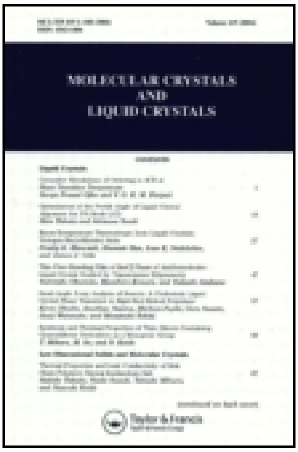

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Ion Complexation Induced High-Spin Associations of Spin-Labeled Crown Ethers: A Reevaluation

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ION COMPLEXATION INDUCED HIGH-SPIN ASSOCIATIONS OF SPIN-LABELED CROWN ETHERS: A REEVALUATION

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Abstract. Between 1978 and 1989, Mukai and coworkers demonstrated that a series of spin-labeled benzo-15-crown-5 derivatives gave triplet ESR spectra in ethanol glasses in the presence of diamagnetic alkali and alkaline earth ions. They proposed that the high-spin coupling resulted from a pair of radicals being brought into close contact by a 1:2 complexation of metal ions with the crown ether moieties. The work of Mukai and his colleagues represents an early example of high-spin coupling induced in radical pairs that assemble around diamagnetic metal ions. Herein, we describe ion binding experiments with simple stable free radicals such as TEMPO and galvinoxyl that lack the crown moiety. The triplet state species that we observe require the possibility of unforeseen mechanisms for previously reported high-spin associations in spin labeled crown ethers.

INTRODUCTION

Several years ago we reported the field dependent hysteresis of the magnetization of heterogeneous solids prepared by precipitating the free radical, tris(2,6-dimethoxyphenyl)methyl, from ether solutions with lithium salts.[1] This observation developed into an approach to molecular magnetic materials[2] that relies on the assembly of paramagnetic tripod ethers by ion binding, thereby inducing magnetic interactions between the unpaired electrons.[3] We reported mixed results with this symmetrical system; however, Gatteschi and coworkers have been exceptionally successful in organizing free radicals with paramagnetic metal ions to produce ferrimagnetic arrays.[4] More recently, they and others have used diamagnetic metal ions as high-spin coupling entities.[5]

Some time ago, in related work, Mukai and coworkers[6] demonstrated that a series of spin-labeled benzo-15-crown-5 derivatives gave triplet ESR spectra in EtOH glasses in the presence of diamagnetic alkali and alkaline earth salts. They proposed that a pair of radicals were brought into close contact by a 1:2 complexation of metal ions by the crown ether moieties, resulting in the observation of triplet states by ESR spectroscopy. Because our chemical system somewhat resembles that of Mukai in its intended mechanism of action, we were prompted to give his results considerable attention. We found, however, that the collected observations of Mukai presented several surprising results:

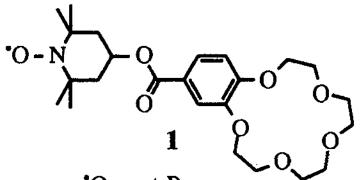
(1) While the nitroxyl **1** and galvinoxyl **2** derivatives of benzo-15-crown-5 gave triplet ESR spectra in the presence of K^+ but not Na^+[7], the analogous verdazyl radical **3** gave triplet spectra in the presence of Na^+ but not K^+.

(2) The phenoxyl radical **4** gave triplet spectra for almost any metal ion including Li^+, Na^+, K^+, Rb^+, Mg^{++}, Ca^{++}, Sr^{++}, and Ba^{++}. The selectivity proposed in the nitroxyl and galvinoxyl systems is ultimately reversed in the verdazyl system **3**, and then obviated in the phenoxyl system which is indiscriminate. This is very unusual in light of the fact that each radical carries the benzo-15-crown-5 moiety.

(3) The zero-field splitting (ZFS) parameters are almost unchanged between metals.

(4) The crown is not essential; veratrole methoxy groups as in **5** were said to be sufficient for binding ions in a fashion reminiscent of the benzo-15-crown-5 analog.

