Molecular structure and magnetic properties of *N*,*N*-bis{4-methoxy-3,5-bis(*N*-*tert*-butyl-*N*-oxyamino)phenyl)}aminoxyl. An approach to a stable and high-spin pentaradical

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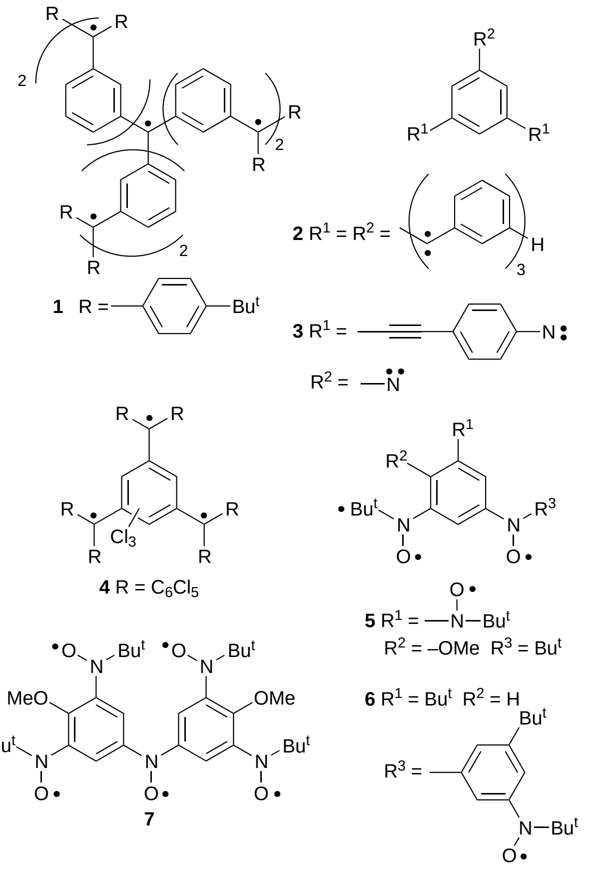
A stable pentaradical, *N*,*N*-bis{4-methoxy-3,5-bis(*N*-*tert*-butyl-*N*-oxyamino)phenyl)}aminoxyl, is prepared and its ground state determined to be a sextet ($S = 5/2$) by SQUID magnetization measurements of the pentaradical diluted in poly(vinyl chloride) matrix.

Poly(triarylmethyl) radical **1** ($S = 7/2$),[1] nonacarbene **2** ($S = 9$),[2] and trinitrene **3** ($S = 3$)[3] are some of the highest-spin organic molecules rivalling high-spin $3d^5$ Mn^{II}, Fe^{III} and $4f^7$ Gd^{III} ions. However, these organic open-shell species are kinetically unstable and can be kept only in solid solution at cryogenic temperature under exclusion of air. Stable counterparts that can be bottled in the neat state under air are limited to perchlorinated triradical **4** ($S = 3/2$).[4] Knowing that the methoxy group, while weakening the ferromagnetic coupling, increases the kinetic stability of **5**,[5] and that **6**[6] is a reasonably stable quartet, we designed pentakis(aminoxyl) radical **7** as a stable, high-spin, and high-spin-density pentaradical.



Pentaradical **7** was prepared in a manner similar to the procedure[6] for triradical **6** by using bis(hydroxyamino) derivatives protected with *tert*-butyldimethylsilyl groups in place of protected monohydroxylamines. A solution of 1-bromo-4-methoxy-3,5-bis[*N*-*tert*-butyl-*N*-(*tert*-butyldimethylsiloxy)-amino]benzene in THF was lithiated with *n*-butyllithium and coupled with 0.5 mol equiv. of pentyl nitrite to give monoradical **7a**† (7.7%) whose EPR spectrum ($\nu_0 = 9.509$ GHz) in benzene showed a hyperfine structure consisting of a triplet of quintets ($a_N = 10$ G, $a_H = 1.85$ G). Monoradical *N*,*N*-bis[4-methoxy-3,5-bis(*N*-*tert*-butyl{*N*-*tert*-butyldimethylsiloxy}-amino)phenyl]aminoxyl **7a** was deprotected in the presence of $NBu^n{}_4F$ followed by oxidation with silver oxide in ether and purification by column chromatography (silica gel/*n*-hexane–diethyl ether). Recrystallization from ether gave indefinitely stable pentaradical **7** as red needles.‡ It is somewhat unstable in dilute benzene and THF solution; a decrease of the EPR signal intensity by 5% was observed after 24 h under ambient conditions. Pentaradical **7** crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with four molecules in the unit cell. An ORTEP drawing and stick model for the molecular and crystal structure of **7** are shown in Fig. 1(*a*) and (*b*), respectively.‡

