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Macrocyclic High-Spin ($S = 2$) Molecule: Spin Identification of a Sterically Rigid Metacyclophane-Based Nitroxide Tetraradical by Two-Dimensional Electron Spin Transient Nutation Spectroscopy**

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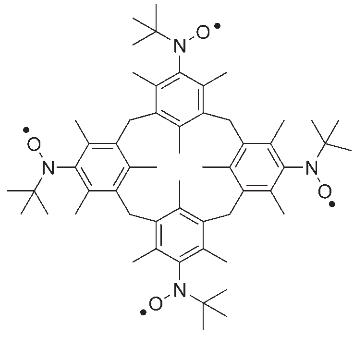
Macrocyclic molecules, such as cyclophanes and calixarenes, have attracted much interest because of their ability to include various guests and the possibility of forming supramolecular assemblies.[1] Calixarenes functionalized by nitroxide radicals, which are widely used as stable spin sources, have been documented,[2–5] revealing their peculiar properties; especially, remarkable changes in continuous-wave (cw)-ESR spectra with and without guests were observed.[3] Calixarene-based high-spin entities, nevertheless, have rarely been well-characterized, particularly in terms of their electronic-spin properties versus their molecular structure. The design and syntheses of well-characterized macrocyclic high-spin systems are an important issue not only for exotic molecular magnetic materials formed by supramolecular assembly,[4] but also for magnetic chemical sensors with multi-sensing sites. The difficulty in studying macrocyclic high-spin systems results from the lack of well-established experimental methods which allow the apparently small exchange or spin–spin interactions to be characterized in supramolecular species which have sizable inclusion pockets. In addition, synthetic macrocyclic systems are frequently contaminated by lower spin species having similar molecular frames. Rajca et al. reported pioneering work on a calix[4]-arene derivative having four nitroxide radicals in the upper (wider) rim of the calixarene skeleton.[5] The X-ray crystal structure of that calixarene derivative revealed that the two diagonally arranged radical sites formed an intramolecular dimeric structure undergoing a strong antiferromagnetic interaction. The spin state of the derivative was only characterized from magnetic susceptibility measurements, which did not give clear and straightforward evidence for the molecular-structure-related microscopic magnetic properties of calixarene-based exchange-coupled systems.

Herein, we show for the first time that nitroxide tetraradical **1** (Scheme 1) with four nitroxide radical sites in the upper rim of the calixarene skeleton is in a quintet state. We have exploited the sterically rigid molecular structure of the macrocyclic skeleton to control intramolecular through-space exchange interactions.[6] Molecule **1** has a unique structure with three methyl substituents in each benzene ring (mesityl groups), giving rise to steric rigidity, and suppressing the flexibility of the skeleton. To unequivocally identify the spin multiplicity of **1** and possibly occurring lower-spin chemical species in an organic glass, 2-dimensional pulse-based electron spin transient nutation (2D-ESTN) spectroscopy developed in our group has been applied. The 2D-ESTN technique gives straightforward information on the spin multiplicity which cannot be derived in terms of cw-ESR spectroscopy.[7]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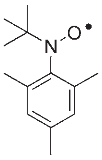
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Scheme 1. Molecular structures of nitroxide radicals, **1** and **2**.

We have prepared both tetraradical **1** and mesityl nitroxide **2** (Scheme 1), which corresponds to a monoradical component of **1**. Compound **2** is used to check any subtle effect of the calixarene structure on the spin structure. Figure 1 shows the X-ray crystal structure of **1**.[8] The structure has a sterically hindered 1,3-alternate conformation giving pseudo-tetrahedral symmetry. The structurally robust macrocyclic structure consists of the metacyclophane derivatives with three methyl groups at the 2-,4-, and 6-positions in each

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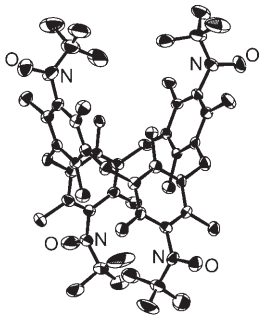

Figure 1. ORTEP representation of **1** with thermal ellipsoids set at 50% probability. Solvents and hydrogen atoms are omitted for clarify.

benzene ring, as reported by C. Klein et al.[9,10] The NO groups of **1** point away from the cavity due to the *ortho*-methyl substituents. The four dihedral angles between the benzene ring and the C-N-O plane of the $(CH_3)_3CNO$ unit are 73.51, 87.39, 68.52, and 89.73°, respectively. The distance between the oxygen atoms in the nitroxide radical moieties ranges from 10.38 to 11.43 Å. Thus, in this macrocyclic system, unwanted robust through-space exchange interactions are reasonably suppressed.