(5) The exclusive *syn* stereochemistry proposed on the basis of ZFS parameters seems strange in the absence of other unspecified forces. Moreover, the crystal structure of the K^+ complex of benzo-15-crown-5 shows *anti*-stereochemistry.[8]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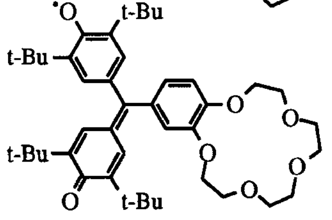
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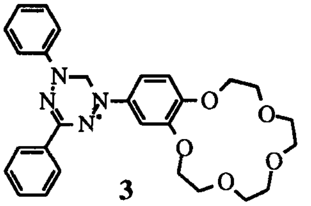
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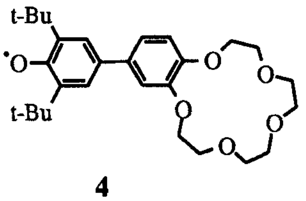
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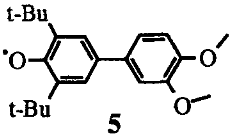
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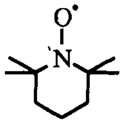
We prepared compounds **2**, **3**, and **5** according to the literature procedures[6] and were able to reproduce Mukai's spectra in each case, thereby confirming the earlier work. However, control experiments carried out using simple nitroxyl, phenoxyl, and galvinoxyl radicals necessitate the possibility of alternative mechanisms for high-spin coupling in compounds that do not involve crown sandwich complexation.

RESULTS

Nitroxyl radicals: X-band ESR studies of ethanol and THF solutions of TEMPO (**6**) (10^{-2} - 10^{-3} M, 100 K) containing 1 eq. KSCN, or even *m*-xylene solutions show $\Delta m_S=2$ signals with small, poorly resolved ZFS in the $\Delta m_S=1$ region. These spectra are qualitatively not different from Mukai's spectra of **1** in the presence of KSCN for which he invoked a sandwich of two molecules of **1** around the alkali metal ion (Figure 1).



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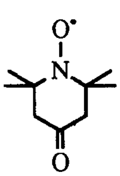

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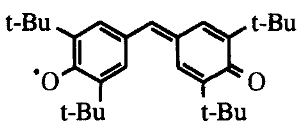

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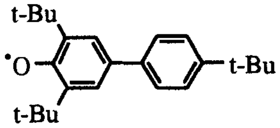

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Galvinoxyl radicals: Commercial galvinoxyl radical **8** was studied as a model for **2**. Solutions of **8** (10^{-2} M, 100 K) in 4:1 ethanol:diethyl ether give triplet spectra with $|D/hc|=0.0046\ \text{cm}^{-1}$ and $|E/hc|=0.0006\ \text{cm}^{-1}$. Surprisingly, the addition of one equivalent of KSCN or NaSCN resulted in a dramatic increase in the intensity of the triplet signal relative to the doublet signal. However, there was no change in the values of the zero-field parameters whether KSCN, KI, NaSCN or no additional ions were added to the solution. Sequestering the added K^+ with 18-crown-6 caused a diminution of the intensity of the triplet components, yet throughout these intensity changes, we never observed a change in the ZFS parameters. We found similar behavior for Mukai's galvinoxyl-crown **2**, which also gives a triplet spectrum in the absence of metal ions.

