

{2,5-Bis[3-(*tert*-butylaminoxyl)-phenyl]-1,1-dimethyl-3,4-diphenylsilole- κ O}bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)manganese(II)

Nans Roques,^a Philippe Gerbier,^{a*} Inhar Imaz,^b Philippe Guionneau^b and Jean-Pascal Sutter^b

^aLaboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637, Université Montpellier 2, CC 007, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France, and ^bICMCB-CNRS UPR 9048, Université Bordeaux I, 87 Avenue du Dr. Schweitzer, 33608 Pessac, France
Correspondence e-mail: gerbier@univ-montp2.fr

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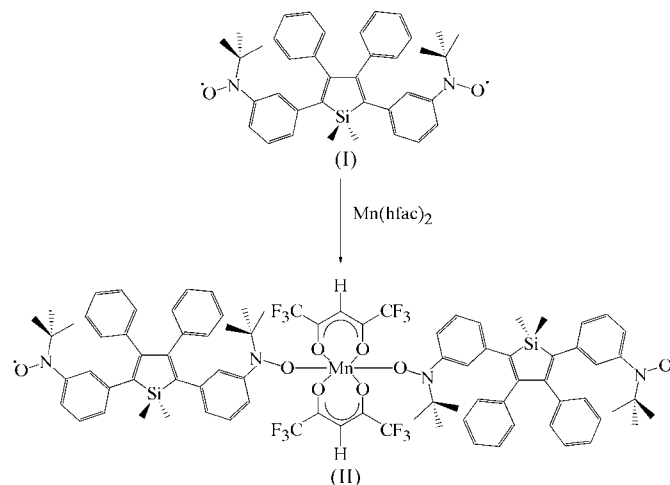
In the structure of the first bis-adduct of 2,5-bis[3-(*tert*-butylaminoxyl)phenyl]-1,1-dimethyl-3,4-diphenylsilole with bis(hexafluoroacetylacetonato)manganese(II), [Mn(C₅HF₆O₂)₂(C₃₈H₄₂N₂O₂Si)₂], the Mn atom lies on a crystallographic inversion centre and is bound to two chelating hexafluoroacetylacetonate ligands and two monodentate nitroxide groups in a distorted octahedral configuration. The silole ligands present a propeller-like arrangement of the benzene rings around the Si-containing five-membered ring. The dihedral angles between the complexed nitroxides and the benzene rings to which they are bound are smaller than those found in the free ligand.

Comment

The design and construction of molecule-based magnetic materials possessing a well defined structural dimensionality along with interesting magnetic properties has been a challenging proposition over the past 20 years (Miller & Epstein, 2000; Veciana & Iwamura, 2000). In this field of research, one of the most successful approaches towards molecule-based magnetic materials involves the coordination of stable organic radicals to high-spin metal ions, such as manganese in the form Mn(hfac)₂ (hfac is hexafluoroacetylacetonate). Following this approach, numerous examples of molecule-based materials possessing a large variety of dimensionalities and architectures (Mathevet & Luneau, 2001) have been reported, on account of the large number of combinations available through variations of the nitroxide radical nature and the organic spacers to which the radical unit(s) is (are) bound.

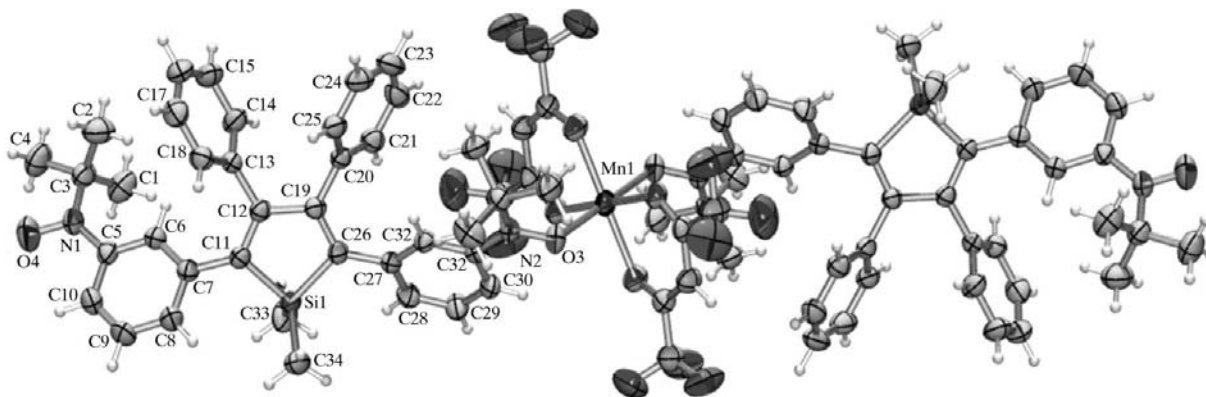
We have previously reported the synthesis, structure and detailed magnetic properties of the first example of silacyclopentadiene (or silole) substituted by two phenyl *tert*-

butyl nitroxide radicals, (I) (Roques *et al.*, 2003). Our goal was to take advantage of the photo-excited triplet state that was evidenced in the silole spacer to generate a reversible light-induced modification of the magnetic behaviour of this molecule (Roques *et al.*, 2004).



