Pulsed EPR Studies of Ion Binding in a Double-Faced Paramagnetic Ionophore: Tris(2,6-di(methoxyethoxy)phenyl)methyl Radical

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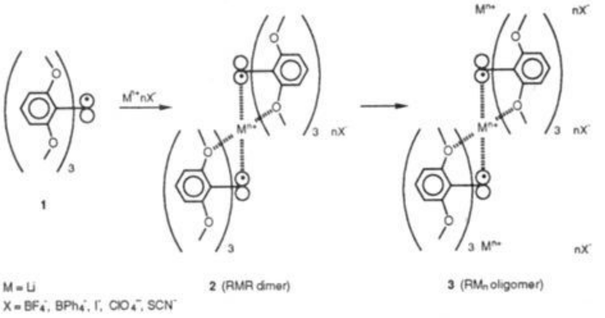
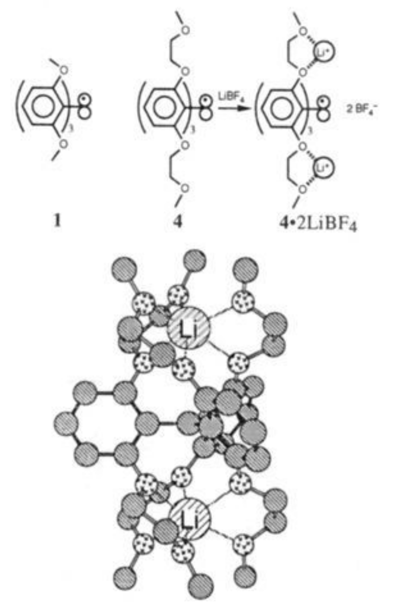
In a recent report[1] we described our initial efforts to assemble magnetic materials based on the tris(2,6-dimethoxyphenyl)methyl radical **1**, first studied by Martin *et al.*[2] Our approach involves ion complexation in the dual ether tripods presented by these hexamethoxytriaryl-Z systems. Magnetic coupling between radical centers is to be mediated by the bound metal cation (e.g., Li^+, Na^+), as shown in Scheme I. X-ray analyses of several tripod ether binding sites have been presented elsewhere.[3]

Scheme I



In this work, the electron spin echo envelope modulation (ESEEM) technique of pulsed EPR spectroscopy has been used to measure weak electron–nuclear hyperfine couplings between the radical centers and coordinated metal cations in **4**, a double octopus[4] analogue of **1**. The ESEEM method provides structural details regarding radical–metal ion distance, the number of metal ions held near a given radical center, and an estimate of the unpaired electron spin density transferred to the metal. Together with magnetic susceptibility data and studies on structurally related diamagnetic systems, these results inform and guide our attempts at rational synthesis of new organic magnetic materials.

Scheme II. (Top) Complexation of $LiBF_4$ by **4** and (Bottom) MNDO Calculated Structure of **4**·$2Li^+$



Radical **4** is constructed by straightforward modification of Martin's original procedures.[5,6] CW-EPR spectra collected for **4** at −70 °C show a 13-line pattern with the splitting between consecutive lines being 1.0 G. This intensity pattern is consistent with the higher resolution results reported for **1** by Sabacky *et al.*[2,7] where 1.06-G coupling to six equivalent meta protons and 2.26-G coupling to three equivalent para protons on the three aryl groups were found. Thus, we believe the aryl ring twists in **4** are essentially similar to those in **1**, which were estimated to be 45–50° rotated out of the coordination plane of the central carbon atom.

Our purpose in synthesizing **4** was to build an analogue of **1** in which chain formation of the type shown in **2** would be blocked. Radical **4** provides a bound M^+ ion with a full coordination sphere of six ether oxygens, effectively "capping" the radical on both faces as shown in Scheme II. Thus, the radical center in **4**·$2M^+X^-$ is encapsulated and should behave as a completely isolated paramagnet. We have verified this expectation by magnetic susceptibility studies of powders of the $LiBF_4$ complex.[8] As expected for an isolated radical, a Curie plot ($1/\chi$ vs T) for **4**·$2LiBF_4$ shows near ideal paramagnetic behavior with μ_{eff} of 1.56 μ_B. The linear fit ($R = 0.997$) to this plot has an intercept (the Weiss constant, Θ) of $\Theta = -3$ K, indicating simple paramagnetism or very weak antiferromagnetic coupling. We attribute the slightly low μ_{eff} value to uncertainty in the exact **4**:$LiBF_4$ ratio and to a small amount of radical oxidation during

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(2) (a) Sabacky, M. J.; Johnson, C. S., Jr.; Smith, R. G.; Gutowsky, H. S.; Martin, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2054. (b) Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 2252.