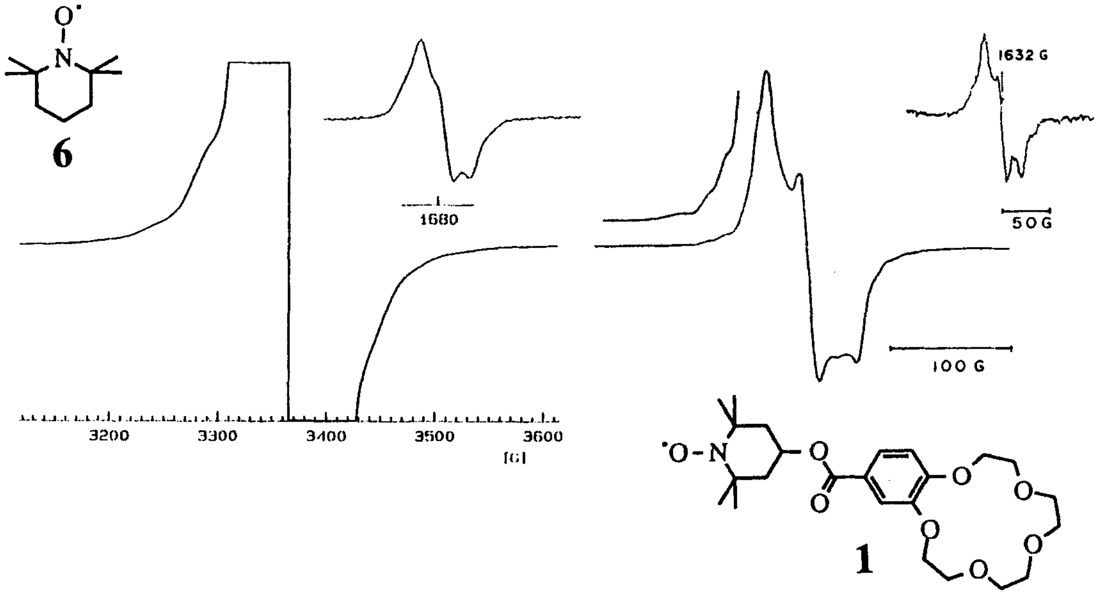

FIGURE 1. Left: ESR spectrum of TEMPO **6** (10^{-1} M) in ethanol at 100 K. Right: Mukai's spectrum of **1** in the presence of 1 eq. KSCN at 77 K.

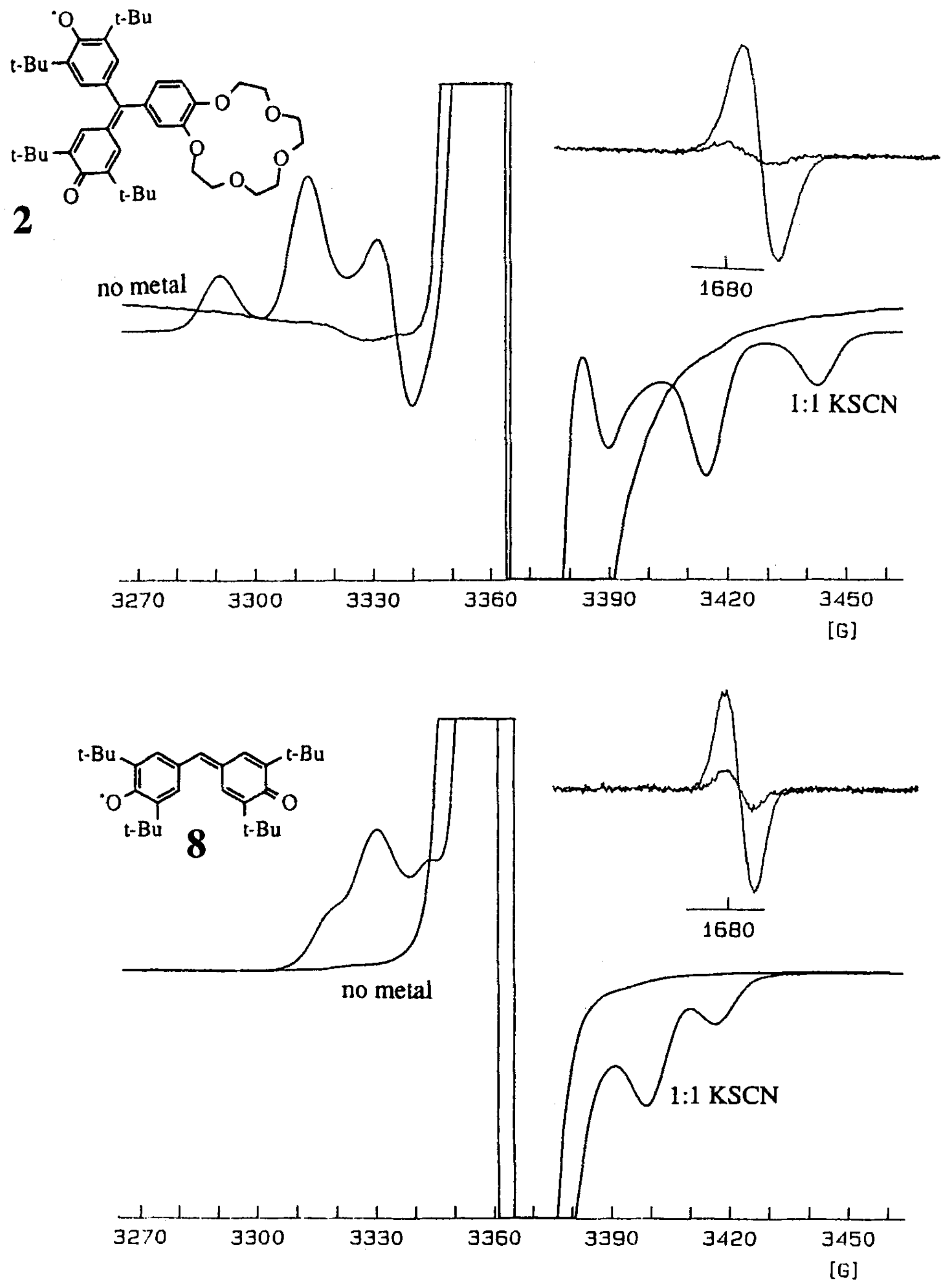

FIGURE 2. ESR spectra of **2** (top) and **8** (bottom) showing in each case the increase in the triplet component of the spectrum on addition of 1 eq. KSCN.

