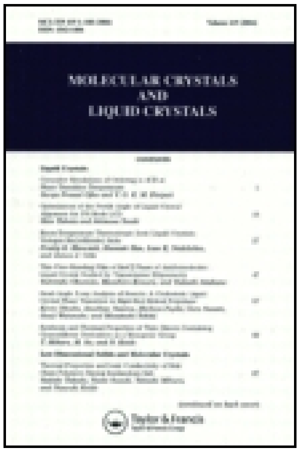

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SYNTHESIS AND MAGNETIC CHARACTERIZATION OF METALLOCENE-SUBSTITUTED α-NITRONYL NITROXIDE RADICALS

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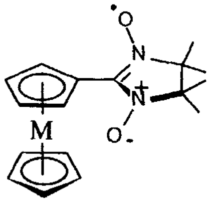
Abstract The synthesis and magnetic characterization of a series of α-metallocenyl nitronyl nitroxide monoradicals (M = Fe, Ru, Os) are reported. Intra- and intermolecular magnetic interactions in this series of compounds have been studied in detail by ESR spectroscopy and magnetic measurements. ESR spectra of monoradicals in dilute solutions under isotropic conditions show a small spin density on the metal centers. In the solid state, the radicals derived from ferrocene and ruthenocene show a paramagnetic behavior with very weak antiferromagnetic intermolecular interactions, as ascertained from magnetic susceptibility measurements. This behavior is rationalized, for the ferrocene derivative, by means of its crystal structure.

INTRODUCTION

The macroscopic magnetic properties of molecular crystals depend both on the microscopic molecular electronic properties and on the intermolecular electronic interactions as a consequence of their solid state structures. It is therefore a challenge to design molecules with the appropriate crystal packing and elements to transmit properly the magnetic interactions in order to obtain molecular based magnets as well as to increase their critical temperatures.

Recently, some purely organic bulk ferromagnets have been synthesized and studied in detail.[1] Among them, a lot of work has been devoted to the family of α-substituted nitronyl nitroxides, the β-phase of *p*-nitrophenyl nitronyl nitroxide[2] being the first example of a free radical with a bulk ferromagnetic transition. Some of us are presently involved in the study of different ways to control the crystal packing and consequently, the magnetic interactions of molecular solids by designing open shell molecules with multiple intermolecular hydrogen bonds.[3] As a result of this study, we recently reported an example of a bulk ferromagnet,[4] the α-phase of 2-hydroxy nitronyl nitroxide radical, in which the intermolecular ferromagnetic interactions were induced by a 3D network of hydrogen bonds.

In the present study we try to develop a new way to induce magnetic interactions between nitronyl nitroxide radicals by attaching them to organometallic moieties. The metallocenes of the iron subgroup (Fe, Ru, Os) were chosen as organometallic rests to which two or more radicals are attached. Before studying such organometallic polyradicals, we considered that it was convenient to know the role played by the central metal in their electronic structures. Therefore, the α-metallocenyl nitronyl nitroxides of iron **1a**, ruthenium **1b** and osmium **1c** were synthesized and studied.



1a; M = Fe

1b; M = Ru

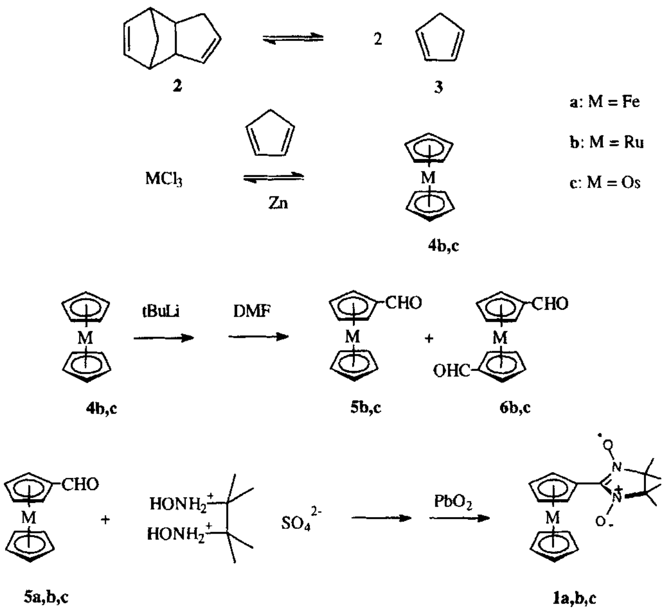
1c; M = Os

Here we will present the ESR study of these monoradical molecules, which yields interesting information about their spin density distributions, in an attempt to show whether the metallocenes are suitable for transmitting magnetic interactions. We will also present the bulk magnetic behavior of the radicals in the solid state giving an explanation of such behavior based on the crystal structure.

RESULTS AND DISCUSSION

Preparation of Metallocene-substituted α-Nitronyl Nitroxides

Radicals **1a-c** were obtained from the corresponding monoaldehydes **5** by the usual procedures depicted in the following scheme.[5]



Electronic Structure of Metallocene-substituted α-Nitronyl Nitroxides

The most interesting aspect of the electronic structure of radicals **1a-c** is the spin density distribution of their unpaired electrons. Since the spin density on a given atom of a free radical is proportional to the hyperfine coupling constant observed in the ESR spectrum for the corresponding nucleus, we have recorded the free tumbling solution ESR spectra of the radicals.