The crystal was found to contain 0.5 of a molecule of diethyl ether per molecule of **7** and it is situated near the radical unit S_{A1}. The molecular structure of **7** has no symmetry axis and two sets of aminoxyl radicals S_A and S_B have *syn* and *anti*§ conformations, respectively, with respect to the benzene ring. The dihedral angles of the central *N*,*N*-diarylaminoxyl radical S_C with the two aryl rings are 23.7 and 32.9° and those of S_A and two S_B with the benzene rings are relatively large [60–76°; Fig. 1(*a*)]. The average distances among the three aminoxyl radical moieties within a molecule are in the range 4.96–5.74 Å to construct a two-triangular five-spin system. As indicated in Fig. 1(*b*), there are two intermolecular short distances i and ii between the radical centers which should be responsible for the appearance of a strong intermolecular antiferromagnetic interaction at low temperature;[8] two molecules make a head-to-tail dimer structure with a separation of 3.35 Å and the resulting dimers align at a distance of 3.69 Å to form a chain structure along the *b* axis.

The X-band EPR spectrum of pentaradical **7** in toluene solution at room temp. showed one broad signal with $\Delta H_{PP} = 20$ G at $g = 2.0064$. In the corresponding spectrum ($\nu_0 = 9.410$ GHz) of **7** in frozen solution at 6.5 K, five signals (318.8, 327.2, 335.3, 343.4, and 351.8 mT) were observed in addition to the signal ($g = 4.019$) due to a $\Delta m_S = 2$ transition. The spectrum was simulated as a sextet with $S = 5/2$ to afford $g = 2.0062$ and zero-field splitting parameters $|D/hc| = 0.0039$ and $|E/hc| = 0.0013$ cm^{-1}.¶ As the temperature was increased from 12 to 100 K, the intensity of the signal at $g = 2$ decreased in accordance with the Curie law, suggesting that the sextet was a ground state.

The magnetic susceptibility of a crystalline sample of pentaradical **7** was measured on a SQUID magnetometer/susceptometer in the temperature range 2–350 K at a constant field of 200 mT. The $\chi_{mol}T$ value at 350 K is 2.09 emu K mol^{-1}

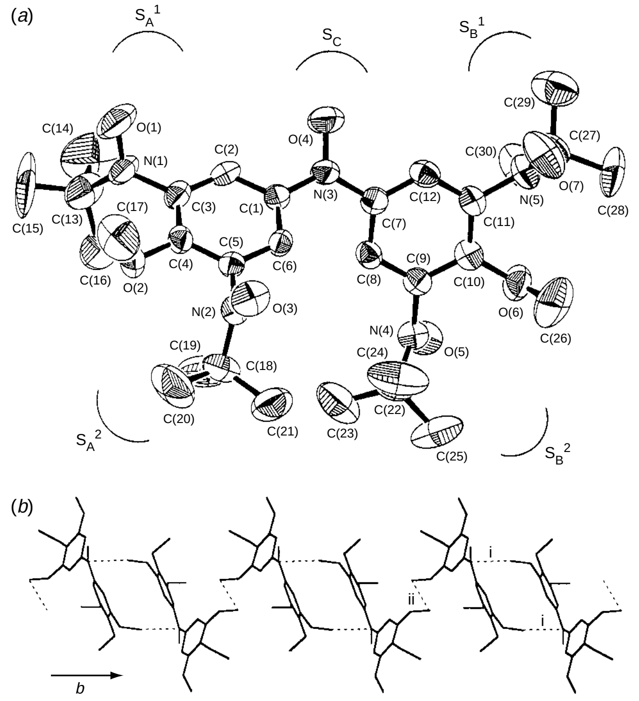


Fig. 1 Molecular and crystal structure of pentaradical **7**: (*a*) ORTEP drawing with thermal ellipsoid plot at the 30% probability level. The diethyl ether molecule of crystallization is omitted for clarity; torsion angles between the benzene ring and the radical N–O bond are 75.8°, −62.9, −63.1 and 60.3° for $S_A{}^1$[O(1)N(1)C(3)C(2)], $S_A{}^2$[O(3)N(2)C(5)C(6)], $S_B{}^1$[O(7)N(5)C(11)C(12)] and $S_B{}^2$[O(5)N(4)C(9)C(10)], respectively. The average distances between the two nitrogens and two oxygens are 5.53, 5.56 and 4.96 Å for $r(S_{A1}S_{A2})$, $r(S_{A1}S_C)$ and $r(S_{A2}S_C)$ and 5.57, 5.74 and 5.04 Å for $r(S_{B1}S_{B2})$, $r(S_{B1}S_C)$ and $r(S_{B2}S_C)$, respectively, and (*b*) a stick model of crystal structure; Bu^t groups are omitted for clarity. Broken lines indicate short contacts (Å) between the atoms of the radical centers; (i) 3.35 and (ii) 3.60.

which is slightly greater than 1.88 emu K mol^{-1} calculated as a spin only value for five isolated radical centers. As the temperature was decreased from 350 K, $\chi_{\text{mol}}T$ values increased gradually and reached a maximum of 2.22 emu K mol^{-1} at 120 K and then decreased sharply. The maximum value is considerably smaller than theoretical 4.38 emu K mol^{-1} for $S = 5/2$ and suggests that intermolecular antiferromagnetic interaction takes place predominantly below 120 K, as expected from the X-ray crystal structure of **7**.

