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be quite remarkable for the lines to be as evenly spaced as we observe on the $g = 4.1$ signal.[18] In addition, as discussed above, we favor a model where the resolved components all arise from a single principal component on the g tensor.

Furthermore, the $g = 4.1$ signal cannot arise from an isolated binuclear Mn complex. The $g = 4.1$ signal appears to arise from an $S = {}^3/_2$ ground-state doublet.[6,7] Antiferromagnetic coupling within either a Mn(III)Mn(IV) or a Mn(II)Mn(III) binuclear complex will produce an $S = {}^1/_2$ ground state. Even if the $g = 4.1$ signal arose from an excited state, one would expect to observe an associated $S = {}^1/_2$ $g \approx 2$ signal whose intensity at a given temperature would be directly proportional to the intensity of the $g = 4.1$ signal. However, such an associated $g \approx 2$ signal is not observed, and in fact, there appears to be an interconversion between the $g = 4.1$ and $g = 2$ multiline EPR forms.[4,8]

On the other hand, an exchange-coupled tetranuclear Mn complex could have either an $S = {}^3/_2$ ground state or an $S = {}^1/_2$ ground state.[6c,10] Additionally, the reduced hyperfine couplings observed in the $g = 4.1$ spectra are consistent with a tetranuclear origin for the signal. The measured ^{55}Mn hyperfine interaction for each ion will scale to the mononuclear hyperfine couplings of the ion by the projection of each individual ion spin on the total spin.[2] To illustrate the reduction of hyperfine couplings that will occur in an $S = {}^3/_2$ tetranuclear complex, we consider as an example a "dimer-of-dimers" model consisting of two dimeric complexes with antiferromagnetic couplings as well as magnetic couplings between the two dimers. Using a simplified vector coupling model in which the interdimer exchange couplings are set equal, we can calculate the predicted values for the Mn hyperfine couplings. Consider the case of a $\mathrm{Mn_1(III)Mn_3(IV)}$ tetramer in which a $\mathrm{Mn_A(III)}$ and a $\mathrm{Mn_B(IV)}$ are strongly antiferromagnetically coupled to give an $S_{\mathrm{AB}} = {}^1/_2$ ground state, and the $\mathrm{Mn_C(IV)}$ and $\mathrm{Mn_D(IV)}$ ions are antiferromagnetically coupled to give an $S_{\mathrm{CD}} = 1$ first excited state. Ferromagnetic coupling between the dimers can then give rise to a total spin $S = {}^3/_2$ ground state.[6b,c,10] Calculation of the projected hyperfine couplings gives $A_{\mathrm{A}} = {}^2/_3A_{(\mathrm{III})}$, $A_{\mathrm{B}} = -{}^1/_3A_{(\mathrm{IV})}$, and $A_{\mathrm{C}} = A_{\mathrm{D}} = {}^1/_3A_{(\mathrm{IV})}$, where $A_{(\mathrm{III})}$ and $A_{(\mathrm{IV})}$ are the hyperfine coupling constants for monomeric Mn(III) and Mn(IV), respectively. This reduction in line spacing and the approximately 2:1 ratio in the magnitude of the effective hyperfine couplings are consistent with our experimental observation of a regular spacing of 36 G between lines. We are commencing EPR simulations of this and other tetranuclear models. At present, we cannot rule out the possibility that different conformations of a Mn trimer could also give rise to both the $g = 4.1$ and multiline signals. However, this would leave a "voyeur" Mn that is always EPR silent in the OEC. With a monomeric origin for the $g = 4.1$ signal discounted by this work, the motivation for considering separate mononuclear and trinuclear centers in the OEC is decreased. Our new observations of resolved hyperfine structure on the $g = 4.1$ signal are strongly suggestive that, under conditions of ammonia inhibition of oxygen evolution, the multiline and $g = 4.1$ EPR signals arise from a common tetranuclear mixed-valence Mn cluster that can present either an $S = {}^1/_2$ or an $S = {}^3/_2$ ground state, depending on slight configurational differences.

Acknowledgment. This work was supported by a grant from the National Science Foundation (DMB-8804526) and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Energy Biosciences of the U.S. Department of Energy, under Contract DE-AC0376SF00098. D.H.K. gratefully acknowledges the receipt of a University of California President's Undergraduate Fellowship (1989–1990). R.D.B. gratefully acknowledges support from the Camille and Henry Dreyfus Foundation.

