

## Mn(II)-Induced Formation and Structural Elucidation of a [3 + 3] Benzene Dimer Derivative from *m*-Phenylenebis(*N*-*tert*-butylaminoxyl)

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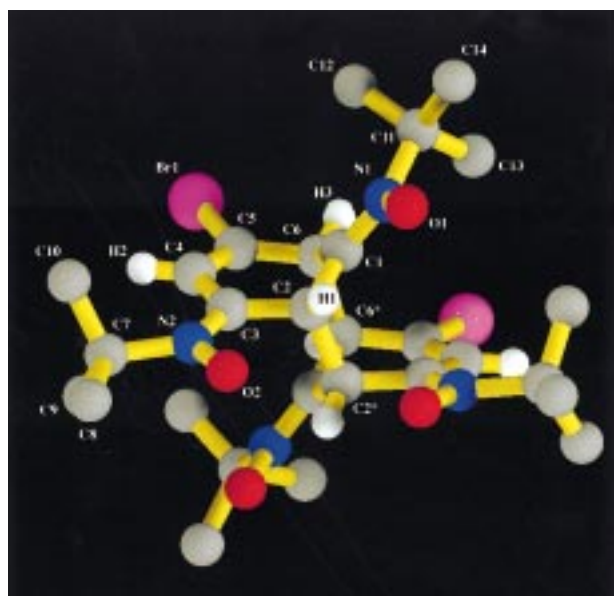
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We have recently developed a strategy for constructing ferrimagnetic polymer complexes by self-assembly of magnetic metal ions with bis- and tris(aminoxyl) radicals serving as bridging ligands.<sup>1</sup> Since a wide variety of magnetic structures having various dimensions and transition temperatures for magnets of at least up to 46 K are obtainable, optimization of the reaction conditions for pure crystalline samples is highly desirable. We report here an interesting side reaction leading to an undesired byproduct that has a unique [3 + 3] benzene dimer structure.

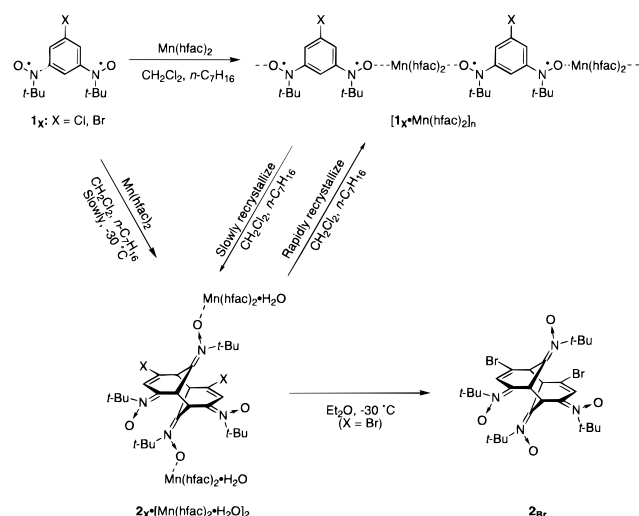
One-dimensional ferrimagnetic complexes,  $[\text{Mn}(\text{hfac})_2 \cdot \mathbf{1}_X]_n$  ( $X = \text{Cl}$  or  $\text{Br}$ ), are typically obtained by the reaction of  $\text{Mn}(\text{hfac})_2$  with  $\mathbf{1}_X$ .<sup>2</sup> When it takes a few days for crystallization, however, black solutions often turn yellow in  $\sim 1$  day and do not afford the expected, black polymer complexes. Instead yellow crystalline precipitates are obtained under these conditions (Scheme 1). A solution of 0.994 g (3.02 mmol) of  $\mathbf{1}_{\text{Br}}$ <sup>3</sup> in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added to a suspension of 1.417 g (3.02 mmol) of  $\text{Mn}(\text{hfac})_2$  in 20 mL of *n*- $\text{C}_7\text{H}_{16}$  at 0 °C and the mixture was stored at  $-30$  °C. After a few days, 2.032 g (1.18 mmol, 85.2%) of yellow needles of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  was obtained.

