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Interpenetrated 3D Polymeric Metal−Radical Networks Built from a Tetranitroxide Radical and Bis(hexafluoroacethylacetonato) Manganese(II)

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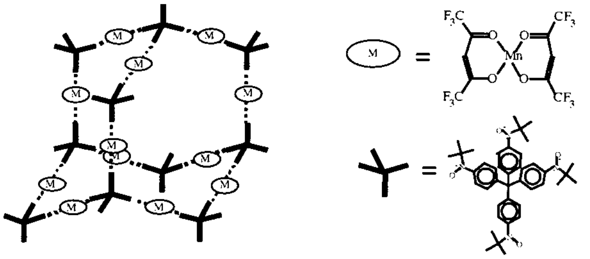
Physical properties in molecular-based materials depend mainly on intermolecular cooperation. Therefore, any progress in mastering the assembly of molecules in the solid state is of general concern to numerous fields such as magnetism as well as electronic or nonlinear optical materials for example.

In the field of molecular-based magnets most of the chemical routes aim to the building of 3D networks as a prerequisite to high Curie temperatures (T_c) below which a material behaves like a magnet.,[1−5] In this frame, the metal−radical approach, in which radicals are used as bridging ligands for metal ions, is particularly appealing for it combines both the versatility of organic and inorganic spin carriers, which moreover interact generally strongly.[4,6] Following this way, and using chelating nitronyl nitroxide radicals, we successfully synthesized and characterized layered 2D compounds with honeycomb structures and T_c below 50 K.[7,8] In an other approach K. Inoue and H. Iwamura, using polynitroxide radicals, have succeeded to synthesize 2D and 3D metal−radical coordination polymers with T_c up 50 K.[9−11] The latter was, to now, the unique example of 3D network among this class of compound.

Taking advantage of these works we synthesized the tetrakis-[4-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]methane (tetranitroxide).[12] Indeed, several publications have shown that the use of molecular blocks based on the substituted tetraphenylmethane unit lead efficiently to the building of organic and inorganic 3D frameworks.[13−17]



We report herein the crystal structure and magnetic properties of {**[Mn(hfac)$_2$]$_2$(tetranitroxide)**}$_n$ (hfac = hexafluoroacetylacetonate) obtained by slow interdiffusion of a heptane solution containing dehydrated Mn^{II}(hfac)$_2$ in a dichloromethane solution of the tetranitroxide[18]

{**Mn(hfac)$_2$]$_2$(Tetranitroxide)**}$_n$ crystallizes in the tetragonal $P4_12_12$ space group.[19] The asymmetric unit which comprises one tetranitroxide ligand and two Mn(hfac)$_2$ units is shown in Figure 1. Both Mn^{II}(hfac)$_2$ units coordinate two nitroxide groups in a *cis* conformation, but the two crystallographically independent maganese(II) ions Mn1 and Mn2 have opposite octahedral configuration respectively Δ and Λ. The crystal structure is shown in Figure 2; it consists of two independent and neutral 3D polymeric metal−radical networks of the diamond type, which interpenetrate in a fashion similar to those found for Zn(CN)$_2$.[14,15]

Each Mn(hafc)$_2$ unit bound two nitroxide groups to have the Mn(II) ions octahedral and act as an anchorage node for two tetranitroxide units which promote the three-dimensional building. Each of the two interpenetrated networks are built separately from four of the eight independent positions of the crystal group.[20] The interpenetrated networks have the effect to fill partially the large cavities induced by the 3D structure and increase the crystal packing. However, the density is still very low ($d = 1.269$ g cm^{-3}) if compared with other hexafluoroacetylacetonato derivatives ($d_{\mathrm{mean}} = 1.60$ g cm^{-3}). As has already been mentioned, the crystal structure is reminiscent of catenane compounds in the way that the two infinite networks interlock.

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(12) **Tetrakis[4-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]methane:** To a solution of tetrakis(4-bromophenyl)methane (1.3 g, 2 mmol) in freshly distilled THF (50 mL) was added *n*-butyllithium (2.5 M in hexane, 4 mL, 10 mmol) at −78 °C. The mixture was warmed slowly at room temperature over a period of 1 h and then cooled again at −78 °C prior to addition of 2-methyl-2-nitrosopropane (800 mg, 4.5 mmol of the dimer). After warming and stirring for 12 h at room temperature, a saturated NH$_4$Cl aqueous solution (20 mL) was added to the resulting mixture. The THF solution was separated, and the aqueous phase was extracted with ethyl ether. After gathering the organic phases, they were washed with water, dried over Na$_2$SO$_4$, and evaporated. The residue containing tetrakis[4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]-methane was dissolved in CH$_2$Cl$_2$ (100 mL) and cooled over ice. An aqueous solution of NaIO$_4$ (900 mg, 4 mmol) was then added and the mixture turned red. After strong stirring for 30 min the organic phase containing a mixture of unreacted material with mono-, bis-, tris- and tetraradicals was separated and the aqueous phase extracted with dichloromethane. The organic phases were gathered and evaporated. The residue was chromatographed on silica with a mixture (1:1) of diethyl ether and petroleum ether. The mono-, bis-, tris-, and tetranitroxide were identified by EPR spectroscopy. The tetranitroxide, was then twice recrystallized by vapor diffusion of ethyl ether in a dichloromethane-saturated solution to give red needlelike crystals which are stable for long period of time. (300 mg, 23%). FW = 664.9 mp = 220−225 °C.