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(18) From the measured pattern of Mn hyperfine lines on the oriented $g = 4.1$ signal, we could describe it as another "multiline" signal. We note that the $g = 4.1$ signal resembles the ammonia-altered multiline form (see ref 11, Figure 2) in that both signals have better resolution of Mn hyperfine features in the higher field regions.

Molecular Engineering in the Design of Short-Range Ferromagnetic Exchange in Organic Solids: The 1,3,5-Triphenylverdazyl System

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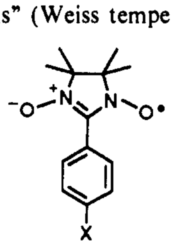
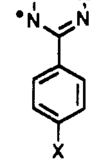
Organic molecular solids composed of open-shell molecules, as a rule, yield bulk paramagnets. If ordering of the unpaired spins occurs, it is generally antiferromagnetic. The few exceptions to the above are metamagnetism (MM) in a bisnitroxy,[1,2] weak ferromagnetism (FM) in a nitronyl nitroxide,[3-5] and weak FM prior to a structural-phase transition that produces antiferromagnetism in galvinoxyl.[6,7]

The report that **1** exhibits "ferromagnetic intermolecular interactions" (Weiss temperature $\theta \sim 1$ K)[3,4] prompted us to determine if introduction of a nitro group in the isoelectronic position of triphenylverdazyl; e.g., **2N**, would also lead to an FM or short-range ferromagnetic (SRFM) organic solid. Here we report the magnetic properties and crystal structures of **2N** and **3** and the rationale for the design of **3**, an organic solid exhibiting SRFM with $\theta = +1.6$ K.



1, X = NO_2



2, X = H; **2N**, X = NO_2

1,3,5-Triphenylverdazyl (**2**) is an unusually stable organic free radical that has been studied extensively.[8,9] Magnetic susceptibility measurements[9] showed it to be an AF coupled system. Electron spin resonance spectroscopy (ESR)[8] and NMR[8] spectroscopy had been performed on a number of verdazyls and multiple verdazyls.[10] In general, the preponderance of spin density is on the four nitrogen atoms,[11,12] which is also observed in **2N** and **3**.[13]

Compounds **2N** and **3** were prepared according to literature procedures.[8,14] In Figure 1a we show that the solid-state structure[15] of **2N** consists of stacks and that the tetraazapentadienyl moieties are arranged for good intermolecular "overlap" within the stacks. Since these are the regions of maximum spin density, it follows from McConnell's model[16] that this solid should exhibit antiferromagnetism. In Figure 2a we show the results of static magnetic susceptibility measurements,[17] which, contrary

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(1) Saint Paul, M.; Veyret, C. *Phys. Lett. A* **1973**, *45*, 362.
(2) Chouteau, G.; Veyret-Jeandey, C. *J. Phys.* **1981**, *42*, 1441.
(3) Awaga, K.; Maruyama, Y. *Chem. Phys. Lett.* **1989**, *158*, 556.
(4) Awaga, K.; Maruyama, Y. *J. Chem. Phys.* **1989**, *91*, 2743.
(5) Awaga, K.; Inabe, T.; Nagashima, U.; Maruyama, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1617; *Ibid.* **1990**, 520.
(6) Awaga, K.; Sugano, T.; Kinoshita, M. *J. Chem. Phys.* **1986**, *85*, 2211.
(7) Kinoshita, M. *Mol. Cryst. Liq. Cryst.* **1990**, *176*, 163.
(8) Kuhn, R.; Trischmann, H. *Monatsh. Chem.* **1964**, *95*, 457.
(9) Azuma, N.; Yamauchi, J.; Mukai, K.; Ohya-Nishiguchi, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2728.
(10) Kuhn, R.; Neugebauer, F. A.; Trischmann, H. *Monatsh. Chem.* **1966**, *97*, 525.
(11) Neugebauer, F. A.; Bruhner, H.; Hausser, K. H. *Tetrahedron* **1971**, *27*, 3623.
(12) Fischer, P. H. H. *Tetrahedron* **1971**, *23*, 1939.
(13) Allemand, P.-M., unpublished results.
(14) All analytical data are in accord with the structures.
(15) $C_{20}N_5O_2H_{16}$: $M_w = 358.38$; orthorhombic; space group *Pmnb*; $Z = 4$; $a = 18.352$ (3), $b = 22.789$ (4), $c = 4.0717$ (7) Å, $V = 1702.9$ Å^3, $D_{\mathrm{calcd}} = 1.40$ g cm^{-3}, $2\theta \leq 45°$; 551 reflections with $I > 3\sigma(I)$, $R = 0.051$, $R_w = 0.058$.
(16) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