An X-ray structure analysis revealed that  $\mathbf{2}_X \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  has a [3 + 3] benzene dimer structure [ $X = \text{Cl}$  or  $\text{Br}$ ;  $\mathbf{2}_X = 3,10$ -dihalo-5,8,11,12-tetrakis(*N*-*tert*-butylimino)tricyclo-[5,3,1,1,2<sup>6</sup>]dodeca-3,9-diene *N,N',N'',N'''*-tetraoxide] (Figure 1).<sup>4</sup> Two crystallographically equivalent manganese(II) ions have an octahedral coordination and are coordinated with four oxygen



**Figure 1.** Molecular structure of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  and  $\text{H}_2\text{O}$  molecules, and hydrogen atoms of *t*-Bu and Mn(II)(hfac)<sub>2</sub> are omitted for clarity.

### Scheme 1



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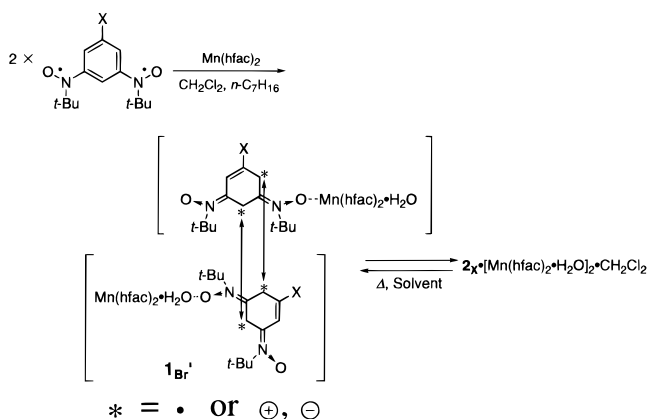
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(4) A yellow needle single crystal of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  (approximate dimensions  $0.20 \times 0.40 \times 0.90$  mm<sup>3</sup>) was mounted on a glass fiber.  $\text{C}_{49}\text{H}_{52}\text{N}_4\text{O}_{14}\text{F}_{24}\text{Cl}_2\text{Br}_2\text{Mn}_2$ ,  $M_r = 1717.53$ , monoclinic, space group  $P2_1/n$ ,  $a = 15.036(3)$  Å,  $b = 9.582(3)$  Å,  $c = 26.118(8)$  Å,  $\beta = 102.23(2)^\circ$ ,  $V = 3677(1)$  Å<sup>3</sup>,  $Z = 4$ . The final cycle of full-matrix least-squares refinement was based on 3680 observed reflections ( $I > 2.0\sigma(I)$ ) and 451 variable parameters and converged with agreement factor of  $R = 0.071$ ;  $\text{GOF} = 4.47$ .

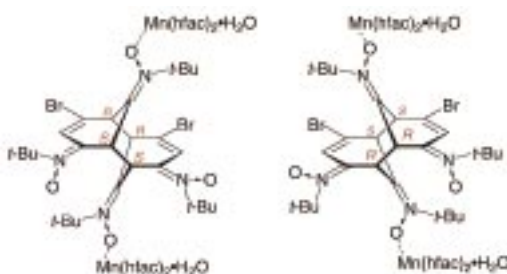
atoms of two hfac ligands, one oxygen atom of water, and one oxygen atom of O(1) of  $\mathbf{2}_{\text{Br}}$ . The Mn–O(1) distance is 2.176(4) Å. Four molecules of  $\text{CH}_2\text{Cl}_2$  are contained in each unit cell. In the  $\mathbf{2}_{\text{Br}}$  moiety, the bonds connecting the two six-membered rings, namely, C(2)–C(2)\* and C(6)–C(6)\*, are 1.55(1) and 1.59(1) Å, respectively. The torsion angles for N(1)–C(1)–C(2)–C(3) and N(1)–C(1)–C(6)–C(5) are 125.9(6) and 119.4(6)°, respectively. Whereas the dimer complex is chiral, both enantiomers are contained in each unit cell (Chart 1). The  $\mathbf{2}_{\text{Cl}}$  complex is isostructural to the bromine derivative.

