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Supplementary Material Available: Physical and spectral data for **3**, **4**, **5**, and **11** plus graphs showing kinetic data on enzyme assays (4 pages). Ordering information is given on any current masthead page.

Magnetic Phase Transitions in Manganese(II) Pentafluorobenzoate Adducts with Nitronyl Nitroxides

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Magnetic phase transitions of molecular materials are currently of large interest, particularly those leading to a permanent magnetic moment. Several different approaches are used in order to obtain three-dimensional order, and among them one particularly interesting is that of assembling in lattice spins with largely different moments, such as $S = 5/2$ and $S = 1/2$, in order to take advantage of the large moments which result either from a parallel or an antiparallel orientation of the individual spins. According to this procedure ferrimagnetic chains have been obtained,[2-6] and eventually three-dimensional ordered ferromagnets have been reported.[3-6]

We have followed an approach which uses metal ion hexafluoroacetylacetonates, $M(hfac)_2$, coupled to nitronyl nitroxides, NITR (NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide, R = methyl, ethyl, propyl, and phenyl), to synthesize one-dimensional ferri- and ferromagnetic chains,[6,7] but, although comparatively strong intrachain interactions are developed, the transitions to three-dimensional magnetic order occur at relatively low temperature due to the fact that the chains are fairly well shielded from each other. In particular we have found that compounds of formula $Mn(hfac)_2NITR$ order ferromagnetically at ca. 8 K.[6]

In order to increase the transition temperature we decided to use metal salts which are more suitable to give intermolecular interactions, and our choice fell on carboxylates which are well known to yield complex magnetic structures.

We found that manganese(II) pentafluorobenzoate dihydrate, $Mn(F_5benz)_2{\cdot}2H_2O$, reacts with NITR[8] radicals (R = methyl and ethyl) to yield blue-violet microcrystalline compounds, as shown by powder diffractograms, of formula $[Mn(F_5benz)_2]_2NITR$,[9] which resisted all our attempts to grow crystals suitable for X-ray analysis but showed interesting magnetic phase transitions at ca. 24 and 20.5 K for R = methyl and ethyl, respectively.

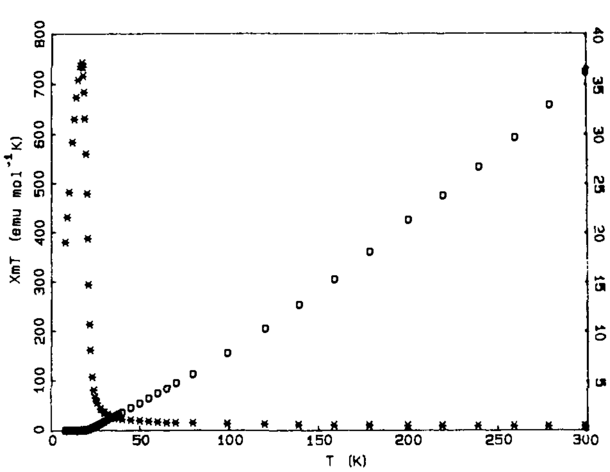


Figure 1. χT (*) and χ^{-1} (O) values for $[Mn(F_5Benz)_2]_2NITEt$ in an external field of 100 Oe.

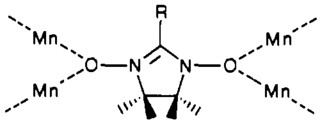
The electronic spectra of $[Mn(F_5benz)_2]_2NITR$ show an intense absorption at 18 500 cm^{-1} typical of the n → π* transition of the radicals,[10] confirming that they do not undergo redox reactions.

