3Aa08S

The Spin Structure of Linked Nitronyl Nitroxide Radicals

H. Heise and F. H. Köhler

Anorganisch-chemisches Institut, Technische Universität München, D-85747 Garching, Germany

Abstract: Solid-state ^{1}H, ^{13}C, and ^{31}P MAS NMR spectroscopy has been used for the investigation of compounds wherein up to three nitronyl nitroxides are linked via various potential coupling units. When the signal shifts are transformed into spin densities, the radicals' spin structure including most of their nuclei can be determined. Effects like changes of the spin sign upon complexation and magnetic interaction between the radicals will be demonstrated.

Nitronyl nitroxides are rather stable organic radicals, which are known for more than 30 years.[1] There was a renaissance of this chemistry, when nitronyl nitroxides were used as ligands bound to paramagnetic transition metal ions and when this resulted in not only ferromagnetic interaction, but also spontaneous magnetization.[2] A bit later, it turned out that in some cases the transition metal ion was not compulsory and that the solid sample of a nitronyl nitroxide alone may become a magnet.[3] This raised the question on the origin of the magnetic interactions. Since theoretical results suggested that Heitler-London-type interactions (summarized as McConnell-I mechanism[4]) are responsible[5], the spin density distribution in the nitronyl nitroxides became a focus of current research.

Therefore, this contribution first briefly compares the advantages and weaknesses of current methods for determining the spin structure of radicals. It will be also demonstrated briefly by showing a simple example, what data can be obtained from NMR spectroscopy.[6] More recent preparative efforts aimed at coupling nitronyl nitroxides in order to change the spin state and to investigate the efficiency of the coupling units. While compounds of this sort are known[7] their spin structure is still essentially unexplored.

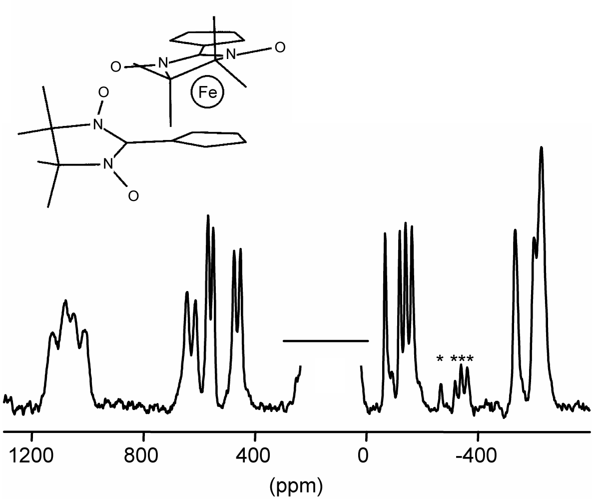

Figure 1. ^{13}C MAS NMR spectrum of two nitonyl nitroxides fixed at ferrocene.

As metallocenes are potential coupling units, ferrocene- and ruthenocene-bridged nitronyl nitroxides have been investigated by using solid-state NMR spectroscopy under magic angle spinning.[8] Figure 1 shows how well resolved the spectra can be. Spectrum analysis reveals that considerable spin density is transferred from the nitronyl nitroxides to the ferrocene ligands. Nevertheless, the signals of the radical moieties appear in ranges that are known from isolated nitronyl nitroxides,[9] while magnetic measurements show antiferro-

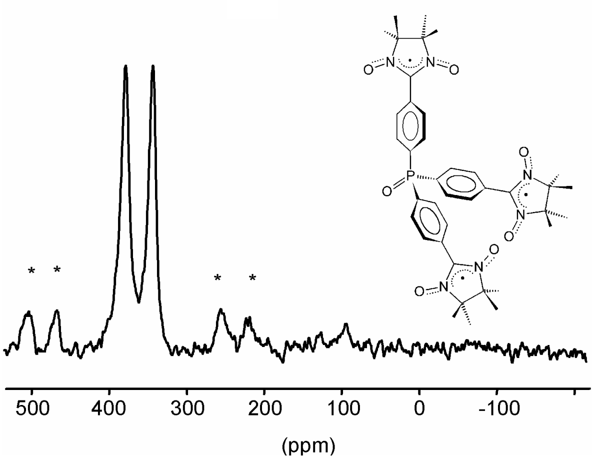

Figure 2. ^{31}P MAS NMR spectrum of the molecule shown.