Rigid-glass cw-ESR spectra of **1** in the $\Delta M_S = \pm 1$ and ± 2 regions are shown in Figure 2. The signal of $\Delta M_S = \pm 2$ is very weak, and the forbidden transitions of neither $\Delta M_S = \pm 3$ nor ± 4 were observed, indicating that these transition probabilities are extremely small as a result of a small *D*-value of the high-spin states from **1**. The probabilities of the forbidden transitions were confirmed by the hybrid eigenfield method. The ESR spectra were simulated with the help of experimental results of the 2D-ESTN measurements described below.

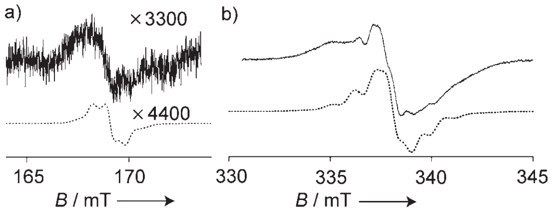

Figure 2. cw-ESR spectra of **1** observed at liquid helium temperatures (upper traces). a) Forbidden transitions of $\Delta M_s = \pm 2$ ($T = 2.7$ K, $\nu_{MW} = 9.49407$ GHz). b) Allowed transitions of $\Delta M_s = \pm 1$ ($T = 3.4$ K, $\nu_{MW} = 9.49409$ GHz). The lower traces show simulated spectra generated by the superposition of both the spectrum arising from the quintet and the one from the quartet species.

To identify the spin multiplicity of **1** in a straightforward manner, two-dimensional field-swept 2D-ESTN spectroscopy was applied to the rigid-glass sample (Figure 3). An echo-detected field-swept fine-structure spectrum is given on the right hand side in Figure 3. From the 2D-ESTN spectra, five nutation frequency components, 16.9, 22.8, 26.8, 32.0, and 39.8 MHz are discriminated. They are denoted by a, b, c, d, and e, respectively, as given in Figure 3. The relative ratios of the observed frequency components are 1:1.35:1.59:1.89:2.36, being consistent with ω_1:$\sqrt{2}\omega_1$:$\sqrt{3}\omega_1$:$2\omega_1$:$\sqrt{6}\omega_1$, as the corresponding theoretical values according to the Equation (S1) given in Supporting Information. The theoretical frequencies $2\omega_1$ and $\sqrt{6}\omega_1$ correspond to the allowed transitions for the quintet high-spin state. The signals of the other frequencies with $\sqrt{3}\omega_1$, $\sqrt{2}\omega_1$, and ω_1 show that partially nitroxide-deficient radicals, that is, tri, di, and mono radicals, were identified as minorities in the sample (Table S1 in the Supporting Information). In Figure 2, the cw-ESR spectrum is compared with a simulated spectrum. Based on the spectral transition assignments from the 2D-nutation spectra, it is confirmed that more than three open-shell species contribute to the experimentally observed spectrum. As shown in the Supporting Information, Figure S4, the cw-ESR spectrum is well explained by the superposition of both $S = 2$ and $S = 3/2$ species whose transitions were dominantly observed in the ESTN spectra (Supporting Information, Figure S3). The results of the 2D-ESTN spectroscopy consistently demonstrate that the mono and di radicals are minor species. It should be noticed that the nutation signals arising from the quintet state are observed at 3.8 K, showing the quintet state is in the ground state or nearly degenerate with singlet ground states. Other thermally accessible intermediate spin states ($S = 1$) from **1** were not detected up to 20 K.[12]

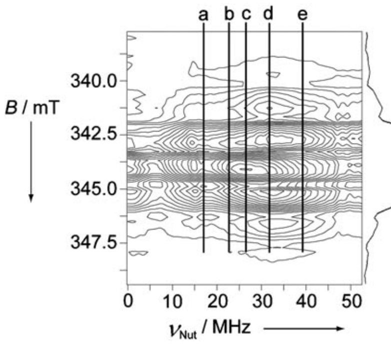

Figure 3. Contour plot of the field-swept 2D nutation spectra of **1** ($T = 3.8$ K, $\nu_{MW} = 9.65684$ GHz); see text for details.