Phenoxyl radicals: We synthesized 4-(4'-*tert*-butylphenyl)-2,6-di-*tert*-butylphenoxyl radical **9**[9] as a model for Mukai's phenoxyls **4** and **5** that lacks coordinating functionalities. Both **4** and **5**, as well as **9**, give similar triplet ESR spectra in ethanol (7.5×10^{-3} M) in the *absence* of added metal ions, with D values that vary between 90 and 100 G. As with the galvinoxyl systems, addition of KSCN to solutions of these radicals increases the relative intensities of the triplet spectral components. Phenoxyl crown **4** is reported to show two sets of ZFS parameters, one major and one minor. We observed that concentrated ethanol solutions (7.5×10^{-3} M) of **5** also show a minor triplet species.

TABLE I. Zero-field Splitting Parameters for Concentrated Glasses of Free Radicals.*

Radical	Conc. (M)	Alkali metal salt	D/hc (cm^{-1})	E/hc in (cm^{-1})
Nitroxyls				
1	5.4×10^{-3}	KSCN	0.0065	0.0004
6	10^{-1}	none	0.0114	0.0011
Galvinoxyls				
2	3×10^{-3}	KSCN	0.0071	0.0008
2	3×10^{-3}	none	0.0069	0.0009
8	10^{-2}	KSCN	0.0047	0.0006
		NaSCN	0.0047	0.0006
8	10^{-2}	none	0.0048	0.0008
Phenoxyls				
4	7.5×10^{-3}	KSCN	major: 0.0026	0.0001
			minor: 0.0093	0.0006
4	7.5×10^{-3}	none	0.0060	0.0006
5	3×10^{-3}	KSCN	major: 0.0031	0.0003
			minor: 0.0090	0.0005
5	7.5×10^{-3}	none	0.0071	0.0003
9	7.5×10^{-3}	KSCN	0.0087	0.0011
9	7.5×10^{-3}	none	0.0077	0.0012

*Ethanol at 100 K

DISCUSSION

Intermolecular dipolar interactions between monoradicals had been studied by Krielick and coworkers[10] several years before Mukai's first report on **1**. From the dipolar relaxation times of di-*tert*-butyl nitroxide radicals in concentrated (2.5×10^{-1}M) CCl_4 solutions they determined that the radicals associate to form short-lived dimers with a small intermolecular separation (~4.7 Å) and a relatively large dipole-dipole interaction (~0.03 cm^{-1}). They postulated that at high concentrations there is always a second radical present in the solvation sphere, and showed that the magnetic susceptibilities of these solutions correspond to the case where $kT \gg J$, indicating that these dimers are weakly interacting biradicals.

Long before our observations of triplet spectra for TEMPO in concentrated glasses, Eaton and coworkers[11] observed half field transitions in solutions of radical **7** in toluene ($7.5x10^{-3}$ M) glasses. This transition was used as a measure of intermolecular spin-spin interactions. For a monoradical, they found that the intensity of the half field transition is proportional to concentration, and solutions of **7** were used as controls to separate the effects of inter- and intramolecular interactions in molecular nitroxide biradicals. They caution that "the half field transition is diagnostic of anisotropic spin-spin interactions in general, not just of molecular triplets."[12] Therefore, care must be used when interpreting Mukai's data; since control experiments with radicals lacking crown moieties were not described, we cannot easily separate the effects of inter- and intra-complex interactions.

Oddly, Mukai and Sogabe studied the triplet ESR spectra of radical pairs of **2** in a crystalline matrix of the corresponding phenol.[13] They attributed the observed ZFS parameters to a specific nearest-neighbor radical pairing. They have clearly demonstrated that well-defined ESR spectra of triplets may result from a pair of free radicals in close van der Waals contact.

CONCLUSION

Our results clearly indicate that a specific pairwise ether binding mechanism is not essential for the production of triplet state spectra from simple monoradicals. The increase in radical pair spectra upon the addition of salt may be a consequence of the hydrophobic effect; perhaps we are salting out greasy dimers. In ethanol, proton bound dimers may be considered as well. Suffice it to say, we are looking at the results of perturbations of complex equilibria. The observed magnetic consequences are in no way a simple consequence of pairwise ion binding as suggested by Mukai.

