

trophilic quinone imine generated from these antitumor agents by oxidative bioactivation.

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A Linear Chain with Alternating Ferromagnetic and Antiferromagnetic Exchange: $\text{Cu}(\text{hfac})_2\text{-TEMPOL}$

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It was recently suggested that $\text{Cu}(\text{hfac})_2\text{-TEMPOL}$ could behave like an alternating linear magnetic chain.¹ We show here that the material indeed behaves in that fashion, and provides an example in which the sign of the exchange also alternates.

The compound bis[(hexafluoroacetyl)acetonato][(4-hydroxy-2,2,6,6-tetramethylpiperidinyl)-*N*-oxy]copper(II), hereafter abbreviated as above, contains² polymeric chains of planar $\text{Cu}(\text{hfac})_2$ units bridged by TEMPOL ligands. Each copper ion is hexacoordinated by four oxygen atoms of two hfac^- ions, one O(H) and one N-O atom of two different TEMPOL ligands, as shown in Figure 1. At high temperatures,¹ the magnetic behavior is characteristic of a system comprised of two independent spin $S = 1/2$ moieties. As the temperature of the sample is decreased, the spins interact ferromagnetically, leading to a spin-triplet ground state for the pair. The exchange constant, based on an analysis using the familiar Bleaney-Bowers expression, was found to be $2J/k = 19$ K, with an estimated standard error of 7 K.¹ The average g value for the adduct was found to be 2.08. At temperatures of 4.2 K and below, one therefore expects the system to consist of spin $S = 1$ units with $\langle g \rangle = 2.08$, and the question is whether there is a (weak) magnetic link between the pairs via the saturated ligand and the hydrogen bond?

The zero-field susceptibility of the compound is illustrated over the temperature interval 50 mK to 4.2 K in Figure 2, and the low-temperature data are shown at higher resolution in Figure 3; the experimental procedures have been described elsewhere.³ The data above 2 K may be fit by the Curie-Weiss law with $\langle g \rangle = 2.1$ and $\theta = 0.21$ K. At lower temperatures the data increase and go through a broad maximum at about 80 mK. This is behavior characteristic of an antiferromagnetic linear chain, which is suggested by the following data analysis.

The curve through the data in the figures is based on the familiar theoretical result for a spin-1 linear chain, the modified classical result of Fisher.⁴ The susceptibility is calculated as

$$\chi = \chi_c \left(\frac{1 + \mu}{1 - \mu} \right)$$

where

$$\chi_c = N g^2 \mu_B^2 S(S+1) / 3kT \quad \mu = \coth K - 1/K$$

$$K = 2J'S(S+1) / kT$$

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(1) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1984**, *106*, 5813. These authors use a spin Hamiltonian of the form $\mathcal{H} = JS_1 \cdot S_2$ and report $J = -13 \pm 5$ cm⁻¹. We use the spin Hamiltonian $-2JS_1 \cdot S_2$ and thus, changing units, $J/k = 19 \pm 7$ K.

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(3) van der Bilt, A.; Joung, K. O.; Carlin, R. L.; de Jongh, L. *J. Phys. Rev. B* **1980**, *22*, 1259-1262.

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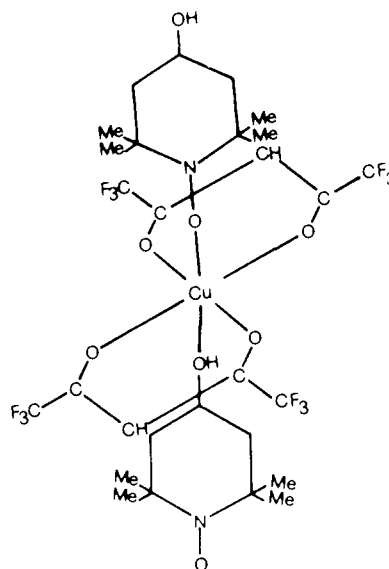


Figure 1. Repeating structural unit (schematic) of the $\text{Cu}(\text{hfac})_2\text{-TEMPOL}$ chain.