The ESR spectra of **1a-c** show five main groups of lines, with relative intensities of 1:2:3:2:1, which result from the coupling of the unpaired electron with two equivalent nitrogen nuclei (I =1). A more detailed analysis of each of these five main groups of lines revealed a complex pattern which arises from the supplementary coupling of the free electron with the twelve methyl hydrogen atoms (I = 1/2). Beside these main groups of lines, other low intensity outer lines (satellite lines) are observed in the ESR spectra of **1a** and **1b**, which result from an additional coupling with the metal centers, as is shown in Figure 1 for radical **1b**. The computer simulation of the free tumbling ESR spectra of radicals **1a-c** has yielded the hyperfine coupling constants summarized in Table I. For the three radicals studied, the values of the coupling constants with the nitrogen atoms and the twelve methyl hydrogen atoms are nearly equal. They are also very similar to the usual values known for other substituted α-nitronyl nitroxides,[6] indicating therefore, that the unpaired electron is mainly distributed on both NO groups and the α-carbon atom.

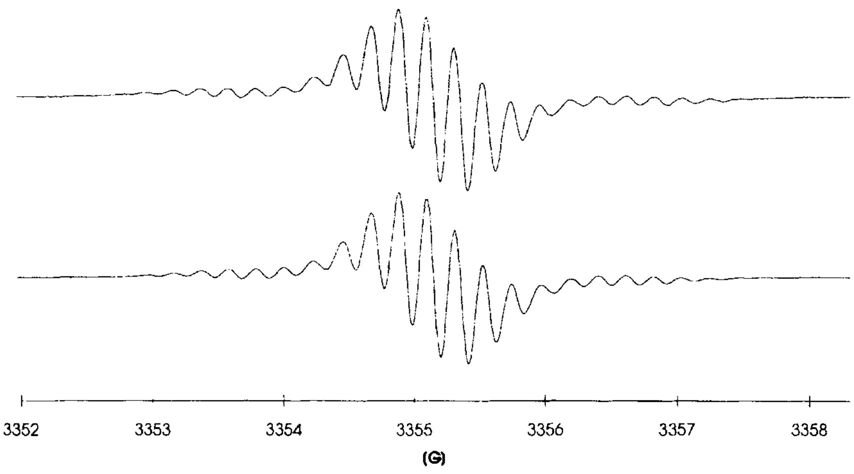


FIGURE 1 Experimental (upper) and simulated (lower) ESR spectra of radical **1b** under free tumbling conditions. The depicted signals correspond to the enlarged central group of peaks of the spectra.

As already mentioned, for radicals **1a** and **b** we have observed a rather large hyperfine coupling constant with the metal nuclei, showing that there is a significant spin density on this metal atom. Both the hyperfine coupling constant with the metal and the spin density for the ruthenocene radical **1b** are lower than for the ferrocene derivative. In spite of that, the satellite lines observed for radical **1b** are more intense than in the spectra of **1a**. This is merely a consequence of the higher isotopic abundance of the nuclei which give rise to hyperfine coupling with the unpaired electron in the case of ruthenium (17% for ^{101}Ru and 12.7% for Ru ^{99}) than in the case of iron (2.64% for ^{57}Fe). By contrast, osmocene radical **1c** does not show any satellite lines, although osmium has two magnetically active isotopes with large enough natural abundance to be observed; i. e., ^{187}Os and ^{189}Os with abundance of 1.64% and 16%, respectively. This result is ascribed to an efficient quadrupolar relaxation phenomenon that takes place during the ESR experiment because osmium is a heavy element with a very large quadrupolar moment.

TABLE I Summary of simulated hyperfine coupling constants (in Gauss) and relative spin densities (A/A_0) on the metal atoms for radicals **1a-c**[a].

	N (I = 1)	H (I = 1/2)[b]	M	$A/A_0 \times 10^3$
1a	7.52	0.21	^{57}Fe (I=1/2): 2.60	9.75
1b	7.52	0.21	^{101}Ru (I=5/2): 0.6	0.85
			^{99}Ru (I=5/2): 0.53	0.85
1c[c]	7.51	0.20	^{189}Os (I=3/2): -	-
			^{187}Os (I=1/2): -	-

[a] A_0 is the expected hyperfine coupling constant for a spin density of 1 on the metal nuclei. [b] Hydrogen atoms that belong to the CH_3 groups. [c] For a correct simulation of osmocene radical **1c** it is necessary to introduce an additional coupling with two equivalent hydrogen atoms with a constant of 0.24 G. Presumably, these hydrogen atoms belong to the cyclopentadienyl ring attached to the radical moiety.