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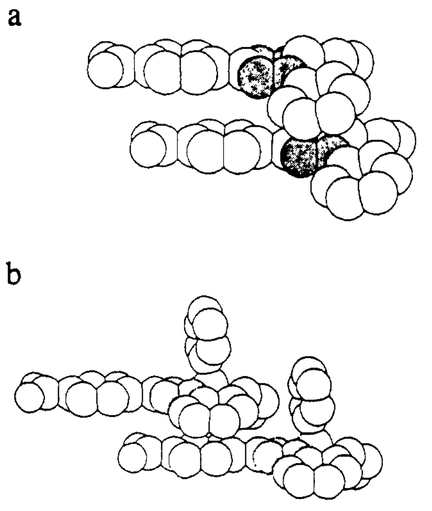
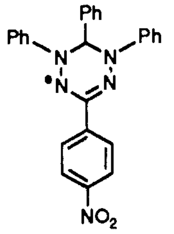


Figure 1. (a) Molecular packing of (nitrophenyl)verdazyl **2N**. The drawing was generated from crystal structure data by using the program CHEM-X. Hydrogen atoms were left out for clarity. Shaded atoms comprise the region of maximum spin density as determined by EPR. (b) Molecular packing of (nitrophenyl)verdazyl **3**. The drawing was generated from crystal structure data by using the program CHEM-X. Shaded atoms comprise the region of maximum spin density as determined by EPR.

to the expectation based on **1** above, but in accord with McConnell's model,[16] show AF behavior. The data are plotted as χT vs T, since this procedure illustrates AF and FM qualitatively most clearly (an upturn or a downturn in ordinate values, as a function of T, corresponds to ferromagnetic or antiferromagnetic behavior, respectively).

If the molecules within a stack of **2N** could be slid relative to one another in the b direction (see Figure 1a), then regions of high-spin density would overlap regions of nodes in adjacent molecules. The McConnell model would then predict[18,19] intrastack FM interactions. We reasoned that placement of a phenyl ring in the 6-position (as in **3**) could produce the desired effect.



3

As depicted in Figure 1b, the "designed" lattice[20] was obtained. As Figure 2b shows, the material exhibits SRFM. However, the product $\chi_{\rm spin}T$ decreases slowly from 300 to 100 K and then *increases* below 100 K to reach a maximum at 2 K. The change in slope at ca. 100 K could be due to a structural-phase transition,[21] but no changes in the ESR line width or in the resonance field were observed at this temperature.

In the 300–100 K temperature region, the $\chi_{\rm spin}$ of **3** follows the Curie–Weiss law with $\theta \sim -6$ K but from 100 to 30 K, the Curie–Weiss law is obeyed with $\theta = +1.6$ K, indicating ferromagnetic interactions between $S = {}^1/_2$ species. There is a strong deviation from the Curie–Weiss law below 30 K with $\chi_{\max} = 0.241$ emu/mol at 2.15 K. The susceptibility data from 6 to 80 K were analyzed with the 1-D Heisenberg model.[22-24] The maximum in χ at 2.15 K suggests the presence of antiferromagnetic coupling between ferromagnetic chains.[25]

