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Article

Low-Valent Low-Coordinated Manganese(I) Ion Dimer: A Temperature Dependent W-Band EPR Study

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W-Band EPR spectra of $[\{HC(CMeNAr)_2\}Mn]_2$ (Ar = 2,6-$^{i}Pr_2C_6H_3$) have been measured at different temperatures. The spectra show a behavior which is typical for an antiferromagnetically coupled dimer with excited states populating upon increasing temperature. By following the intensity variation of the different features of the spectra with temperature, we attributed different groups of resonances to the $S = 1$, 2, and 3 states of the dimer. Their corresponding spin Hamiltonian parameters were derived from simulations. The zero-field-splitting parameters measured in this way were $D_{S=1} = 1.57$ cm^{-1} and $E_{S=1} = 0.064$ cm^{-1}, $D_{S=2} = 0.266$ cm^{-1} and $E_{S=2} = 0.0045$ cm^{-1}, and $D_{S=3} = 0.075$ cm^{-1} and $E_{S=3} = 0$. On the basis of the molecular structure of the system, we could estimate that zero-field splitting (ZFS) is the result of anisotropic exchange and single-ion anisotropic contributions of similar magnitude ($|D| \approx 0.2$ cm^{-1}). These results allow a deeper insight into the electronic structure of the Mn(I) centers in low-coordination environments, further supporting the electronic structure of Mn(I) to be $4s^13d^5$, as previously indicated by DFT calculations.

Introduction

Organometallic complexes containing low-valent transition metal ions have been extensively investigated because of their potential involvement in catalytic processes such as olefin hydrogenation, hydroformylation, and polymerization.[1] In this framework, biomimetic complexes containing low-valent manganese are interesting because of their photochemistry as well as their significance in free-radical chemistry.[2]

Moreover, transition metal complexes containing low-coordinate metal centers have attracted some interest both from the fundamental and the applicative point of view. One prominent example is the reduction of dinitrogen to ammonia at the active site of the Fe−Mo cluster which occurs at a trisulfide coordinated Fe(II) center.[3] This has prompted chemists to create synthetic analogues with this unusual coordination geometry to fully analyze the electronic properties of this active site.[4] Following these efforts, a large reduction of the quenching of the orbital contribution to the magnetic moment which is caused by the smaller ligand-field effects in these systems has recently been observed in low-coordinated Fe(II) complexes.[5]

There is then an obvious interest in preparing new complexes containing low-valent and low-coordinated metal ions. Recently $[\{HC(CMeNAr)_2\}Mn]_2$ **(1)**, was obtained, containing the bulky β-diketiminate ligands,[4,6] which have been reported to have a high stabilization effect for these systems.[7] The coordination environment around each man-

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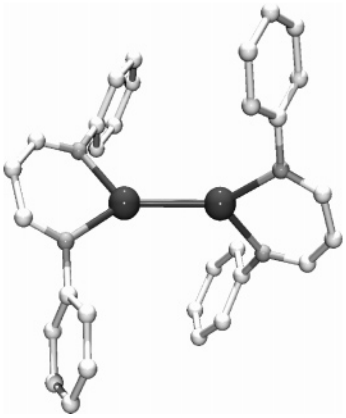

Figure 1. PovRay view of **1**: dark gray, Mn atoms; medium gray, N atoms; light gray: C atoms. ^{i}Pr groups and hydrogen atoms have been omitted for sake of clarity.

ganese center is a planar arrangement and consists of two nitrogen atoms of the chelating ligand and of the second manganese atom. The planes containing the coordination sphere of the two manganese centers are almost orthogonal to each other, forming a dihedral angle of 84.5° (Figure 1). The investigation of the electronic and magnetic properties of **1** lead to the conclusion that this is the first compound with Mn(I) in a high-spin configuration. Both DFT calculations and experimental data indicated a quite large antiferromagnetic coupling between the two units, which on the basis of the DFT results were shown to have an open shell ($3d^5 4s^1$) configuration on the Mn(I) ions. The interaction between the two singly occupied 4s orbitals results in a highly reactive single Mn−Mn σ bond that represents the HOMO of the molecule.[7] The remaining unpaired electrons, formally on 3d magnetic orbitals, are less strongly coupled resulting in a temperature-dependent magnetic moment. The magnetic data were fitted with a spin Hamiltonian $\mathbf{H} = J\mathbf{S}_a\mathbf{S}_b$ ($S_a = S_b = 5/2$ and $J = 110$ cm^{-1}).