In order to confirm the presence of a spin density on the metal atoms of radicals **1a-c** we also recorded and simulated their ESR spectra in frozen solution. As shown in Figure 2, it has been possible to simulate by computer these spectra obtaining the principal values of the **g** and **A** tensors which are summarized in Table II. All these values are compared to those of α-phenyl nitronyl nitroxide radical (PHNN). The **g** values for **1a-c** are lower than in the case of PHNN, indicating larger spin orbit couplings for all these α-metallocenyl nitronyl nitroxides than in PHNN. It is therefore reasonable to ascribe this spin orbit coupling to the participation of metallocene metal orbitals in their SOMOs. An additional proof of this assignment is the lower principal **g** values of **1c** when compared with those of **1a** and **b**, which is in accordance with the larger size of the osmium atom. This fact confirms the hypothesis that in the case of the osmocene radical there is also a spin density on the osmium atom.

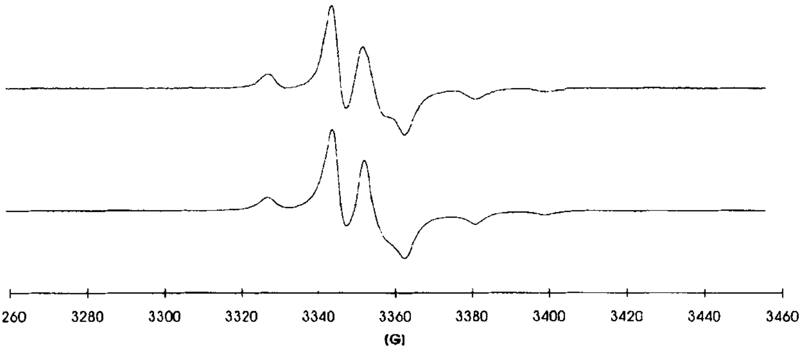


FIGURE 2 Experimental (upper) and simulated (lower) frozen solution ESR spectra of radical **1b**.

TABLE II Principal values of the **g** tensor and the hyperfine coupling tensor with two equivalent nitrogen nuclei for radicals **1a-c** obtained by simulation. A_{ii} values are given in Gauss.

	g_x	g_y	g_z	A_{xx}	A_{yy}	A_{zz}
PHNN	2.0030	2.0072	2.0100	18.5	1.5	1.5
1	2.0018	2.0070	2.0080	17.5	3.3	2
2	2.0013	2.0070	2.0082	18	3.3	2
3	1.9988	2.0072	2.0072	18	1.3	1.3

Solid State Magnetic Properties and Crystal Packing

As show in Figure 3, magnetic susceptibility measurements of radicals **1a** and **1b** show paramagnetic behaviors with small negative Weiss constants (θ = -0.67 K for **1a** and θ = -3.03 K for **1b**) indicating very weak intermolecular antiferromagnetic interactions.

The quasi ideal paramagnetic behaviors of **1a** and **1b** already described can be rationalized for **1a** by studying its crystal packing. As shown in Figure 4, the presence of the bulky metallocenyl groups forces the nitronyl nitroxide units of radical **1a** to remain at distances from each other -the shortest distance found between spin carrying O-N-C-N-O units was 3.8 Å - which are too large to allow significant magnetic exchange interaction between two neighboring radical molecules.

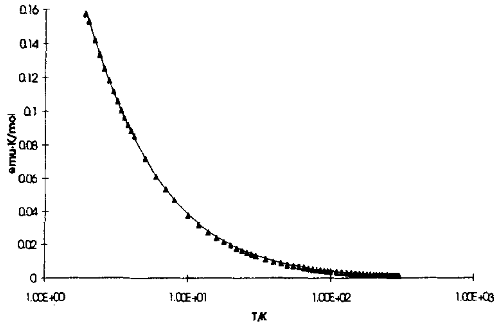


FIGURE 3 Temperature dependence of paramagnetic susceptibility of **1a**.

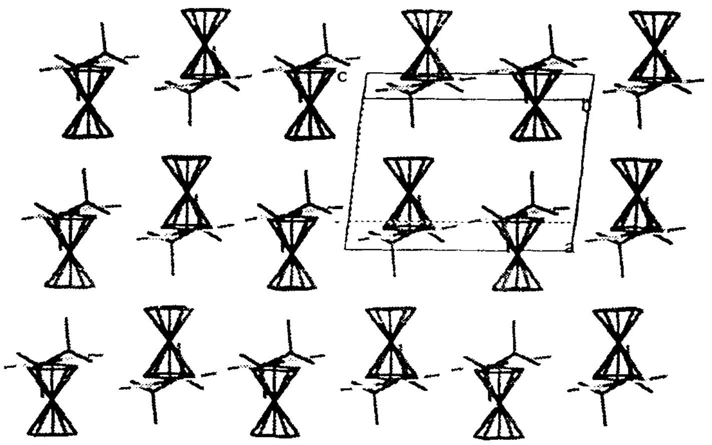


FIGURE 4 Projection of an *ac* layer of the crystal structure of radical **1a**.

CONCLUSIONS

The results presented here show clearly that the attachment of an α-nitronyl nitroxide radical to a metallocene produces a certain spin density on the metal atom, opening the possibility to use metallocenes as bridge units to transmit magnetic interactions.

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