(3) Kahr, B.; Jackson, J. E.; Ward, D. L.; Jang, S.-H.; Blount, J. F. *Acta Crystallogr.* **1992**, *B48*, 324.

(4) (a) Vögtle, R.; Weber, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 753. (b) Vögtle, F. *Chimia* **1979**, *33*, 239. (c) Tümmler, B.; Maass, G.; Vögtle, F.; Sieger, H.; Heimann, U.; Weber, E. *J. Am. Chem. Soc.* **1979**, *101*, 2588.

(5) Synthesis of **4**: 1,3-bis(2-methoxyethoxy)benzene was prepared by the reaction of resorcinol and 2-chloroethyl methyl ether with K_2CO_3 in refluxing acetone (^1H NMR ($CDCl_3$, 300.1 MHz) δ 3.42 (s, 6H), 3.72 (m, 4H), 4.07 (m, 4H), 6.51 (m, 3H), 7.13 (t, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 58.75, 66.74, 70.54, 101.24, 106.65, 129.34, 159.48; MS *m/e* 226 ($C_{12}H_{18}O_4$); yield 42%). A solution of 2,6-bis(2-methoxyethoxy)phenyllithium was prepared by the addition of *n*-butyllithium in hexane (1.2 equiv) to a solution of 1,3-bis(2-methoxyethoxy)benzene in sodium-dried diethyl ether at −78 °C followed by stirring at room temperature under Ar for 48 h. Dimethyl carbonate in benzene (0.3 equiv) was added, and the reaction mixture was refluxed for 3 days under Ar. The reaction mixture was poured into ice–water; and the organic phase was concentrated to yield tris(2,6-dimethoxyphenyl)carbinol as an oil. A solution of this crude material in diethyl ether was treated with a small amount of concentrated HBF_4, and the resulting blue precipitate was filtered and dried to give $4^+BF_4^-$ salt as a crystalline solid (^1H NMR ($CDCl_3$, 300.1 MHz) δ 3.15 (s, 18H), 3.20 (m, 12H), 3.92 (m, 12H), 6.50 (d, 6H), 7.56 (t, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 58.37, 68.39, 69.80, 105.35, 111.30, 141.19, 161.82; yield 11.9%).

(6) The salt $4^+BF_4^-$ was reduced with a $CrCl_2$ solution prepared from $CrCl_3\cdot 6H_2O$ and Zn/Hg in 10% HCl solution. Radical **4** was extracted into ether, washed with water twice, dried with $MgSO_4$, and chromatographed with ether on silica gel to give a pure solution of radical **4**.

(7) Our own CW-EPR spectrum of **1**, obtained under the same conditions as were used for **4**, shows a 13-line pattern with 1.1-G splittings. The small decrease in splitting (1.1 G for **1**, 1.0 G for **4**) suggests a slightly steeper (*ca.* 5°) aryl ring twist in **4** than the 47° estimated for **1**.[2a]

(8) Magnetic susceptibility measurements in the temperature range from 1.8 to 350 K at −55 to 55 kG were performed on a MPMS Quantum Design SQUID magnetometer. Samples for susceptibility measurements were prepared by the addition of tris(2,6-dimethoxyphenyl)methyl radical in diethyl ether to a solution of $LiBF_4$ in THF under Ar. The resulting red-brown precipitates were filtered and dried under vacuum.