The IR spectra suggest that the pentafluorobenzoates are not monodentate, but we cannot distinguish the chelate and bridging structures because the differences of the frequencies in the two types of coordination are too small.[11]

The temperature dependence of the inverse molar susceptibility of $[Mn(F_5benz)_2]_2NITEt$, shown in Figure 1, is loosely reminiscent of that of a bulk ferromagnet, with θ ca. 25 K, but the continuous variation of the slope of χ^{-1} vs T indicates that the Curie-Weiss law is not followed and suggests the presence of short range order typical of low-dimensional magnetic materials. The behavior of $[Mn(F_5benz)_2]_2NITMe$ is similar.

The room temperature value of $\chi T = 8.28$ emu mol^{-1} K is lower than that expected for two spins 5/2 and one spin 1/2, all with isotropic g equal to the free electron value, completely uncorrelated (9.15 emu mol^{-1} K) indicating the presence of antiferromagnetic coupling between the spins of manganese(II) and that of radical, as has been previously observed in a few manganese(II)-nitroxide complexes.[12-14] χT increases slowly on lowering temperature indicating that the Mn_2NITR moieties are not isolated.

A possibility to reconcile the stoichiometry of the complex and the magnetic properties is that of a structural pattern as shown below, in which each radical is bound to four different manganese ions, each of them being shared by two different radicals.



Antiferromagnetic coupling between manganese and radicals keeps all the metal spins parallel to each other, yielding a large uncompensated moment at low temperature. With these blocks

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(9) The compounds were synthesized suspending 0.25 mmol of $Mn(F_5Benz)_2{\cdot}2H_2O$ in 40 mL of hot toluene and adding 0.25 mmol of the radical. After stirring for 10 min at 50-60 °C the suspension turned from pink to violet color. The fine microcrystalline precipitate was filtered and dried under vacuum. Anal. Calcd for $[Mn(F_5Benz)_2]_2NITEt$: Mn, 9.75; C, 38.98; H, 1.49; H, 2.46. Found: Mn, 9.98; C, 38.14; H, 1.61; N, 2.39. Anal. Calcd for $[Mn(F_5Benz)_2]_2NITMe$: Mn, 9.87; C, 38.40; H, 1.33; N, 2.49. Found: Mn, 10.02; C, 38.38; H, 1.65; N, 2.58.

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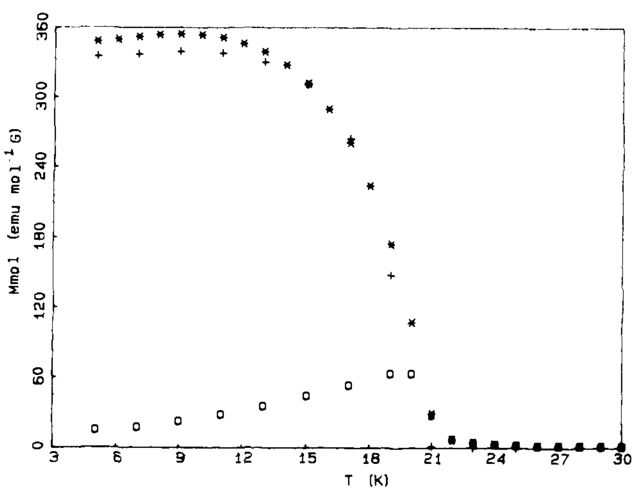

Figure 2. (*) FC magnetization; (+) remnant magnetization; (O) ZFC magnetization of $[Mn(F_5Benz)_2]_2$NITEt in low field (H = 1 Oe).

either chain or layer structures can be built, but it is not possible to suggest a crystal structure owing to the large number of different coordination modes of the carboxylates.

If we compare the χT values in the paramagnetic region of $[Mn(F_5benz)_2]_2$NITR with those of the ferrimagnetic manganese radical chains we see that the values for the latter start to increase at higher temperature than those of the two present compounds suggesting that in these the coupling is smaller. On the other hand, the powder EPR spectra of $[Mn(F_5benz)_2]_2$NITR show a single line at $g = 2$ which is much narrower than those observed for $Mn(hfac)_2$NITR chains (35 G against 150 G) implying that the exchange narrowing regime is more efficient for the present compounds.[15,16] These results can be attributed to a magnetic dimensionality larger than one for $[Mn(F_5benz)_2]_2$NITR, which makes the narrowing mechanism more efficient than in linear chain systems.

