Experimental Section

$[Co_2(CO)_8]$ (2.5 g, Strem Chemicals, Inc.) was dissolved in dry toluene (30 mL) under air-free conditions, filtered, and then loaded into a syringe. Trioctylphosphane oxide (TOPO, 5 g, Strem Chemicals, Inc.) was placed in a 100 mL flask and dried under vacuum at 150 °C. The temperature was then brought down to 50 °C, and the solution of $[Co_2(CO)_8]$ was quickly injected into the flask while vigorously stirring under a nitrogen atmosphere. The temperature was slowly increased to 110 °C. This was accompanied by evolution of carbon monoxide and by a color change of the reaction mixture from deep blue to black. After completion of the reaction the heating mantle was removed, and the mixture was allowed to cool to room temperature. The product of the reaction was isolated as a black powder and was thoroughly washed with hexane and methanol and dried under nitrogen.

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Keywords: clusters · cobalt · structure elucidation · X-ray scattering

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A Triphenylamine Derivative with Three *p*-(*N*-*tert*-Butyl-*N*-oxylamino)phenyl Radical Units and Yet a Doublet Ground State[**]

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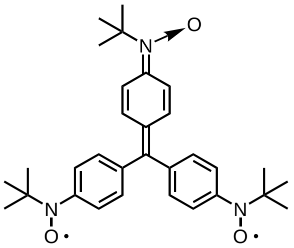
Intramolecular ferromagnetic interactions of electron spins in polyradicals are of current interest in the design of molecular ferromagnets.[1] Previously, we reported that the oxidation of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]methane with silver(I) oxide gave the quinonoid diradical **1**, which has a robust triplet ground state.[2] When the methane carbon atom in **1** is replaced with a nitrogen atom to make tris[*p*-(*N*-*tert*-butyl-*N*-oxylamino)phenyl]amine (**2**), a quinonoid structurerequires a zwitterionic structure. Hückel MO calculations show that tris(*p*-methylenephenylene)methane, a simplified model of **1**, has two degenerate SOMOs similar to those of trimethylenemethane (TMM).[3] Since the corresponding amine has one more π electron than the methane, the former is expected to become isoelectronic with the anion radical of the latter and therefore exist as a doublet monoradical. We report here the synthesis, structure, and magnetic properties of **2**.



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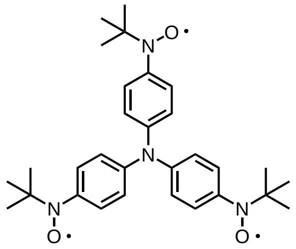

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Triradical **2** was obtained by oxidation of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine with Ag_2O. A single crystal for an X-ray diffraction measurement was obtained by slow evaporation of a solution of **2** in *n*-heptane/dichloromethane.[4] The molecule has no threefold axis passing through the central nitrogen atom (Figure 1). The *p*-phenylene rings are tilted by 29.8°, 34.3°, and 57.3° from the plane formed by C1, C11, and C21. The intramolecular distances between the oxygen atoms of the oxylamino groups are 9.73

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

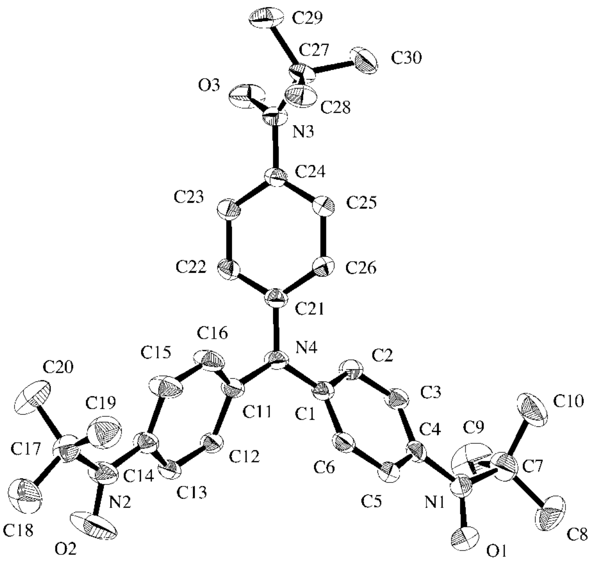


Figure 1. ORTEP drawing of **2** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N4–C1 1.412(4), N4–C11 1.421(4), N4–C21 1.428(4), N1–O1 1.291(3), N2–O2 1.285(4) N3–O3 1.294(3), N1–C4 1.417(4), N2–C14 1.414(4), N3–C24 1.413(4); C1-N4-C11 122.1(2), C1-N4-C21 118.9(2), C11-N4-C21 118.7(2), O1-N1-C4 116.9(2), O2-N2-C14 116.9(3), O3-N3-C24 116.6(2).