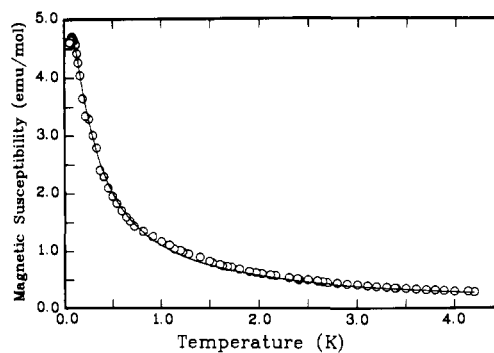


Figure 2. Magnetic susceptibility of the compound, along with the fit described in the text.

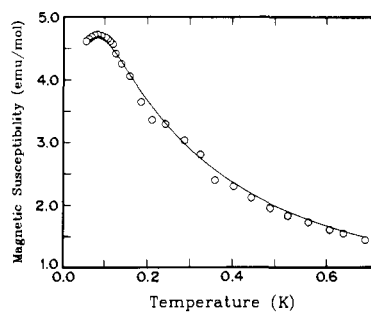


Figure 3. Low-temperature data, along with the fit. Note that the origin is offset.

and the fit, for $S = 1$, yields $\langle g \rangle = 2.2$ (1) and $2J'/k = -78$ (2) mK. This is quite a weak exchange constant but is reasonable for the proposed rather lengthy superexchange path. An analysis similar to this one has been provided on high-field magnetization data on (4-benzylpiperidinium)- CuCl_3 .⁵

The ratio of the exchange constants is $2J'/2J = -0.078/19 = -0.004$, and this is the alternation parameter α as written in the usual Hamiltonian,

$$H = -2J \sum_{i=1}^{N/2} (\vec{S}_{2i} \cdot \vec{S}_{2i-1} + \alpha \vec{S}_{2i} \cdot \vec{S}_{2i+1})$$

A number of chains with alternation parameter $0 < \alpha < 1$ have been reported recently,⁶ but this is one of the few examples in

(5) de Groot, H. J. M.; de Jongh, L. J.; Willett, R. D.; Reedyk, J. *J. Appl. Phys.* **1982**, *53*, 8038-8039.

which the sign of α is negative. That is, not only the magnitude of the exchange constant alternates, but the sign also alternates along the chain from ferromagnetic to antiferromagnetic. We note that measurements such as these would not have been possible for a system with α of this magnitude but positive, for the low-temperature diamagnetism of the singlet ground state of the pair would preclude the observation of the antiferromagnetic interpair interaction. A molecule of this sort is copper acetate-pyrazine.^{7,8}

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Registry No. Cu(hfac)₂-TEMPOL, 72692-66-1.

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(7) Valentine, J. S.; Silverstein, A. J.; Soos, Z. G. *J. Am. Chem. Soc.* **1974**, *96*, 97-103.

(8) An alternative attempt was made to analyze the magnetic behavior in terms of the zero-field splitting of the $S = 1$ ground state. Using the appropriate relationship for the susceptibility of a powder,⁹ a fit of the data above 80 mK was obtained with $D = 0.31$ (1) cm⁻¹. However, the calculated behavior then remains constant at lower temperatures, in contrast with the decrease in the experimental data. Furthermore, this value of D is twice that (0.157 cm⁻¹) measured by EPR spectroscopy.¹ Thus, even if zero-field splitting effects are operative, it is possible to conclude that they do not provide the dominant effect in determining the magnetic behavior. The chains are also too far apart for interchain interactions to give rise to the observed effects.