The fine-structure parameters and *g*-values for the quintet species ($S = 2$) derived from the spectral simulation method are: $|D| = 0.0014\ \text{cm}^{-1}$, $|E| = 0.00017\ \text{cm}^{-1}$, $g_{xx} = 2.0062$, $g_{yy} = 2.0062$, and $g_{zz} = 2.0056$. To consider the molecular structure of **1** in the rigid glass, *D*-value calculations using the point dipole–dipole approximation were performed based on a four-spin cluster model.[11] There are other possible orientations of the NO moieties in the rigid glass in addition to those in the crystal structure of **1**. Considering distortion from the macrocyclic skeleton of the crystal structure of **1**, the most reasonable and probable fine-structure parameters have been calculated to be $D = -0.00140\ \text{cm}^{-1}$ and $|E| = 0.00014\ \text{cm}^{-1}$. The corresponding structure is as follows; the three NO sites are inside the cavity and the remaining one outside as shown in the Supporting Information, Figure S5. The structure obtained for tetraradical **1** in the rigid glass is different from the one determined by the X-ray analysis, as given in Figure 1. Another dominant species identified is the triradical molecule. The fine-structure parameters of triradical were determined by the spectral simulation method:[13]

$|D| = 0.00155\ \text{cm}^{-1}$ and $|E| < 0.0001\ \text{cm}^{-1}$. Those parameters for triradical were also reasonably reproduced by the spin-cluster model based on the molecular structure with one NO-spin-deficient site, such as NOH. The D-value calculations of tetraradical **1** and the single NO-site deficient triradical are given in the Supporting Information, Table S2–4. It is indicated that tetraradical **1** has somewhat flexible structure even in the sterically hindered macrocyclic skeleton in the glass.

In conclusion, we have characterized the electronic-spin and molecular structure of tetraradical **1** which has a sterically-controlled molecular structure by using cw- and pulsed-ESR spectroscopy. 2D-ESTN spectroscopy has been applied to identify the spin multiplicity of **1** in a straightforward manner, illustrating its spectroscopic usefulness for open-shell entities featuring small fine-structure parameters arising from small spin-dipolar interactions of multicentered high spins, such as polyradicals. It was indicated that the steric hindrance introduced by mesityl groups yields a relatively rigid macrocyclic molecule with four nitroxide radicals, generating the high-spin quintet state. The systems based on flexible macrocycles, in which the sterically controlled conformation is relevant to inclusion phenomena, are easily tunable, in which the exchange interaction is modulated by external stimuli, such as ligation or ionic capture.[12] The high-spin states of macrocyclic compounds, combined with their inclusion properties, allow the exploration of spin-sensing multifunctional materials.

Experimental Section

Experimental procedure: Detailed information on the syntheses, ESR/2D-ESTN measurements, **D**-tensor calculations, and DFT calculation, are given in Supporting Information.

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Keywords: electron spin transient nutation · EPR spectroscopy · high-spin systems · macrocycles · radicals

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[8] X-ray crystal structure analysis of **1**: An orange-red block ($0.5 \times 0.1 \times 0.15$ mm) of **1** for the X-ray crystal structure analysis was prepared by slow evaporation of a diethyl ether solution of **1**. Diffraction data were obtained with $2\theta_{\text{max}} = 55.0°$ at 24°C. $C_{56}H_{80}N_4O_4{\cdot}C_4H_{10}O$, $M_r = 947.38$, Triclinic, space group $P\bar{1}$, $a = 12.22(1)$, $b = 15.62(1)$, $c = 15.76(1)$ Å, $\alpha = 62.68(3)$, $\beta = 84.65(4)$, $\gamma = 83.16(4)°$, $V = 2651(4)$ Å^3 and $\rho_{\text{calcd}} = 1.144\ \text{g cm}^{-3}$ for $Z = 2$. Anisotropic temperature factors were applied for non-hydrogen atoms. Hydrogen atoms with isotropic thermal parameters were refined as riding models. Refinement converged at $R = 0.107$ and $R_w = 0.159$ for 5032 observed reflections, with $I > 3\sigma(I)$ and 690 variables. CCDC 669668 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] The location and fine-structure parameters of the thermally accessible triplet states from tetraradical **1** were theoretically calculated, and are in agreement with the experimental result.

[13] It is noted that minor contributions from quartet species with slightly different fine-structure parameters to the observed spectrum are not included in the present spectral simulation.