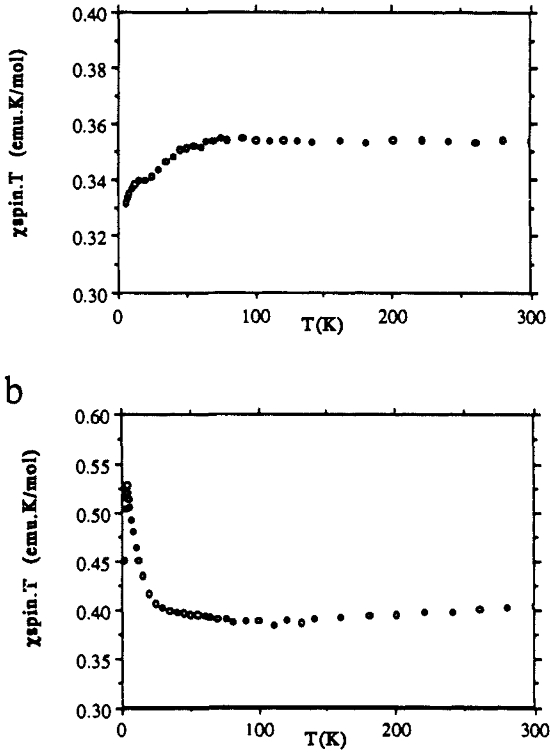


Figure 2. (a) Plots of the product of magnetic susceptibility and temperature vs temperature for (nitrophenyl)verdazyl **2N**. (b) Plots of the product of magnetic susceptibility and temperature vs temperature for (nitrophenyl)verdazyl **3**. In both plots, the values of χ were corrected for diamagnetic contributions.

We have shown above that a combination of structure analysis and specific modification by molecular engineering can lead to the preparation of molecular solids with remarkably different magnetism, culminating in a case of short-range organic ferromagnetism.[26]

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Supplementary Material Available: Unit cell orientations and tables of positional and thermal parameters of verdazyls **2N** and **3** (12 pages); listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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(17) Regional Facility, administered by C. A. Reed.

(18) Only a number of intermolecular overlaps can be applicable as in Iwamura's case (ref 19).

(19) Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293.

(20) $C_{26}N_5O_2H_{20}$: $M_w = 434.38$; triclinic, $P\bar{1}$; $Z = 2$; $a = 12.777$ (2), $b = 13.199$ (1), $c = 6.597$ (1) Å; $\alpha = 84.28$ (2), $\beta = 83.93$ (2), $\gamma = 87.31$ (1)°; $V = 1100.1$ Å^3; $D_{\rm calcd} = 1.32$ g cm^{-3}; $2\theta \leq 40°$; 783 reflections with $I > 3\sigma(I)$; $R = 0.15$. Refinement of this structure is still in progress. Besides a limited number of data, a reason for the high R value could be the quality of the crystal and that the average change in the intensity of standard reflections was 8%. The latter remains unexplained but could be due to a phase transition occurring at, or near, the temperature of data collection.

(21) If there were a phase transition, then the property–structure correlation with the room-temperature crystal structure would not apply.

(22) The experimental data can be fit by a Pade expansion series for the $S = {}^1/_2$ Heisenberg model $\chi(K) = [Ng2\mu_B2/4k_BT][(1 + 5.80K + 16.90K^2 + 29.38K^3 + 29.83K^4 + 14.04K^5)/(1 + 2.80K + 7.01K^2 + 8.65K^3 + 4.57K^4)]^{2/3}$, where $K = J/2k_B$. The best fit was obtained with $J/k_B = +2.2$ K, a value that compares well with J given by the molecular fit theory $\theta = {}^2/_3 ZS(S+1)\cdot J/k_B = J/k_B = +1.6$ K if $Z = 2$ and $S = {}^1/_2$.

(23) Baker, G. A.; Rushbrooke, G. S.; Gilbert, H. E. *Phys. Rev.* **1964**, *135*, 1272.

(24) Bonner, J. C.; Fischer, M. E. *Phys. Rev.* **1964**, *135*, A640.

(25) The above equation (footnote 22) was then modified by considering antiferromagnetic interchain interactions (j) $\chi' = \chi/(1 - 2Zj\chi/Ng^2\mu_B^2)$, where Z, the number of nearest neighbors, was set at 4, $J/k_B = +2.9$ and $j/k_B = -0.19$ (and thus, $J/j = 15.6$); but this mean-field correction does not give reliable fits below 6 K.

(26) The ultimate test is determination of magnetization curves. Results from measurements in collaborations (Cornell, Zaragoza) will be forthcoming.