One of the key issues in the elucidation of the electronic structure of these complexes is the determination of their magnetic anisotropy which could not be derived from the temperature dependence of the magnetic susceptibility and X-band EPR spectra. Therefore, we decided to characterize complex **1** by high-field high-frequency EPR spectroscopy at the W-Band. One of the advantages of this technique over conventional EPR is its ability to resolve the anisotropies of different multiplets, even in the presence of large zero-field splitting and integer spin states, thus giving access to information which would not be accessible by conventional EPR.[8] This makes HF-EPR particularly well suited for the analysis of exchange-coupled homodinuclear species that have a series of integer spin states for some of which conventional EPR might be unable to resolve the zero-field splitting (ZFS). We present here the first determination of ZFS parameters obtained by W-Band EPR spectroscopy of a Mn(I) dimer for three of the states resulting from the magnetic coupling between the ions. We qualitatively relate these values to single-ion properties and to the anisotropy of the exchange interaction.

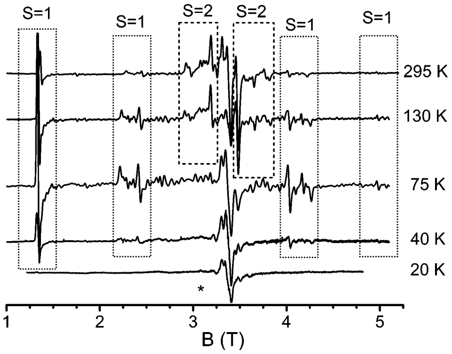

Figure 2. Temperature dependence of the EPR spectrum of **1**. The boxes show the series of signals belonging to the $S = 1$ (dotted) and $S = 2$ (dashed) states, respectively. The star indicates the spurious signal coming from the Mn(II) paramagnetic impurity present in the sample.

Experimental Section

Synthesis. Samples of **1** in crystalline form were obtained as previously described in ref 7.

EPR Spectroscopy. W-band (94 GHz) EPR spectra were recorded on polycrystalline powder samples of **1** with a Bruker ELEXSYS E600 CW spectrometer equipped with a 6 T split-coils superconducting magnet (Oxford Instruments). We used a Teraflex resonator with a cylindrical cavity operating in TE_{011} mode. A continuous flow ESR910 ^{4}He cryostat by Oxford Instruments was used to work at variable temperatures between 20 and 130 K. Because of the extreme air and light sensitivity of **1**, the sample was prepared in a glovebox in the absence of strong light by grinding freshly filtered crystals. These were transferred to a quartz tube which was sealed with wax and then inserted into a Schlenk flask to bring it close to the spectrometer. Transfer of the quartz tube to the sample holder and insertion into the cryostat under helium flow was performed in about 30 s to minimize the possible degradation of the sample. It was found out that, if it was stored under helium or nitrogen flow, the sample was stable for about 1 day. A preliminary remark has to be made concerning the quality of the spectra we obtained; because of the high reactivity of complex **1** it was impossible to completely block the powder and avoid partial orientation of the microcrystalline grains, a phenomenon that manifested itself in an increased “noise” of the spectra. However, apart from this effect, the measured spectra showed a satisfactory and reproducible powder pattern.

Simulation of the Spectra Variable-temperature spectra were simulated using a program written by H. Weihe.[9] The program is based on full diagonalization of the matrix of the chosen spin Hamiltonian.

Results

The temperature-dependent powder W-Band EPR spectra of **1** are shown in Figure 2.

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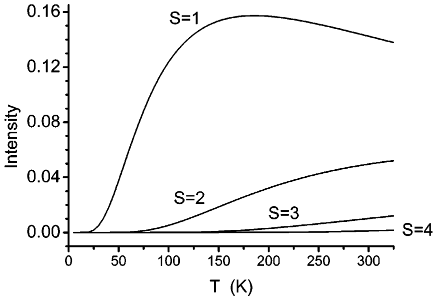

Figure 3. Expected intensity, on an arbitrary scale, of the EPR signal for excited multiplets of two coupled $S = 5/2$ spins assuming $J = 110$ cm^{-1}.