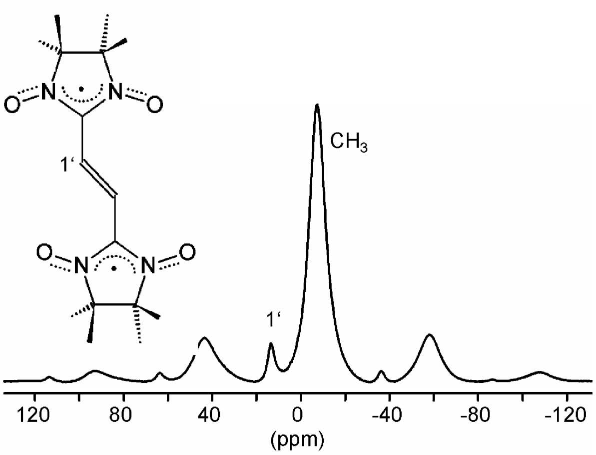

Figure 3. ^{1}H MAS NMR spectrum of ethylene -bridged nitronyl nitroxides.

magnetic interaction. For a ruthenocene-bridged biradical it turns out that conformational changes may lead to signal shifts that could also result from antiferromagnetic interactions.

When nitronyl nitroxides are linked via a phosphorus atom, potential donors for transition metals result.[10] ^{31}P MAS NMR studies (see Fig. 2) uncover a sign change of the spin density at phosphorus, when a nitronyl nitroxide-substituted phosphane is coordinated to a metal fragment. The magnetic interaction across the phosphorus is weak.

Conjugated non-aromatic bridges are more efficient couplers between two nitronyl nitroxides. This is obvious from strongly reduced NMR signals shifts (e. g. Fig. 3).[11] Temperature-dependent ^{13}C MAS NMR studies are shown to be a valuable tool for the determination of magnetic interactions. The interaction constant thus obtained agrees with those determined by independent methods.

References

1 J. H. Osiecky, E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 1078 (1968).

2 A. Caneschi, D. Gatteschi, R. Sessoli, *Acc. Chem. Res.*, **22**, 392 (1989).

3 P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama, M. Kinoshita, *Chem. Phys. Lett.*, **180**, 327 (1991). K. Itoh, M. Kinoshita, Eds., *Molecular Magnetism*, Kodansha, Tokyo and Gordon and Breach Science Publishers, Australia, 2000, chapter 5.

4 H. M. McConnell, *J. Chem. Phys.*, **39**,1910 (1963).

5 J. J. Novoa, M. Dumal, *Struct. Bonding (Berlin)*, **100**, 33, (2001).

6 F. H. Köhler in *Magnetism: Molecules to Materials, Models and Experiments*; J. S. Miller, M. Drillon, Eds.; Wiley-VCH, Weinheim, 2001.

7 J. Veciana, H. Iwamura, *MRS Bulletin*, 36, 41 (2000). P. M. Lahti, Ed. *Magnetic Properties of Organic Materials*; Marcel Dekker, New York, 1999.

8 C. Sporer, H. Heise, K. Wurst, D. Ruiz-Molina, H. Kopacka, P. Jaitner, F. H. Köhler, J. J. Novoa, J. Veciana, submitted to *Chem. Eur. J.*

9 H. Heise, F. H. Köhler, F. Mota, J. J. Novoa, J. Veciana, *J. Am. Chem. Soc.*, **121**, 9659 (1999).

10 C. Rancurel, H. Heise, F. H. Köhler, U. Schatzschneider, E. Rentschler, J. Vidal, J. Veciana, J.-P. Sutter, manuscript in preparation.

11 C. Stroh, R. Ziessel, H. Heise, G. Raudaschl-Sieber, F. H. Köhler, P. Turek, N. Claiser, C. Lecomte, manuscript in preparation.