(O1–O2), 11.30 (O2–O3), and 11.41 Å (O3–O1), whereas the shortest intermolecular distance between O1 and O2′ of neighboring molecules is 4.84 Å.[4, 5]

The X-band ESR spectra of **2** in degassed 2-methyltetrahydrofuran (MTHF) were measured in the temperature range 8.5–300 K. At 300 K the ESR spectrum centered at $g = 2.006$ consisted of a septet in a ratio of 1:3:6:7:6:3:1 ($|a_N| = 4.06$ G) due to hyperfine coupling with the three equivalent nitrogen nuclei (Figure 2). This suggests that the exchange interaction is much larger than the hyperfine interaction ($|J| \gg |a_N|$).

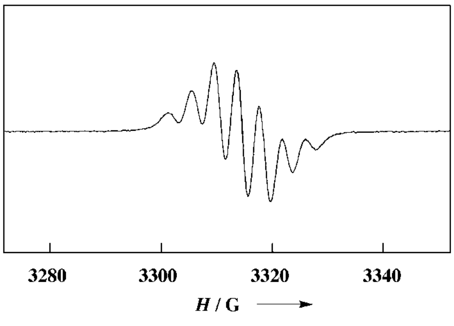


Figure 2. X-band ESR spectrum of **2** (10 mM in MTHF) at 300 K (9.327 GHz).

In a frozen solution **2** showed a large main peak with a very weak outer shoulder in the $g = 2$ region, but no signal arising from the $\Delta m_s = 2$ or 3 transitions. The intensity of the main peak decreased as the temperature was increased in the range 8.5–100 K, which is in good agreement with Curie's law. This result is not inconsistent with a quartet ground state of **2**. However, it is not possible to determine rigorously whether the ground state is quartet, doublet, or degenerate quartet/doublet.

Figure 3 shows the temperature dependence of the molar paramagnetic susceptibility (χ_{mol}) of **2** at 500 G as a plot of $\chi_{mol}T$ versus T. The observed $\chi_{mol}T$ values remained almost constant from 100 down to 20 K and are in good agreement with the theoretical value (0.375 emu K mol^{-1}) expected for an assembly of single isolated spins. As the temperature was decreased below 20 K, the $\chi_{mol}T$ values increased continuously to a value of 0.58 emu K mol^{-1} at 2 K.

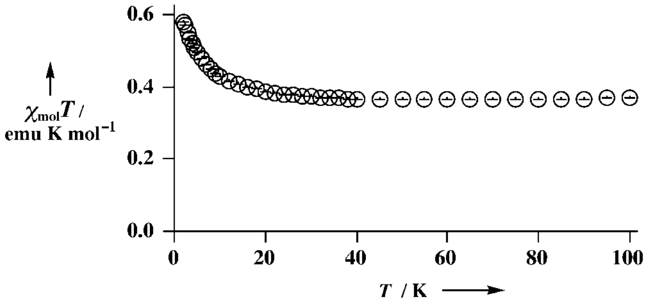
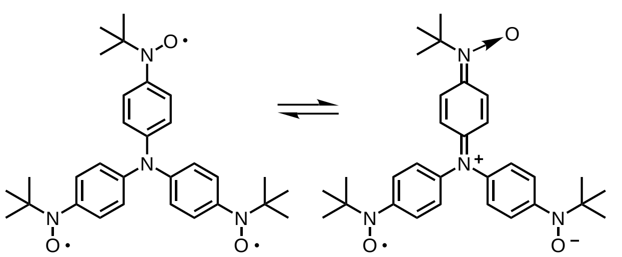


Figure 3. Plot of $\chi_{mol}T$ versus T for **2** at 500 G.

Further proof of the ground-state spin multiplicity of **2** was furnished by similar magnetic susceptibility measurements on dilute samples (5%) of **2** in poly(vinyl chloride), in which possible intermolecular coupling would be considerably diminished. Under these conditions, the continuous increase in the $\chi_{mol}T$ values below 20 K was absent, which suggests that there is no intramolecular magnetic interaction populating the quartet state at the cryogenic temperature and that the ground state must be a doublet state.[6] The doublet–quartet energy gap is estimated to be greater than 100 K (>0.2 kcal mol^{-1}).

Ab initio MO calculations at the B3LYP/6-31G level were performed on models in which all three *N-tert*-butyl groups in **2** were replaced with methyl groups and the structures were optimized. The doublet was found to be more stable than the quartet by 0.84 kcal mol^{-1}. Whereas the central amine nitrogen atom does not carry high net spin density in either state (Mulliken spin density of 0.0093 and 0.0314 for the doublet and quartet respectively), it has high α and β spin densities in the 100th magnetic orbital and the 99th doubly occupied MO, respectively, in the doublet ground state. This demonstrates the operation of a superexchange mechanism through the lone pair of electrons on the central nitrogen atom, with two spins on the oxylamino radical centers coupled antiferromagnetically and one spin remaining intact. A superexchange mechanism has been invoked in organic dicarbenes,[7] but there are none in which the interaction has been demonstrated to be as strong as in **2**. Any contribution of a quinonoid structure for **2** to the equilibrium illustrated in Scheme 1 is thus estimated to be very small.[8]

In conclusion, the doublet ground state of the triphenyl amine **2** carrying three *N-tert*-butyl-*N*-oxylamino groups in the *para* positions indicates that not only the topology but also the number of the π electrons is important in defining ferromagnetic couplers for molecular-based magnets.[1]



Scheme 1. Equilibrium of the triradical and zwiterionic structures of **2**.