With the idea of further pursuing these investigations, we report here the synthesis and structure of the first manganese bis-adduct of (I), the title complex, (II). It is worth noting that (II) is only the second example of a *tert*-butyl nitroxide-based mononuclear manganese complex (Rajca *et al.*, 2001). This discrete unit is a promising model for the exploration of photo-induced magnetic states in low-dimensional metal-organic magnetic materials.

Complex (II) was obtained as dark-red diamond-like blocks by reacting silole (I) with Mn(hfac)₂ (see *Experimental*). Structure examination reveals a linear bis-adduct structure, (I)–Mn(Hfac)₂–(I) (Fig. 1). The Mn²⁺ ion coincides with an inversion centre and is bound to two chelating hfac ligands and two monodentate nitroxides in a distorted octahedral configuration, as previously reported in the literature (Iwamura *et al.*, 1998; Inoue *et al.*, 2000) for extended one- and two-dimensional structures. The distortions from regular octahedral geometry about the Mn atom are rather small, with no bond angle deviating by more than 6° from its ideal value. The largest distortions involve the pincer angles of *ca* 84° for the chelating hfac ligands. The Mn–O bond distances lie in the range 2.119 (2)–2.176 (2) Å. These are typical values for Mn²⁺ complexes of hfac and nitroxide ligands (Shibata *et al.*, 1985; Dickman *et al.*, 1986). Coordination of the nitroxide ligands to the metal centre affords pronounced changes in its structure. As usually observed in tetraarylsiloles, the molecule of (II) displays a propeller-like arrangement of the four benzene rings (Yamagushi *et al.*, 2000). However, the C2 symmetry axis that passes through the central Si atom in the structure of (I) is lost (Roques *et al.*, 2003). The dihedral angles between the five-membered silole ring and the benzene rings bearing the nitroxide radicals are 45.92 (9) and 35.61 (9)°, the latter being considerably smaller than the value of 49° encountered in the parent molecule. Another difference is observed in the dihedral angles made by the nitroxide groups

**Figure 1**

The structure of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For clarity, only selected atoms have been numbered; unlabelled atoms are related to labelled atoms by the symmetry code $(-x, -y, -z)$.

and the benzene rings to which they are bonded. While in the parent silole the dihedral angles are similar to that found here for the free nitroxide [$16.1(4)^\circ$], the complexed nitroxides in (II) are only twisted by angles of $7.3(4)^\circ$. These structural modifications are ascribed to the presence of the bulky hfac ligands in the coordination sphere of the metal centre.

In conclusion, compound (II) is the first bis-adduct of 2,5-bis[3-(*tert*-butylaminoxyl)phenyl]-1,1-dimethyl-3,4-diphenylsilole with bis(hexafluoroacetato)manganese(II) to have been synthesised and structurally characterized. Experiments are currently underway in our laboratory to use this bis-adduct as a building block to construct magnetic chains. Our efforts are also directed at studies of the photo-excited magnetic states of this metal-organic radical species.

Experimental

A sample of $\text{Mn}(\text{hfac})_2 \cdot \text{H}_2\text{O}$ (12 mmol) was suspended in *n*-heptane (30 ml) and the mixture was refluxed for 24 h to remove water by azeotropic distillation. To the cooled solution was added bis-nitroxide (I) (12 mmol) in freshly distilled dichloromethane (10 ml). After stirring for 10 min, the resulting deep-brown solution was concentrated to *ca* 5 ml under reduced pressure. The dark microcrystalline powder which formed during the concentration step was removed by filtration, and the resulting filtrate was allowed to evaporate to dryness, yielding dark-red diamond-like crystals of (II) after 4 d.

Crystal data

$[\text{Mn}(\text{C}_5\text{HF}_6\text{O}_2)_2(\text{C}_{38}\text{H}_{42}\text{N}_2\text{O}_2\text{Si})_2]$	$Z = 2$
$M_r = 1642.7$	$D_x = 1.351 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 14.784(2) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$b = 13.402(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 21.084(4) \text{ \AA}$	Diamond, dark red
$\beta = 104.88(1)^\circ$	$0.30 \times 0.10 \times 0.10 \text{ mm}$
$V = 4037.4(13) \text{ \AA}^3$	

Data collection

Nonius KappaCCD area-detector diffractometer	30037 measured reflections
φ scans, and ω scans with κ offsets	8261 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4786 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.921$, $T_{\max} = 0.973$	$R_{\text{int}} = 0.071$
	$\theta_{\text{max}} = 26.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 0.9718P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
8261 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
512 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.00020 (5)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn1—O1	2.119 (2)	Mn1—O3	2.176 (2)
Mn1—O2	2.141 (2)		
O1—Mn1—O2	84.40 (8)	O2—Mn1—O3	94.91 (9)
O1—Mn1—O3	92.11 (8)		

All H atoms were positioned geometrically ($\text{C—H} = 0.96 \text{ \AA}$ for the H atoms of methyl groups and $\text{C—H} = 0.93 \text{ \AA}$ for the other H atoms) and allowed to ride on their parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3007). Services for accessing these data are described at the back of the journal.

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