Resonance structure  $\mathbf{1}_{\text{Br}}'$  must be responsible for the reaction leading to the dimer complex (Scheme 2),<sup>5</sup> either dimerization of  $\mathbf{1}_{\text{Br}}'$  or attack of  $\mathbf{1}_{\text{Br}}'$  to free and complexed  $\mathbf{1}_{\text{Br}}$ . In the absence of  $\text{Mn}(\text{hfac})_2$ , there is no dimerization but only a disproportionation reaction of  $\mathbf{1}_{\text{Br}}$  observed.<sup>3a</sup> Either at  $-30$  °C or at room temperature,  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  was obtained if crystallization was sufficiently slow ( $\sim 2$  days) and  $[\text{Mn}(\text{hfac})_2 \cdot \mathbf{1}_{\text{Br}}]_n$  was obtained when crystallization was fast ( $\sim 30$  min) (Scheme 1). The yellow color of a  $\text{CH}_2\text{Cl}_2/n$ -heptane (1:1) solution of  $\mathbf{2}_X$

## Scheme 2



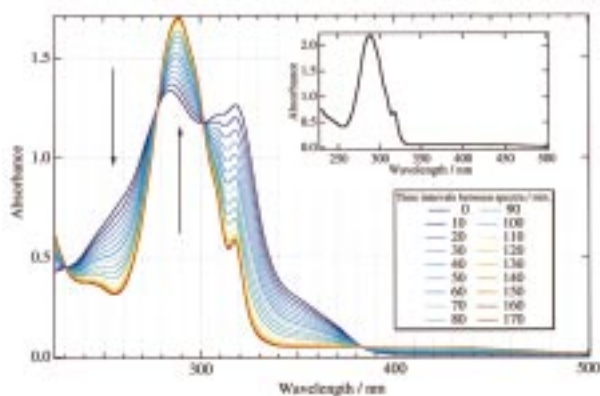
## Chart 1



$[\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  turned deep brown when the temperature was increased to room temperature. Whereas the one-dimensional ferrimagnetic complex  $[\text{Mn}(\text{hfac})_2 \cdot \mathbf{1}_{\text{Br}}]_n$  is a kinetic product and precipitates out of the solution at the earlier stage of the reaction, the yellow crystal of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  appears to be a thermodynamic product.

Another interesting feature of this work is the liberation of dimer ligand  $\mathbf{2}_{\text{Br}}$  free from manganese ions. When 540 mg (0.314 mmol) of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  was dissolved in 20 mL of  $\text{Et}_2\text{O}$  and the solution was stored at  $-30^\circ\text{C}$ , a white powder of  $\mathbf{2}_{\text{Br}} \cdot 2\text{H}_2\text{O}$  [150 mg (0.216 mmol, 68.8%)] free of  $\text{Mn}(\text{hfac})_2$  precipitated out in 30 min (Scheme 1).<sup>6</sup> Spectroscopic data on  $\mathbf{2}_{\text{Br}}$  are in good agreement with its structure.<sup>7</sup> Absorptions at 317 nm are assigned to the  $\pi-\pi^*$  transition for the  $\text{C}=\text{N}$  chromophores. The spectrum of  $\mathbf{2}_{\text{Br}}$  in  $\text{CH}_2\text{Cl}_2$  is time-dependent and converted eventually to that of monomeric biradical  $\mathbf{1}_{\text{Br}}$  ( $\pi-\pi^*$  transition characteristic of the arylaminoxyl at 290 nm) by showing four isobestic points at 235, 278, 302, and 381 nm as shown in Figure 2. The result indicates that the dissociation process of  $\mathbf{2}_{\text{Br}}$  into two molecules of  $\mathbf{1}_{\text{Br}}$  is very clean. The two water molecules of hydration appears to be crucial for the stability of  $\mathbf{2}_{\text{Br}} \cdot 2\text{H}_2\text{O}$ ; it is stable in water at  $100^\circ\text{C}$  but starts to decompose by dissociation even at  $-78^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  when dehydrated by molecular sieves.