In order to exclude the contribution of the intermolecular antiferromagnetic interaction at low temperature, a sample of **7** doped in poly(vinyl chloride) (PVC) matrix was prepared and employed for a SQUID measurement. The field dependence of a PVC film‖ containing 2% **7** was investigated at 2, 4, and 6 K and the M/M_S *vs.* H/T plot is shown in Fig. 2 together with a theoretical curve obtained on the basis of the Brillouin function** for $S = 5/2$. The theoretical curve fitted the experimental data reasonably well indicating that the five aminoxyl radicals interact ferromagnetically to produce a sextet state.

In summary, stable pentaradical **7** was successfully prepared and its molecular structure was revealed by X-ray structure analysis. Its magnetic properties revealed that ferromagnetic interactions occur predominantly among the five spins within a molecule to produce a sextet ground state. However, the exchange coupling parameters (J) among them could not be estimated quantitatively from a $\chi_{\text{mol}}T$–T plot since the intermolecular antiferromagnetic interaction among the pentaradical molecules at low temperature caused by short intermolecular contacts between radical centers in the crystalline state was very strong.

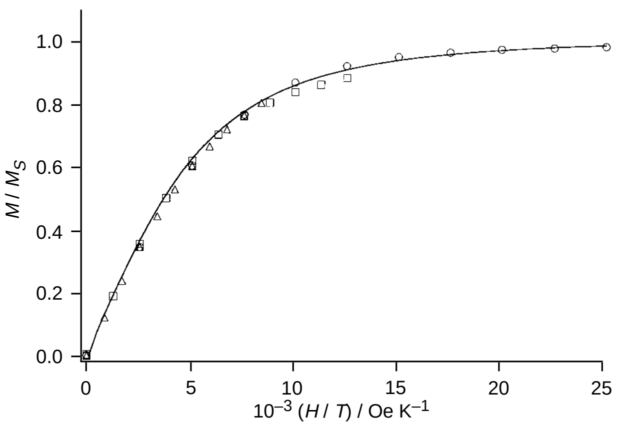


Fig. 2 Field dependence of the magnetization at 2 (○), 4 (□), and 6 K (△) as expressed by M/M_S *vs.* H/T plots for pentaradical **7**. The solid curves are theoretical ones for $S = 5/2$ as described in text.

Footnotes and References

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† **7a**: mp (decomp.) 85–87 °C, FABMS (*m*-nitrobenzyl alcohol matrix) *m*/*z* 1049 (M$^+$ + 1), Anal. Calc. for $C_{54}H_{106}N_5O_7Si_4$: C, 61.71; H, 10.18; N, 6.67. Found: C, 62.08; H, 10.17; M, 6.37%.

‡ **7**: mp (decomp.) 139–141 °C, FABMS (*m*-nitrobenzyl alcohol matrix) *m*/*z* 592 (M$^+$ + 3), 591 (M$^+$ + 2), Anal. Calc. for $C_{30}H_{46}N_5O_7 \cdot 0.5C_4H_{10}$.O: C, 61.41; H, 8.19; N, 11.18. Found: C, 61.42; H, 8.21; N, 11.19%. *Crystal data* for **7**: $C_{30}H_{46}N_5O_70.5C_4H_{10}O$, $M = 625.78$, monoclinic, space group $P2_1/n$ (no. 14), $a = 16.101(2)$, $b = 12.537(4)$, $c = 19.232(2)$ Å, $\beta = 113.687(8)°$, $U = 3555(1)$ Å^3, $T = 296$ K, $Z = 4$, $D_c = 1.169$ g cm^{-3}, μ(Cu-Kα) = 6.83 cm^{-1}, 5729 total (5516 independent) reflections, $R = 0.072$ and $R_{ws} = 0.071$ for 404 reflections with $I > 3\sigma(I)$. Direct methods and refinement converged using the full-matrix least squares method of the TEXAN Ver. 1.6 program (Molecular Structure Corperation). CCDC 182/633.

§ The *anti* conformation is the first example in this series of methoxy substituted phenyl aminoxyl diradicals.[7]

¶ The simulation for the EPR fine structure was performed by using a program based on the second-order perturbation theory and provided by Professors K. Ito and K. Takui of Osaka City University.

‖ PVC films containing 1% of **7** were also prepared and similar M/M_S *vs.* H/T plots were obtained.

** $M = Ngj\mu_B B_J(x)$, where $B_J(x) = [(2J+1)/2J] \coth [(2J+1)/2J]x - 1/2J \coth (1/2J)x$ and $x = gJ\mu_B H/k_B T$.

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