With the exception of a small paramagnetic impurity at $g = 2.00$, most probably caused by Mn(II) species resulting from the partial oxidation/degradation of the sample, the intensity of the spectrum at 20 K is virtually zero. This behavior is a signature of antiferromagnetic coupling resulting in an $S = 0$ ground state, as expected on the basis of the magnetic properties of **1**.[7] The presence of a detectable amount of paramagnetic impurity was already shown by magnetic susceptibility measurements. The increase in the intensity of the spectrum on increasing temperature is clearly the result of progressive population of different excited states. In particular, the spectrum observed at 40 K should be assigned to the $S = 1$ state. Indeed, for the two $S = 5/2$ spins coupled by an antiferromagnetic interaction, $J \approx 110$ cm^{-1}, as measured by the temperature dependence of the magnetic susceptibility, the relative intensities of the resonances coming from the higher excited states should be very close to zero at this temperature (see Figure 3). No evidence of the $S = 2$ or $S = 3$ states should be visible up to 100 or 250 K, respectively, so that the spectra belonging to these states can be easily identified with the new features appearing in the spectra observed at 130 and 295 K (Figure 2).

Because of the strong exchange coupling, we can safely treat the three populated spin states separately, using the second-order spin Hamiltonian $\mathbf{H}_i = \mu_B \mathbf{S}_i \mathbf{g}_i \mathbf{B} + D_i \mathbf{S}_{iz}^2 + E_i(\mathbf{S}_{ix}^2 - \mathbf{S}_{iy}^2)$ for each S_i multiplet and obtaining the global spectrum as the Boltzmann weighted sum of all the spectra.

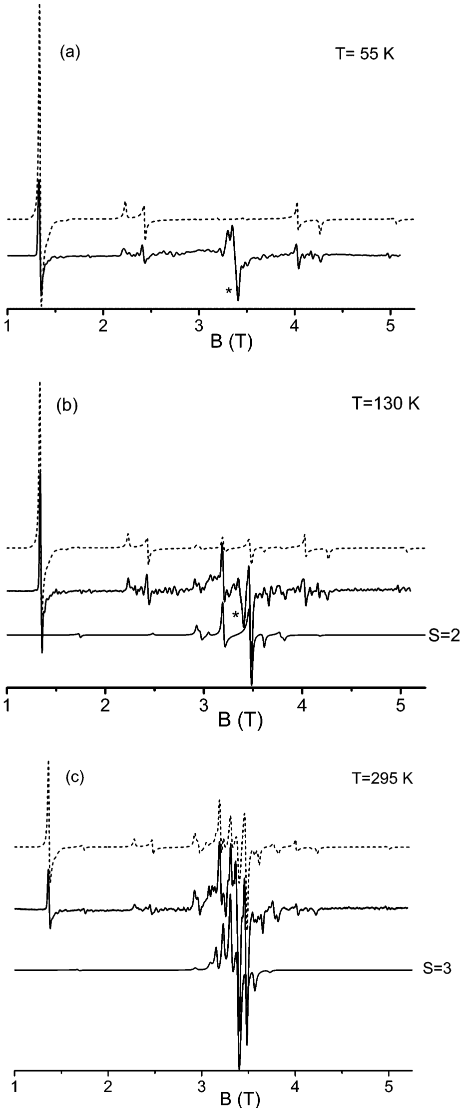

Figure 4. (a−c) Experimental (solid line) and simulated (dashed line) spectra at 55, 130, and 295 K. The lower trace in the 130 and 295 K spectra show the detail of the simulated contribution of the $S = 2$ and 3 multiplets, respectively. The asterisk indicates the signal attributed to the paramagnetic impurity.

Table 1. Best Simulation Parameters of W-Band Spectra for the Three Different Multiplets

	$S = 1$ (55 K)	$S = 1$ (300 K)	$S = 2$	$S = 3$
$\lvert D\rvert^a$	1.63	1.57	0.266	0.075
$\lvert E\rvert^a$	0.066	0.064	0.0045	0.00
g_x	2.00	2.00	2.00	2.004
g_y	2.00	2.00	2.00	2.004
g_z	2.02	2.02	2.02	2.02

[a] Values for D and E are in cm^{-1}.