A number of studies have been conducted on the dimerization of aromatic compounds.<sup>8,9</sup> Most of these compounds are formed



**Figure 2.** Time dependence of UV spectra for  $\mathbf{2}_{\text{Br}}$  in  $\text{CH}_2\text{Cl}_2$  at  $10^\circ\text{C}$ . Inset shows the UV spectrum of authentic  $\mathbf{1}_{\text{Br}}$ .

by a Diels–Alder-type cycloaddition reaction, i.e.,  $[2 + 2]$  or  $[2 + 4]$ .<sup>10</sup> Whereas catalysis of these reactions by Lewis acidic metal ions is also documented,<sup>11</sup> the structure of the complexes formed by the transition metal ions with the substrates are less well-known. Some reports have described the  $[3 + 3]$  cycloaddition of organic molecules but not of aromatic compounds.<sup>12</sup> Our work presented here on spectroscopic and crystallographic characterization of the  $\text{Mn}(\text{II})$ -induced aromatic  $[3 + 3]$  cycloaddition is second only to spectroscopic characterization of an aromatic  $[3 + 3]$  cycloaddition by Severin and Bohn.<sup>9</sup> The structural elucidation of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  would help shed light on the mechanistic detail of Lewis acid-catalyzed cycloaddition and free-radical reactions.<sup>13</sup>

Dimerization was also observed for the chlorine derivative  $\mathbf{1}_{\text{Cl}}$ , under similar conditions, and  $\mathbf{2}_{\text{Cl}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$  was characterized crystallographically by X-ray structure analysis in our preliminary work. The characterization of free benzene dimer derivative  $\mathbf{2}_{\text{Cl}}$  is now in progress.

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**Supporting Information Available:** Supporting Information includes spectral data and a description of the X-ray diffraction determination, molecular structure, and magnetic properties of  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2 \cdot \text{CH}_2\text{Cl}_2$ . Spectral data for  $\mathbf{2}_{\text{Br}}$  are available (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(6) Free  $\mathbf{2}_{\text{Br}}$  appears to be soluble in  $\text{Et}_2\text{O}$  but  $\mathbf{2}_{\text{Br}} \cdot 2\text{H}_2\text{O}$  is not. Hence, when  $\mathbf{2}_{\text{Br}} \cdot [\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}]_2$  is dissolved in  $\text{Et}_2\text{O}$ , the dissociated free  $\mathbf{2}_{\text{Br}}$  and  $\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}$  would hydrate the former and precipitated out  $\mathbf{2}_{\text{Br}} \cdot 2\text{H}_2\text{O}$  within 30 min. The  $\text{Mn}(\text{hfac})_2$  moieties are considered to be dissolved in  $\text{Et}_2\text{O}$  and left in solution.

(7)  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{OD}$ ,  $-30^\circ\text{C}$ )  $\delta$  1.588 (s, 18H), 1.596 (s, 18H), 4.787 (s, 2H), 6.089 (s, 2H), 7.626 (s, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{OD}$ ,  $-30^\circ\text{C}$ )  $\delta$  28.26, 29.14, 37.56, 52.35 (*tert*-butyl), 73.67, 73.71 (C2, C6), 118.6 (C5), 128.0 (C4), 140.0, 142.3 (C1, C3); IR (KBr) 1645 ( $\nu_{\text{C}=\text{N}}$ ), 1215 ( $\nu_{\text{N}-\text{O}}$ ), 745  $\text{cm}^{-1}$  ( $\nu_{\text{C}-\text{Br}}$ ). Anal. Calcd for  $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$ : C, 48.42; H, 6.68; N, 8.07. Found: C, 48.64; H, 6.74; N, 7.98.

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