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(18) {**[Mn(hfac)$_2$]$_2$(tetranitroxide)**}$_n$. (hfac = hexafluoroacetylacetonate) Mn(hfac)$_2$·2H$_2$O (50 mg, 0.01 mmol) was dissolved in 10 mL of boiling heptane to azeotropically remove hydratation water molecules. After complete dissolution a few drops of dichloromethane were added to avoid crystallization upon cooling at room temperature. The resulting solution was put in a test tube (10 × 200 mm) on the top of a solution of the tetranitroxide (33 mg, 0.005 mmol) in 10 mL of dichloromethane. Small dark crystals were obtained after 10 days of interdiffusion of the solutions. Anal. Calcd for Mn$_2$C$_{61}$H$_{56}$F$_{24}$N$_4$O$_{12}$: Mn, 6.85; C, 45.71; H, 3.52; F, 28.45; N, 3.50; O, 11.98. Found: Mn, 6.80; C, 45.65; H, 3.57; F, 28.63; N, 3.48.

(19) **Crystallography:** Data collected at room temperature on a Bruker SMART CCD diffractometer ($\lambda = 0.71073$?) were processed through the SAINT reduction software to give 67398 measured reflections and 21301 independent. The structure was solved and refined on F^2 using the SHELXTL software. C$_{61}$H$_{56}$N$_4$O$_{12}$F$_{24}$Mn$_2$, MW = 1602.98, dark red, parallelepiped crystal, tetragonal, $P4_12_12$ (No 92), $a = 20.1716(5)$ and $c = 41.230(2)$ Å, $V = 16776.2(9)$ Å^3, $Z = 8$, $R(\mathrm{int}) = 0.1053$, $R(F) = 0.0761$ [$I < 2\sigma(I)$], $wR(F^2) = 0.2495$ (all data).

(20) ($x, y, z; -x, -y, z + {}^1/_2; -y + {}^1/_2, x + {}^1/_2, z + {}^1/_4; y + {}^1/_2, -x + {}^1/_2, z + {}^3/_4$) and ($y, x, -z; -y, -x, -z + {}^1/_2; -x + {}^1/_2, y + {}^1/_2, -z + {}^1/_4; x + {}^1/_2, -y + {}^1/_2, -z + {}^3/_4$).

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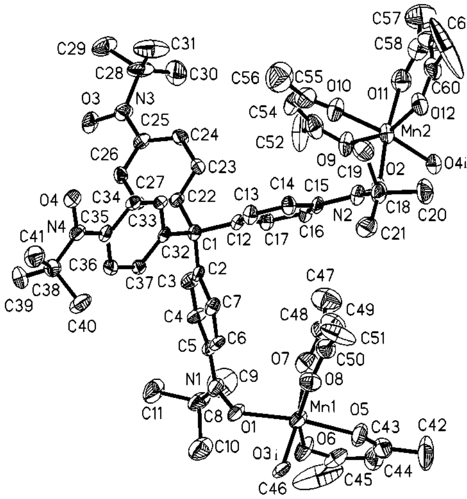

Figure 1. Molecular building block $\{[\mathrm{Mn(hfac)_2}]_2(\text{tetranitroxide})\}$. The fluorine atoms are omitted for clarity. Selected bonds (Å) and angles (deg). O−N = 1.288(4)−1.302(4), Mn1−O3*i* = 2.096(2), Mn1−O1 = 2.105(2), Mn2−O4*ii* = 2.098(2), Mn2−O2 = 2.098(2)•, Mn1−O(hfac) = 2.131(3)−2.161(4), Mn2−O(hfac) = 2.106(3)−2.142(4), Mn−O−N = 128.5(3)−131.1(3). $i = y - {}^{1}/_{2}, -x + {}^{1}/_{2}, z - {}^{1}/_{4}$, $ii = y + {}^{1}/_{2}, -x + {}^{1}/_{2}, z - {}^{1}/_{4}$.