In this respect, the features of the spectrum of the $S = 1$ state are quite clear: in addition to a strong resonance line at 1.35 T, two partially split perpendicular transitions are observed to be almost symmetrical around $g = 2.00$ ($B = 3.33$ T) at 2.35 and 4.20 T, respectively, while a parallel transition is observed around 4.95 T. In the strong field approximation, the two parallel and perpendicular high-field transitions for the $S = 1$ spin system should be separated by $D/2$,[10] and this allowed us to estimate $D = 1.61$ cm^{-1} as the starting value for the simulation. At the same time, the small splitting observed for the perpendicular transition can easily be attributed to a small transverse term in the spin Hamiltonian; the separation between the lines in first approximation is equal to $2E$. Figure 4a shows the best simulation of the 55 K spectrum (see Table 1 for the actual values of the parameters) obtained by considering the $S = 1$ state to be the only populated paramagnetic state at this temperature. With those parameters, we calculated that the strong transition at 1.35 T can be assigned to the formally forbidden $M_S = -1 \rightarrow 1$ transition. It is quite obvious that, despite the use of high magnetic fields, the determination of the sign of the ZFS cannot be accomplished. Indeed, because of the quite high temperature needed to observe a spectrum, depopulation effects within each multiplet are negligible. On the other hand, the large ZFS observed for an integer spin state would not have been resolved in a standard X-band EPR spectrum.

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This has indeed been a limiting factor in the investigation of coupled Fe(III) dimers in the past, for which the ZFS of the triplet state was usually too large to be observed.[11]

The determination and correct simulation of the features belonging to the $S = 1$ spectrum allow an easier assignment of the $S = 2$ spectrum. This is clearly observed to be less extended than the $S = 1$ one and thus can be anticipated to be characterized by a smaller D value. The separation between subsequent perpendicular transitions suggests $D \approx 0.3$ cm^{-1}, with a very small transverse anisotropy term indicated by their unresolved splitting. For this multiplet, the spin Hamiltonian parameters were obtained by simulating the spectrum at 130 K (see Table 1) where the $S = 3$ contribution should still be negligible (Figure 3).

Finally, the $S = 3$ spectrum could be identified in the 295 K experimental scan as a fine structure around $g = 2.00$, and it shows a very small extension of the spectrum. Because of the large overlap of its lines with those from the $S = 2$ state, its parameters (see Table 1) were determined with less confidence than those of the $S = 1$ and $S = 2$ states.

An interesting point related to the spectrum at 295 K is the reduction of the ZFS pertaining to the $S = 1$ state which manifests itself as a somewhat smaller extension of the spectrum at this temperature (see Figure 2). As a consequence, the best simulation at this temperature was obtained by imposing a reduction of about 5% with respect to the parameters obtained at 55 K, indicating a detectable temperature dependence of the ZFS. This difference may be the result of both single-ion and dipolar contributions which, being a function of the Mn−Mn bond length, should be quite sensitive to temperature variation.

It should be stressed here that for all of the measured temperatures the relative intensities of the spectral features belonging to different multiplets are well accounted for by the Boltzmann weighted population calculated assuming $J = 110$ cm^{-1}. Thus, the EPR spectra can be taken as an independent confirmation of the validity of the value of the antiferromagnetic exchange coupling constant obtained by magnetic studies.

Discussion

The ZFS anisotropy of exchange coupled pairs originates from three different contributions, namely single-ion anisotropy, through-space interactions (i.e., dipolar), and through-bond interactions between the two paramagnetic centers

$$\mathbf{H}_{\mathrm{ZFS}} = \mathbf{S}_{\mathrm{a}}\mathbf{D}_{\mathrm{a}}\mathbf{S}_{\mathrm{a}} + \mathbf{S}_{\mathrm{b}}\mathbf{D}_{\mathrm{b}}\mathbf{S}_{\mathrm{b}} + \mathbf{S}_{\mathrm{a}}\mathbf{D}_{\mathrm{ab}}^{\mathrm{dip}}\mathbf{S}_{\mathrm{b}} + \mathbf{S}_{\mathrm{b}}\mathbf{J}_{\mathrm{ab}}^{\mathrm{ex}}\mathbf{S}_{\mathrm{b}} \qquad (1)$$

where we neglected the antisymmetric term and higher-order contributions for the sake of simplicity. The zero-field splitting of each coupled state with spin S_i is related to $\mathbf{D}_{\mathrm{a}}$, $\mathbf{D}_{\mathrm{b}}$, $\mathbf{D}_{\mathrm{ab}}$, and $\mathbf{J}_{\mathrm{ab}}^{\mathrm{exc}}$ by the general tensorial relation

$$\mathbf{D}_{S_{\mathrm{i}}} = d_{\mathrm{a}}\mathbf{D}_{\mathrm{a}} + d_{\mathrm{b}}\mathbf{D}_{\mathrm{b}} + d_{\mathrm{ab}}\mathbf{D}_{\mathrm{ab}}^{\mathrm{dip}} + d_{\mathrm{ab}}\mathbf{J}_{\mathrm{ab}}^{\mathrm{exc}} \qquad (2)$$