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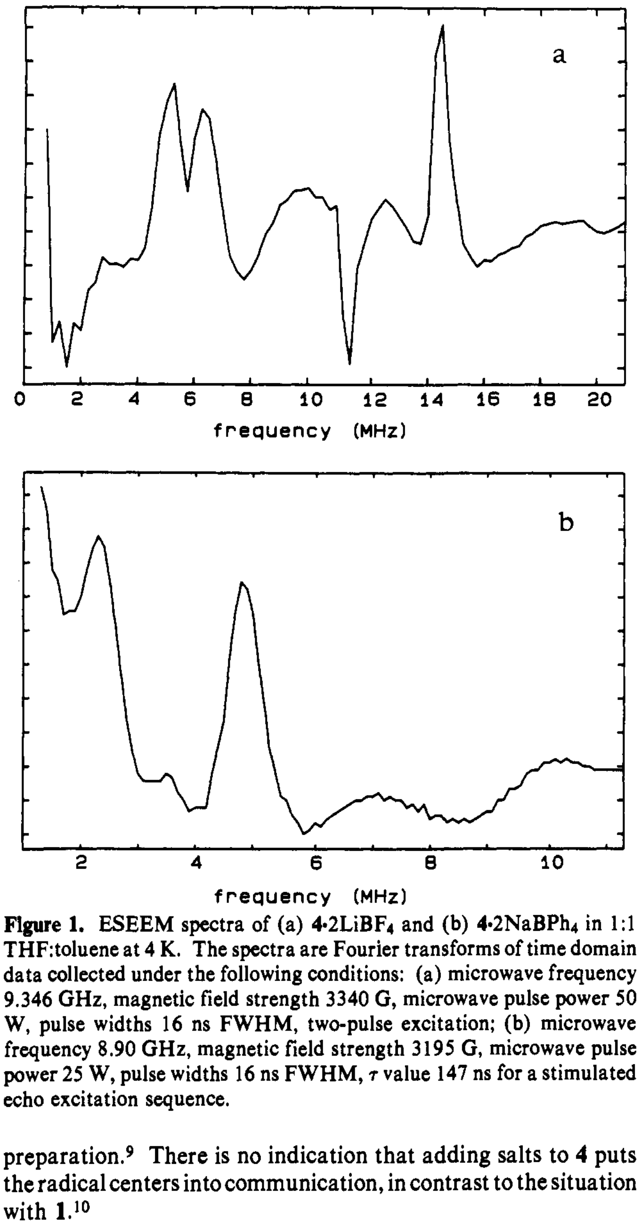

Figure 1. ESEEM spectra of (a) 4·2LiBF$_4$ and (b) 4·2NaBPh$_4$ in 1:1 THF:toluene at 4 K. The spectra are Fourier transforms of time domain data collected under the following conditions: (a) microwave frequency 9.346 GHz, magnetic field strength 3340 G, microwave pulse power 50 W, pulse widths 16 ns FWHM, two-pulse excitation; (b) microwave frequency 8.90 GHz, magnetic field strength 3195 G, microwave pulse power 25 W, pulse widths 16 ns FWHM, τ value 147 ns for a stimulated echo excitation sequence.

Table I. ESEEM Complexation Data for **4** with Various Salts

salt	A_{iso} (MHz)	r_{eff} (Å)	r_{MNDO}	no. of bound M$^+$	spin density on M$^+$ (%)
LiBF$_4$	0.9	3.5 ± 0.2	3.45	2	0.3^a
LiI	1.0	3.4 ± 0.2	3.45	2	0.3^a
NaBPh$_4$	2.4^b	3.8 ± 0.2^c	*d*	2^c	0.3
NaI	2.4^b	3.8 ± 0.2^c	*d*	2^c	0.3

^{a} MNDO finds a spin density of 0.22% on the bound ^{7}Li ions, in reasonable agreement with experiment. Unfortunately, without suitable reference systems, we cannot judge the significance of this value. ^{b} A larger splitting of 6.0 MHz is also observed in the Na salt + **4** samples. This result strongly suggests a complex with only one Na$^+$ bound, inducing pyramidalization at the radical center and hence decreased distance and increased overlap between the radical center and Na$^+$. The presence of radical centers that show this stronger coupling contributes to the masking of the sum combination peak in our two-pulse ESEEM spectra. ^{c} Values for r_{eff} are calculated assuming that two Na$^+$ cations are coupled. If only a single Na$^+$ nucleus is coupled, the calculated dipole–dipole distance decreases to 3.3 Å, a distance that seems unlikely based on CPK molecular models and MNDO studies. ^{d} MNDO parameters are not available for Na, so these structures were not calculated.

preparation.[9] There is no indication that adding salts to **4** puts the radical centers into communication, in contrast to the situation with **1**.[10]