Experimental Section

Tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine: To a solution of tris(*p*-bromophenyl)amine (2.0 g, 4.15 mmol) in THF (40 mL) was added *tert*-butyllithium (1.6 M pentane solution, 18.2 mL) at −78 °C. The mixture was warmed to 0 °C over 10 min and then cooled again to −78 °C. 2,2-Dimethylnitrosoethane (1.45 g, 16.6 mmol) was added, and the mixture was warmed to room temperature and stirred for 1 h. Saturated aqueous ammonium chloride and ether were added, and the organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was washed with dichloromethane to afford tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine (0.77 g, 37 %) as a white powder. M.p. 153 °C (decomp.); ^1H NMR (270 MHz, [D$_6$]DMSO): $\delta = 8.20$ (s, 3 H), 7.92 (d, $J = 8.57$ Hz, 6 H), 6.84 (d, $J = 8.57$ Hz, 6 H), 1.06 (s, 27 H); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): $\delta = 145.34$, 143.74, 125.29, 122.23, 59.19, 25.99; FAB MS calcd for $C_{30}H_{42}N_4O_3$: 506.3257, found: 506.3256.

2: To a solution of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine (100 mg, 0.20 mmol) in dichloromethane (30 mL) was added an excess of freshly prepared Ag_2O (ca. 300 mg), and the mixture was stirred for 2 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure at ambient temperature. The residue was subjected to chromatography on aluminum oxide with dichloromethane as eluent and recrystallized from *n*-heptane/dichloromethane (2/1) to give **2** as dark violet crystals (86 mg, 87 %). M.p. 190–192 °C; FAB MS: *m*/*z* 503 [M^+]; elemental analysis calcd for $C_{30}H_{39}N_4O_3$: C 71.54, H 7.80 N 11.12; found: C 71.44, H 7.79, N 11.08.

Magnetic measurement: Fine crystalline or polymer film samples were mounted in a capsule (Japan Pharmacopoeia NO. 5, ∅4.5 × 11 mm) and measured on a Quantum Design MPMS-5S SQUID susceptometer at 500 G. Corrections for the diamagnetic contribution were made with Pascal's constants.

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[4] Crystallographic data for **2**: $C_{30}H_{39}N_4O_3$, $M_r = 503.66$, monoclinic, space group *Cc*, $a = 13.11(1)$, $b = 23.081(5)$, $c = 10.410(2)$ Å, $\beta = 116.80(5)^\circ$, $V = 2810(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.190\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.77\,cm^{-1}$. Data were collected on a Rigaku RAXIS-IV imaging plate area detector at −100 °C with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71071$ Å). The structure was solved with direct methods and refined to $R = 0.039$, $R_W = 0.054$ for 2461 observed reflections ($I > 3.00\sigma(I)$) and 335 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101263. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] Symmetry operation: $x, -y, 1/2 + z$.

[6] The origin of the ferromagnetic interaction between the neighboring molelucles in crystals may be located at O1−C12′ and O3−C25′ (3.272(4) and 3.131(3) Å, respectively) along the chain made by the molecules aligned in the direction of the *c* axis.

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[8] Triradical **2** exhibits a characteristic broad band between 450–800 nm ($\lambda_{max} = 534$ nm, $\varepsilon = 5500\,M^{-1}cm^{-1}$), but its absorption coefficient is relatively weak compared with that of quinonoid system **1** ($\lambda_{max} = 554$ nm, $\varepsilon = 20400\,M^{-1}cm^{-1}$).[2] The X-ray crystal structure shows that the *p*-phenylene rings have a slight tendency to assume a quinonoid structure, and there are signs of shortened bond lengths in the bonds connecting a aminoxyl nitrogen atoms with the benzene rings (1.43–1.45 Å is typical of phenylaminoxyl groups).[9, 10] However, compared with the carbon analogue **1**, where two *p*-phenylene rings exhibit quinonoidal bond alternations of 0.05 Å, any bond alternation is less than 0.02 Å in **2**. The dihedral angles between the benzene rings and the central trigonal nitrogen plane are somewhat larger for a quinonoid structure.

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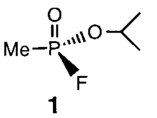
Monitoring Chemical Warfare Agents: A New Method for the Detection of Methylphosphonic Acid**

Jon A. Ashley, Chao-Hsiung Lin, Peter Wirsching,* and Kim D. Janda*

Issues surrounding chemical warfare agents are currently of great importance with regard to national security and world affairs. The lethal compounds **1** (sarin), **2** (soman), and **3** (VX)



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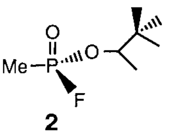

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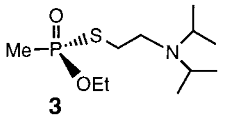

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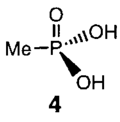

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