Below 40 K an abrupt increase in the slope of χT is observed, suggesting that the system approaches a magnetic phase transition. Low field (0–1 Oe) magnetization measurements were performed with a SQUID magnetometer,[17] and the results for $[Mn(F_5benz)_2]_2$NITET are shown in Figure 2. The data show that the compound orders three dimensionally below 20.5 K. Analogous measurements on $[Mn(F_5benz)_2]_2$NITMe show a transition at 24 K. In Figure 2 we report also the remnant and the zero field cooling (ZFC) magnetizations. Both the high remnant magnetization and the low ZFC one indicate scarce mobility of the domain walls. This may be due to the fact that the measurements were performed on polycrystalline powders. The hysteresis loop at 4.2 K, shown in Figure 3 for $[Mn(F_5benz)_2]_2$NITMe, indicates that both the coercitive field and the residual magnetization are fairly large. Moreover fluxmetric measurements at 4.2 K have shown that for both compounds the remnant magnetization is stable in time.

Magnetization curves at 10 K in the field range 0.5–45 KOe show an initial saturation to $M \cong 5000$ emu mol^{-1} G in a field of 500 Oe, then a second saturation to $M \cong 10\,000$ emu mol^{-1} G in a field of 10 000 Oe and finally a linear increase without reaching a saturation in the maximum field available of 45 000 Oe, inducing as to exclude the ferromagnetic nature of the transition. The slopes of the $M(H)$ curves above 10 kOe indicate the presence of antiferromagnetic interactions whose value can be roughly evaluated from the equation[18]

$$\chi_\perp = \frac{dM}{dH} = \frac{N_g^2\mu_B^2}{2z|J_{AF}|}$$

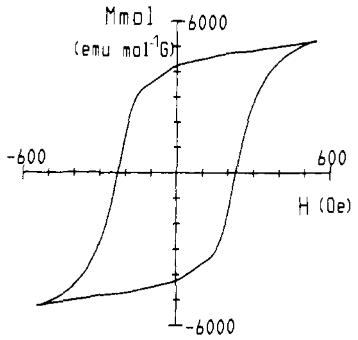

Figure 3. Hysteresis loop for $[Mn(F_5Benz)_2]_2$NITMe at 4.2 K.

yielding $2z|J_{AF}|/k \simeq 4$ K, where z is the number of nearest neighbors.

These data are in agreement with either ferrimagnetism or weak ferromagnetism. Spin canting has previously been observed in manganese(II) compounds[19,20] and has been attributed to local anisotropy (i.e., the principal axes of the zero field splitting tensor are not equally oriented for ions occupying not equivalent positions). If we consider the value of magnetization reached in low magnetic field (500 Oe) as corresponding to the saturation of the magnetic moments arising from the misalignment of the spins we find that it corresponds to an unusually high value of canting.

A ferrimagnetic structure with a net moment lower than that expected for spin $S = 5/2 + 5/2 - 1/2$ can explain the present data, but no unique choice is possible due to the lack of information on the crystal structure and of single crystal measurements.

The present results show that substitution of hexafluoroacetylacetonates with carboxylates in manganese radical species increases dramatically the magnetic transition temperature, raising it at the highest value so far reported in molecular materials which have a well defined and constant chemical analysis.

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Total Synthesis of (+)-Koumine, (+)-Taberpsychine, and (+)-Koumidine

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(–)-Koumine (1), the principal medicinal constituent of the Chinese plant *Gelsemium elegans* Benth., was first isolated in 1931.[1] In 1981 its structure was elucidated by single-crystal X-ray crystallography.[2] The absolute stereochemistry[3] was established by partial synthesis from vobasine.[4] Here we report the total

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