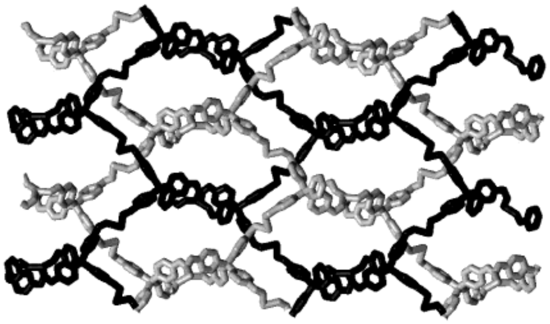

Figure 2. The crystal structure showing the two interpenetrated 3D networks projected along [010] direction. The hfac and *tert*-butyl groups are omited for clarity.

The product of the magnetic susceptibility with temperature ($\chi_{\mathrm{mol}}T$) is 4.0 emu K mol^{-1} at 300 K for the molecular unit $\{[\mathrm{Mn(hfac)_2}]_2(\text{tetranitroxide})\}$[21] (see Figure 3). Upon cooling it decreases only a little down to 60 K (3.75 emu K mol^{-1}), and more abruptly below. The value at 300 K is smaller than expected if the two manganese(II) ions ($S = {}^{5}/_{2}$) and the four nitroxide radicals ($S = {}^{1}/_{2}$) were magnetically independent ($\chi_{\mathrm{mol}}T = 10.50$ emu K mol^{-1}). Furthermore, in the range 300−60 K $\chi_{\mathrm{mol}}T$ is consistent with strong antiferromagnetic couplings between the manganese(II) ions and the two coordinated nitroxide radicals.

This leads to a ground spin state $S = {}^{3}/_{2}$ ($\chi_{\mathrm{mol}}T = 3.75$ emu K mol^{-1} for two $S = {}^{3}/_{2}$). The decrease observed below 60 K suggests that the resulting spin $S = {}^{3}/_{2}$ are weakly and antiferromagnetically coupled in the solid state which prevents any magnetic behavior. Accordingly, the temperature dependence of the magnetic susceptibility was fitted considering three spin units $S2-S1-S3$ ($S1 = {}^{5}/_{2}$ and $S2 = S3 = {}^{1}/_{2}$) in which $S1$ is antiferromagnetically coupled (J) with $S2$ and $S3$ [$F(J,T)$].[22] An additional coupling ($Z'J'$) based on the molecular field approximation was introduce in the fitting process (χ_{fit}) to take into account the magnetic behavior at low temperature.[23,24] The best fit was obtained for $J = -200$ cm^{-1}, $Z'J' = -0.1$ cm^{-1}, $g = 2.05$. A value of −200 cm^{-1} for the manganese(II)−nitroxide interaction is in agreement with previous finding.[6] The −0.1 cm^{-1} value for $Z'J'$ could be reasonably attributed to through-space intermolecular interactions rather than the coupling through the tetranitroxide. Indeed, the shortest intramolecular distance between the manganese(II) ions through the tetranitroxide bridging ligand calculated by summing all of the bond lengths is 20.907(3) Å, while the shortest intermolecular distance is 10.027(3) Å. Moreover the central sp^3 carbon (C1) is not expected to mediate strong superexchange interactions.

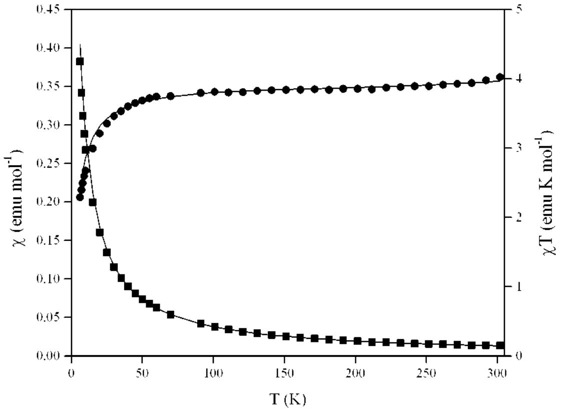

Figure 3. Temperature dependence of the magnetic susceptibility χ_{mol} (●) and of its product with temperature $\chi_{\mathrm{mol}}T$ (■). The solid lines represent the best-fit curves.

Despite the lack of spontaneous magnetization the present compound is a rare example of 3D metal−radical coordination polymer. Furthermore, it highlights the strength and usefulness of metal coordination chemistry in supramolecular engineering.

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Supporting Information Available: Crystallographic data for compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] The magnetic susceptibilities were measured on the polycrystalline sample in the temperature range 2−300 K with a Quantum Design MPMS SQUID magnetometer at a field strength of 0.5 T. The data were corrected for atomic diamagnetism using Pascal constants.

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[24] $\chi_{\mathrm{fit}} = 2\{F(J,T)/[1 - (2Z'J'/Ng^2\beta^2)F(J,T)]\}$ with $F(J,T)$ defined in ref 22.