheses.[2a,b] Compound **2** was synthesized using tetrakis(4-bromophenyl)silane, which was metallated and treated with excess 2-methyl-2-nitrosopropane[4] to give tetrakis(4-*N*-*tert*-butyl-*N*-hydroxylaminophenyl)silane, then oxidized with lead dioxide in diethylether, to give red needles of **2** that were stable for months in air at −20 °C.

A solution phase EPR spectrum of **2** in degassed toluene exhibited a nonet consistent with coupling of four electrons to the nitrogen atoms with an exchange strength substantially larger than the nitrogen hyperfine coupling, $J \gg a_N$. The peak to peak splitting $\Delta H_{pp} = 0.30 \pm 0.02$ mT is in good agreement with the expected value of one-quarter of the hyperfine coupling $a_N \cong 1$ mT for a phenyl *tert*-butylnitroxide unit in a symmetrical tetraradical. ΔH_{pp} is significantly smaller in **2** than in **1a**,[2] 0.3 *versus* 0.4 mT, consistent with the delocalization of nitroxide spin into the phenyl rings in **2**. At 77 K, the spectrum of **2** showed only a featureless single peak in the $g \approx 2$ region and a weak $\Delta M_s = 2$ peak at 166 mT; the latter demonstrates the presence of exchange coupling between the radical spin sites. The lack of resolvable zero field splitting is consistent with time-averaged centrosymmetry.

In an effort to determine the magnetic role of silicon as an *intramolecular* exchange linker, we carried out UB3LYP/6-31G* hybrid density functional[5] computations on a model system with *para*-SiH$_3$ attached to phenylnitroxide using Gaussian 98.[6] Silicon has only a (−)0.4% computed spin density population. For the triplet biradical analog for **2**, there is less than (−)0.1% spin density at the silicon atom, whereas the singlet and triplet states are almost degenerate (2 J mol^{-1} favoring of the singlet), consistent with the observed weak exchange behavior in the silicon linked systems.‡

Nakjima *et al.* showed that the higher temperature portion of the Curie–Weiss plot of reciprocal magnetic susceptibility ($1/\chi$) *versus* absolute temperature (T) for **1a** yields C = 1.55 emu K (Oe mol)$^{-1}$, and $\theta = -3.5$ K.[2c] At low temperature, there was a significant downturn that the authors attributed to trigonal spin cluster formation with net $S = 1$. It was not clear whether the cluster formation was intramolecular, intermolecular, or a mixture of exchange behaviors. By comparison, Fig. 1 shows the Curie–Weiss plot of $1/\chi$ *versus* T that we obtained for **2**. At temperatures above 50 K, the plot is linear with a slope of C = 1.45 emu K (Oe mol)$^{-1}$ and a Weiss constant of $\theta = -1.15$ K (inset, Fig. 1). For both **1a** and **2**, the Curie constant C is consistent with the value of 1.5 expected for a system consisting of four $S = 1/2$ spin units, rather than a robustly exchange

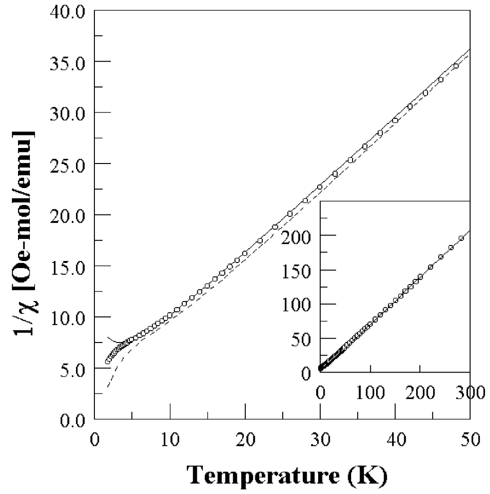

Fig. 1 Curie–Weiss plot of reciprocal paramagnetic susceptibility *vs.* absolute temperature (○) for **2**, compared with a Heisenberg $S = 1/2$ chain fit for two alternating AFM interactions (—) and alternating AFM and FM interactions (- - -). Lower inset shows Curie–Weiss data (○) with a linear fit to data at $T > 50$ K (—).

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† Electronic supplementary information (ESI) available: EPR spectra, X-ray crystallographic data and packing views, synthetic and characterization details for **1a** and **2**, χT plot for **2**, and computational summaries for model systems. See http://www.rsc.org/suppdata/cc/b1/b107430j/

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coupled $S = 2$ state. At 5–50 K, an upward deviation in the plot for **2** indicates the onset of antiferromagnetic exchange (AFM) interactions not observed in **1a**,**b**; below 5 K the plot turns downward again, as reported[2c] for both **1a** and **1b**.