Addition of a 10-fold excess of LiBF$_4$ to 10^{-6} M THF solutions of **4** results in the complex **4**·2LiBF$_4$. Because no new hyperfine coupling could be resolved in the CW-EPR spectrum after this treatment, the ESEEM technique was used to look for weak ^{7}Li hyperfine coupling to the paramagnetic center.[11] ESEEM data were collected on a home-built spectrometer described elsewhere.[12] A two-pulse (90°–τ–180°) ESEEM spectrum of **4**·2LiBF$_4$ collected at a microwave frequency of 9.35 GHz and a magnetic field strength of 3340 G is shown in Figure 1a. The prominent doublet centered at 5.6 MHz shows a splitting of approximately 1.0 MHz. When ESEEM data were taken at 8.52 GHz with a field strength of 3052 G, the center of the doublet shifted to 5.0 MHz, consistent with its assignment to ^{7}Li. Also present in the spectrum of Figure 1a are ^{7}Li sum and difference combination frequencies centered at 11.2 and 1.2 MHz, respectively, and a peak near 14.3 MHz due to weakly coupled protons. An analysis of modulation frequencies and depths using the formalism of Shubin and Dikanov showed that this splitting arose from two ^{7}Li$^+$ ions coupled to the radical center with an effective dipole–dipole distance of 3.5 Å and an isotropic hyperfine coupling of 0.4 G.[13] Because the line width of the sum combination peak is independent of hyperfine anisotropy, the amplitudes and damping factors for the fundamental peaks (5.0 and 6.2 MHz) relative to that of the sum combination line can be used to determine the dipole–dipole distance. With this distance set, the absolute intensities of the lines can be used to determine the number of nuclei that give rise to the coupling.[14,15] Analogous studies of **4**·2NaBPh$_4$ and **4**·2NaI complexes gave similar findings; a stimulated echo spectrum of **4**·2NaBPh$_4$ is shown in Figure 1b. Two peaks centered at 3.6 MHz, the ^{23}Na larmor frequency, and split by approximately 2.5 MHz are observed. The lack of a pronounced sum combination peak in the two-pulse ESEEM data precludes an independent determination of dipole–dipole distance and the number of coupled Na$^+$ ions. Computer simulation of these ESEEM data are consistent with an isotropic hyperfine coupling of 2.4 MHz and an effective dipolar distance of 3.8 Å assuming that two ^{23}Na ions couple to the radical. The Li$^+$–radical center distances from ESEEM analysis using the point dipole–dipole approximation are in good agreement with those obtained from MNDO calculations (see Scheme II).[16] The measured ^{7}Li and ^{23}Na hyperfine coupling constants can be compared with their atomic values to estimate an unpaired spin density of approximately 0.3% for both Li and Na.[17] These results are summarized in Table I. The nontrivial spin densities and hence M$^+$–e$^-$ interactions in these Li$^+$R·Li$^+$ complexes bode well for the metals' functioning as *couplers* of neighboring radical centers, as suggested in **2**.

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(9) Like **1**, radical **4** oxidizes on treatment with Li salts in air, as evidenced by the appearance of the blue color of the corresponding triarylmethyl cation in each case.

(10) Treatment of **1** with CdCl$_2$ leads to antiferromagnetic coupling. Jang, S.-H.; Jackson, J. E., manuscript in preparation. See also ref 1.

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(14) The position and width of the sum combination peak show that ^{7}Li nuclear quadrupole couplings are negligible and that our use of the perturbation treatment of ref 12 is valid. Also supporting the presence of two coupled ^{7}Li cations are faint combination lines observed in stimulated echo spectra. (McCracken, J.; Pember, S. O.; Benkovic, S. J.; Villafranca, J. J.; Miller, R.; Peisach, J. *J. Am. Chem. Soc.* **1988**, *110*, 1069–1074.)

(15) Note that no coupling is seen in ^{10}B, ^{11}B, or ^{19}F nuclei of the BF$_4^-$ counterions; thus splittings do not simply arise via nonspecific coupling to magnetic nuclei near the radical.

(16) MNDO (Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.) calculations were run in the MOPAC program (Stewart, J. J. P. *MOPAC*, Version 4.00, QCPE No. 455, 1987).

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