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Oxidative Decomposition of 1,1'-Azoadamantane by Thianthrene Cation Radical. Carbocationic Chemistry from a Free Radical Source

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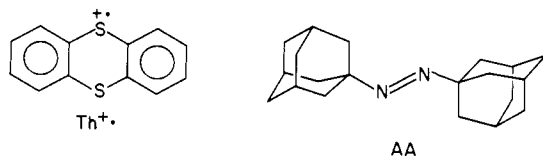
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In the course of studies in the trapping of free radicals, we have discovered that azoalkanes are readily oxidized by aromatic cation radicals in acetonitrile at room temperature. The mechanism of this novel reaction is examined here for the particular case of thianthrenium perchlorate (Th⁺·ClO₄⁻) and 1,1'-azoadamantane

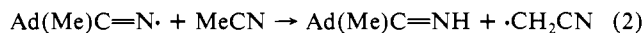


(AA). *trans*-AA undergoes conventional thermolysis into adamantyl radicals (Ad·) in solution at reasonable rates only if heated in the region 280-300 °C.^{4,5} In contrast, reaction of this very stable azoalkane with Th⁺ at room temperature leads to rapid

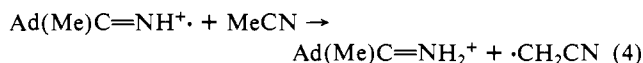
and quantitative evolution of nitrogen.⁶ The major products (Table I) are characteristic of adamantyl cations (Ad⁺) while the minor ones imply a small free radical component of the reaction. In other words, predominantly carbocationic chemistry is observed from an azoalkane, a traditional source of free radicals.⁷

While Th⁺ was reduced quantitatively to thianthrene (Th), the major product from AA was *N*-adamantylacetamide, which was isolated in 90% yield as its perchloric acid salt (cf. Table I). Without doubt, this product arose from hydration, during workup, of a Ritter-type intermediate (AdN⁺·CMe) from reaction of Ad⁺ with solvent acetonitrile. The small amount of 1-adamantanol (0.6%) must have been formed also from Ad⁺ by reaction with water either adventitiously in the solvent or added later. Together, these products show that 91% of the adamantyl groups appeared as the cation. Three other products containing the adamantyl group were obtained: adamantane (AdH), 0.2%, 1,1'-biadamantyl (AdAd), 2.5%, and 1-adamantyl methyl ketone, AdCOMe, 5.5%. Thus, we have accounted for 99% of the adamantyl groups in the AA.

The formation of AdCOMe and AdH but not of the other products was completely suppressed by inclusion of a small amount (0.020 M) of BrCCl₃ in the solvent. The concomitant appearance of 1-bromoadamantane suggests that adamantyl radicals which would normally have given AdH and AdCOMe were trapped by bromine atom abstraction from BrCCl₃.^{8,9} The source of AdCOMe was found to be the ketimine Ad(Me)C=NH. Ketimines are known to hydrolyze readily during isolation.¹⁰ Addition of an authentic sample of Ad(Me)C=NH after reaction was complete resulted in its quantitative hydrolysis to AdCOMe on workup. On the other hand, an authentic sample of Ad(Me)C=NN=C(Me)Ad survived the reaction and workup conditions; hence, AdCOMe is not derived from hydrolysis of this azine. The ketimine may arise from iminyl radicals which are known to abstract hydrogen atoms both intra- and intermolecularly¹¹⁻¹³ in competition with their dimerization.^{11,14} Iminium cation radicals^{12,13}



are better hydrogen abstracting agents, however (eq 3 and 4), and



these are more viable intermediates in our system. The necessary protons could easily derive from hydrolysis of some of the thianthrenium perchlorate¹⁵⁻¹⁷ by the small amount of adventitious water in the solvent.

UV irradiation of AA in hydrocarbon solvents at 65 °C produces Ad· which mostly dimerizes to AdAd or abstracts hydrogen to give AdH.⁵ Since these products are very minor in the present work, it appears that either Th⁺ oxidizes Ad· with great facility

(6) The reactions were carried out by injecting acetonitrile (30 mL) into a mixture of solid thianthrenium perchlorate and AA.

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