In all of these systems, the magnetic behavior suggests short-range interactions, but of an indeterminate nature. We turned to crystallography to try to understand possible interactions that dominate the observed behavior.

Whereas tetraradical **1a** crystallizes in the triclinic $P\bar{1}$ space group, **2** crystallizes in the tetragonal $P4_2/n$ space group.§ The intramolecular approaches between nitrogen atoms in **1a** are 8–10 Å (depending upon the Si–O–TEMPO conformation in the crystal), whereas the closest intermolecular O···O approaches can be as short as 4.0–4.3 Å. Phenylnitroxide rotational disorder makes difficult a precise correlation of crystal packing and magnetic properties in **2**, but depending upon nitroxide group orientation, the closest intramolecular approach between nitrogen atoms is *ca.* 10.2 Å. Unlike **1a**, the closest intermolecular inter-radical radical O···O approaches in **2** of 3.69 and 4.07 Å can form an alternating zig-zag chain parallel to the (001) direction, four per molecule (Fig. 2). The longer distances in **1a** are consistent with its simple Curie–Weiss magnetic behavior above 10 K,[2c] whereas **2** shows significant AFM interactions below 30 K.

The magnetic data for **2** were fit to an alternating $S = 1/2$ Heisenberg chain model[7] for two different limiting interaction schemes. An antiferromagnetic alternating chain gives $J_1/k = -7.0$ K and $\alpha = J_2/J_1 = 0.9$ (Fig. 1, solid line). On the other hand, if alternating ferro- and antiferro-magnetic interactions are assumed, then $|J_1|/k = 3.5$ K and $\alpha = -0.85$ (Fig. 1, dashed line).¶ The presence of short chain segments with an odd number of elements due to the crystallographic disorder in the nitroxide groups would limit longer range propagation of the exchange interactions, giving either or both types of behavior, and leading to the observed Curie–Weiss behavior.

In summary, the magnetism of both **1a** and **2** at higher temperature is consistent with clusters of four weakly coupled radicals: if the central silicon atom provided strong exchange linkage, the magnetic susceptibility analysis would have shown $S = 2$ spin state formation. As the temperature is lowered, short-range interactions are observed. Our crystallographic results for **1a** are consistent with the spin cluster model proposed by Nakajima *et al.*[2c] The crystal and magnetic data for **2** suggest formation of short, intermolecularly exchange coupled $S = 1/2$ chains. This is consistent with the weak computational intramolecular exchange linking capability of silicon. Further study is needed to determine whether any of the overall, low temperature AFM exchange behavior that is observed in **2** is attributable to intramolecular, silicon-mediated effects, rather than closer-range through-space interactions.

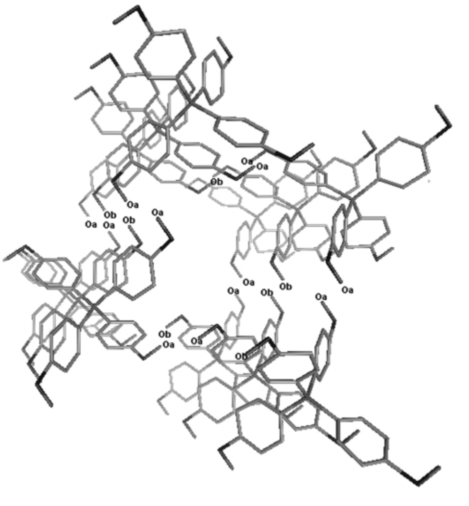

Fig. 2 Crystallographic *ab*-plane of **2** showing the alternating chain of nitroxide oxygen atoms along the (001) direction, where r(Oa–Oa′) = r(Ob–Ob′) = 4.07 Å, r(Oa–Ob′) = 3.69 Å, r(Oa–Ob) = r(Oa′–Ob′) = 7.06 Å. Oa and Ob show the oxygen atoms of the nitroxide groups, but do not show nitroxide rotational disorder, which can disorient the alignment of the N–O units. Hydrogen atoms and *tert*-butyl groups are omitted for clarity.

The results for **1a** and **2** suggest that silicon-linked tetraradicals could be useful as 3-D room temperature exchange linker units for hybrid organic–inorganic magnetic materials. Even in the absence of robust intramolecular exchange coupling among radical spins within **1** and **2**, there is sufficient magnetic exchange in the solid state to show promise for coordination complexes. Pursuit of such materials, and extension to other main group exchange-linking elements with varying radical spin-bearing units, is underway.

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Notes and references

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§ CCDC reference numbers 172624 and 172625. See http://www.rsc.org/suppdata/cc/b1/b107430j/ for crystallographic data in CIF or other electronic format.

¶ Includes a contribution of 6% paramagnetic residuals.

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