The literature relating structure to anisotropic spin-spin interactions in concentrated solutions of free radicals is scant.[14] One way to test alternative dimeric structures would be to use computational models to generate test structures based on *tert*-butyl/*tert*-butyl associations and perhaps proton-bound dimers, and calculate ZFS parameters using realistic models for spin density. Such alternative models, coupled with structural and magnetic studies of Mukai's complexes in the solid state, together will provide a more realistic picture of the high-spin associations previously reported.

REFERENCES

1. S.-H. Jang, R. A. Bertsch, J. E. Jackson, B. Kahr, Mol. Cryst. Liq. Cryst. 211, 289 (1992).
2. O. Kahn, Molecular Magnetism (VCH Publishers, New York, 1993); J. S. Miller, A. J. Epstein, Angew. Chem., Int. Ed. Engl., 33, 385 (1994).
3. S. -H. Jang, S. Antonelli, B. Kahr, J. E. Jackson, submitted for publication.

4. A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, C. Zanchini, Inorg. Chem. 28, 1969 (1989); A. Caneschi, D. Gatteschi, J. P. Renard, P. Rey, R. Sessoli, Inorg. Chem. 28, 1976 (1989); A. Caneschi, D. Gatteschi, J. P. Renard, P. Rey, R. Sessoli, Inorg. Chem. 28, 3314 (1989); A. Caneschi, D. Gatteschi, R. Sessoli, Acc. Chem. Res. 22, 392 (1989).
5. A. Ozarowski, B. R. McGarvey, C. Peppe, D. G. Tuck, J. Am. Chem. Soc. 113, 3288 (1991); D. M. Adam; A. L. Rheingold, A. Dei, D. N. Hendrickson, Angew. Chem. Int. Ed. Engl. 32, 391 (1993); H. Oshio, T. Watanabe, A. Ohto, T. Ito, U. Nagashima, Angew. Chem. Int. Ed. Engl. 33, 670 (1994); S. Bruni, A. Caneschi, F. Cariati, C. Delfs, A. Dei, D. Gatteschi, J. Am. Chem. Soc. 116, 1388 (1994).
6. K. Ishizu, H. Kohama, K. Mukai, Chem. Lett. 227 (1978); K. Mukai, N. Iida, Y. Kumamoto, H. Kohama, K. Ishizu, Chem. Lett. 613 (1980); K. Mukai, T. Yano, K. Ishizu, Tetrahedron Lett. 22, 4661 (1981); K. Mukai, N. Iida, K. Ishizu, Bull. Chem. Soc. Jpn. 55, 1362 (1982); K. Mukai, M. Yamashita, K. Ueda, K. Tajima, K. Ishizu, J. Phys. Chem. 87, 1338 (1983); K. Mukai, M. Tanii, Y. Yurugi, K. Tajima, K. Ishizu, Bull. Chem. Soc. Jpn. 58, 322 (1985); K. Tajima, M. Miyoshi, M. Furutani, Y. Fujimura, K. Mukai, K. Ishizu, Bull. Chem. Soc. Jpn. 62, 2061 (1989); K. Tajima, H. Shimizu, T. Morita, H. Tomoda, K. Mukai, K. Ishizu, Org. Mag. Res. 21, 376 (1983).
7. This is consistent with the reported binding properties of benzo-15-crown-5 (S. Kopdow, T. G. Hogen-Esch, J. Smid, Macromolecules, 6, 133 (1973)).
8. P. R. Mallison, M. R. Truter, J. Chem. Soc. Perkin II, 1818 (1972).
9. A. Rieker, K. Scheffler, Ann. 689, 78 (1965).
10. M. S.Davies, C. Mao, R. W. Kreilick, Mol. Phys. 29, 665 (1975).
11. S. S. Eaton, K. M. More, B. M. Sawant, G. R. Eaton, J. Am. Chem. Soc. 105, 6560 (1983).
12. G. R. Eaton, S. S. Eaton, in Biological Magnetic Resonance, ed. L.J. Berliner. Vol. 8, p. 339 (Plenum Press, New York, 1989).
13. K. Mukai, A. Sogabe, J. Chem. Phys. 72, 598 (1980).
14. W. Broser, H. Kurreck, W. Niemeier, Tetrahedron, 32, 1183 (1976).