where d_{a}, d_{b}, and d_{ab} are the projection coefficients which depend on S_i, S_{a}, and S_{b}.[12] As eq 2 is a tensorial relation, single crystal data at different temperatures are usually needed to separate the different contributions. A usual method for obtaining the value and the orientation of the single-ion ZFS tensor is to substitute one of the paramagnetic centers with a diamagnetic analogue.[13] On the other hand, the dipolar contribution is usually calculated in the frame of the point dipole approximation which holds quite well for pairs of metal ions, where the unpaired spin densities may be safely assumed to be localized on the ions themselves. For complex **1,** the possiblity of recording single-crystal EPR data was out of question because of the extreme air sensitivity of the compound. However, the extreme simplicity of the molecular structure of **1** allowed us to draw some obvious assumptions about the anisotropy axis direction, thus solving the problem. Referring to Figure 1, if we assume an idealized C_{2v} symmetry, the 2-fold symmetry axis which coincides with the Mn−Mn bond will be one of the principal directions of both the single-ion anisotropies and the global one.[14] Following ligand-field arguments, we can assume that the second and third principal directions of the single-ion anisotropy will be determined by the π interactions of Mn(I) with the ligands. Thus, one will intuitively lie in the plane of the C_3N_2Mn ring, and the other will be perpendicular to it. In this framework, we consider the single-ion ZFS tensors on the Mn ions to differ only in their orientation, not in their principal values. One of the tensors is rotated by 85° around the Mn−Mn direction with respect to the other one. It has to be noted that the Mn−Mn direction is obviously also the principal direction of the dipolar tensor. The situation is depicted in Figure 5.

As we mentioned above, the dipolar term can be calculated at the simplest level of approximation by using the point-dipole model, which yields $D_{xx,yy}^{\mathrm{dip}} = 0.088$ cm^{-1} and $D_{zz}^{\mathrm{dip}} = -0.176$ cm^{-1}.

To evaluate the exchange-determined anisotropy, which comes from spin−orbit coupling, mixing excited states into the ground state, the so-called *Moriya approximation*[15] is commonly used, which estimates the $\mathbf{J}_{ij}^{\mathrm{ex}}$ tensors through the relation $\mathbf{J}_{ij}^{\mathrm{ex}} \propto (\Delta\mathbf{g}/g_{\mathrm{e}})^2 J$. It is then usually assumed that $\mathbf{J}_{ij}^{\mathrm{ex}} \approx 0$ for centers with $g \approx \mathrm{g}_{\mathrm{e}}$ (like organic radicals and S ions such as Mn(II), Fe(III), Gd(III)).[12] However neglecting this term for large J values (>30 cm^{-1}) can lead to serious drawbacks, so we will also consider this contribution to the total anisotropy in the following. The only assumption we made was the collinearity of $\mathbf{J}_{\mathrm{exc}}$ with the global

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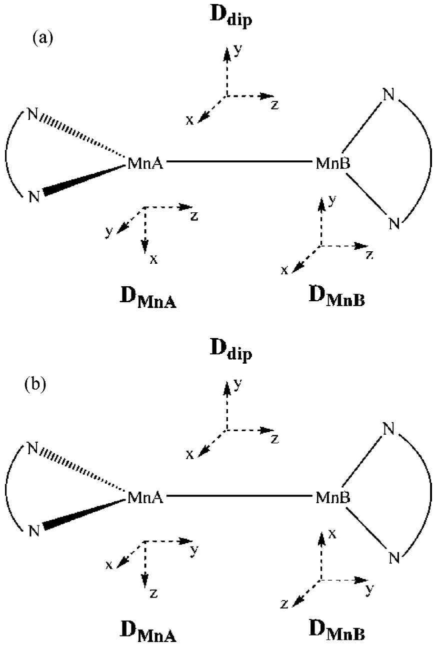

Figure 5. Relative orientation of dipolar and single-ion contributions for the decomposition of the zero-field-splitting tensors of the three coupled states: (a) single-ion *z* axis parallel to the Mn−Mn bond (corresponding to entries I and II in Table 2) and (b) single-ion *z* axis of Mn centers perpendicular to MnN_2 plane (corresponding to entries III and IV in Table 2).

Table 2. Calculated Single-Ion and Exchange-Determined Contribution on the Basis of Different Assumptions for the Orientation of Local Tensors[a]

	D_{Mn} (cm^{-1})	D_{exc} (cm^{-1})
I	−0.19(0)	0.24(0)
II	0.19(2)	+ 0.11(3)
III	−0.19(2)	+ 0.11(3)
IV	+0.19(1)	+ 0.24(0)

[a] I: $D_{S=1}$, $D_{S=2}$, and $D_{S=3} > 0$ collinearity of local *z* axes. II: $D_{S=1}$, $D_{S=2}$, and $D_{S=3} < 0$ collinearity of local *z* axes. III: $D_{S=1}$, $D_{S=2}$, and $D_{S=3} > 0$ collinearity of local *x* axes. IV: $D_{S=1}$, $D_{S=2}$, and $D_{S=3} < 0$ collinearity of local *x* axes.

anisotropy of the system. Rewriting eq 2 for the three spin states $S_i = 1$, 2, and 3 by using the appropriate d_a, d_b, and d_{ab} values, we obtain a system of linear equations whose solutions depend on the choice that is made for the relative orientations of the principal directions of the single-ion anisotropy with respect to the global one and to the sign of the latter. The problem is strongly simplified if we assume that the tilt between the two planes is exactly 90° because this leads to a simple swap of two of the single-ion anisotropy axes on the two Mn(I) centers (see Figure 5). Furthermore, in this assumption, the single-ion *E* terms of the two centers perfectly cancel each other, and we can then neglect them.

Even with this simplification there are 16 different possible combinations because of the uncertainty on the sign of the global anisotropy for the three multiplets. However, only 4 of the corresponding linear systems have best fit solutions of good quality. All of them are obtained for the combinations (see Table 2) derived assuming the same sign for the global anisotropy of the three coupled states. The coupled state $|D|$ values obtained with the four sets of parameters reported in Table 2 are $D_{S=1} = 1.58$ cm^{-1}, $D_{S=2} = 0.275$ cm^{-1}, and $D_{S=3} = 0.068$ cm^{-1} (*D* is defined as $^3/_2$ of the largest principal component of the **D** tensor), which are in very good agreement with the values actually obtained by simulations in the strong-exchange picture. Finally, the four combinations give very similar estimates for $|D_{Mn}|$ and $|D_{exc}|$ so that the results obtained can be considered to be reliable. As far as the *E* term is concerned, it is clear from what we said that any transverse term of the coupled state should have its main source in the exchange-determined contribution. Even if the simplified model we have adopted is insufficient to account for all the details of the spectra we might conclude that the simulations parameters suggest a E_{exc}/D_{exc} value of ~0.1.

The value of D_{Mn} obtained through the outlined procedure deserves some comment. In ref 7, the question of whether the ground state of the Mn(I) configuration was ^{5}D, ^{7}S, or ^{6}S (the 4s electrons being involved in the σ bond between the two Mn(I) centers) was essentially solved by results of DFT calculation in favor of the latter hypothesis. On the basis of the value obtained for D_{Mn} we can rule out the ^{5}D hypothesis for Mn(I) center (i.e, a high-spin $3d^6$ configuration). Indeed, in a low-coordination environment like that experienced by the Mn(I) centers in **1**, the orbital component ($L = 2$) of the ^{5}D state should be only partially quenched, resulting in a large anisotropy. On the other hand, even if the value of D_{Mn} is a bit larger than that reported for oxo-bridged Mn(II) dimers,[16] it is in the range expected for ^{6}S ions[17] and thus lends further support to the hypothesis of the $S = 5/2$ spin configuration obtained using DFT calculations.

Conclusions

We have successfully obtained for the first time HF-EPR spectra of a Mn(I)-containing species. The temperature-dependent spectral behavior of the dimer molecule $[\{HC(CMeNAr)_2\}Mn]_2$ confirmed the existence of a relevant exchange coupling (ca. 100 cm^{-1}) between the two metal centers, as previously shown by magnetic measurements. Simulations of the spectra at different temperatures allowed us to obtain the zero-field-splitting parameters for the excited multiplets $S = 1$, 2, and 3. Despite the impossibility of obtaining single-crystal spectra we were also able, on the basis of simple assumptions, to obtain an estimate of the different contributions to the zero-field splitting of the coupled states. The results we obtained suggest a non-negligible role of the exchange-determined term and indicate a quite small value of the single-ion anisotropy ruling out the possibility of a $3d^6$ configuration for Mn(I) centers and confirming the results formerly obtained by DFT calculations.

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