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Bis(hexafluoroacetylacetonato)manganese(II) complex of 1,1-dimethyl-2,5-bis-(3-*N*-*tert*-butyl-*N*-phenylaminoxyl) –3,4-diphenylsilolacyclopentadiene

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Abstract

In the structure of the first bis-adduct of hfac [1,1-dimethyl-2,5-bis-(3-*N*-*tert*-butyl-*N*-phenylaminoxyl) –3,4-diphenylsilolacyclopentadiene] with bis(hexafluoroacetylacetonato)manganese(II), the manganese atom lies on a crystallographic inversion centre and is bound to two chelating hfac ligands and two monodentate nitroxide groups in a distorted octahedral configuration. The silole ligands present a propeller-like arrangement of the phenyl rings around the silicon-containing five membered ring. The dihedral angles between the complexed nitroxides and the phenyl 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 twenty years (Miller *et al.*, 2000; Veciana *et al.*, 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 = hexafluoroacetylacetonate). Following this approach, numerous examples of molecule-based materials possessing a large variety of dimensionality and architecture (Mathevet *et al.*, 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 already 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 herein the synthesis and structure of the first manganese bis-adduct of (I): complex (II). It is worth noting that II is only the second example of a *tert*-butyl nitroxide based mononuc-

lear 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) is obtained as dark red diamond-like blocks by reacting silole 1 with $\text{Mn}(\text{hfac})_2$ (see experimental section). Structure examination reveals a linear bis-adduct structure, $\text{I}-\text{Mn}(\text{Hfac})_2-\text{I}$ (Fig. 1). The Mn^{2+} 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 Mn 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 of 2.119 (2)- 2.176 (2) Å. These are typical values for Mn^{2+} complexes of hfac and nitroxide ligands (Shibata *et al.*, 1985; Dickman *et al.*, 1986). Coordination of the nitroxide ligands to the metal centre affords strong changes in its structure. As usually observed in tetraarylsiloles, the molecule displays a propeller-like arrangement of the four benzene rings (Yamagushi *et al.*, 2000). However, the C_2 symmetry axis that passes through the central silicon atom in the structure of (I) is lost (Roques *et al.*, 2003). The dihedral angles between the five membered silole ring and the phenyl rings bearing the nitroxide radicals are $45.92(9)$ and $35.61(9)^\circ$, the latter being considerably smaller than the value of 49° encountered in the parent molecule. Another difference is observed for the dihedral angles made by the nitroxide groups and the phenyl 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 center.

To conclude, compound II is the first bis-adduct of 1,1-dimethyl-2,5-bis-(3-*N-tert*-butyl-*N*-phenylaminoxyl) -3,4-diphenylsilolacyclopentadiene with bis(hexafluoroacetylacetonato)manganese(II) to have been synthesized 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 30 ml of *n*-heptane and the mixture was refluxed for 24 h to remove water by azeotropic distillation. To the cooled solution was added 12 mmol of bis-nitroxide silole (I) in 10 ml of freshly distilled dichloromethane. After stirring for 10 min, the resulting deep brown solution was concentrated to *ca* 5 ml under reduced pressure. The dark microcrystalline powder formed during the concentration step was removed by filtration, and the resulting filtrate let to evaporate to dryness to yield dark red diamond-like crystals of (II) after four days.

Refinement

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

Computing details

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, 1990); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and Mercury (CCDC); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

Figures

Figure 1. The structure of complex (II), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. For clarity, only the manganese atom and the atoms belonging to the silole ligand have been labelled.

(nans1)

Crystal data

$C_{86}H_{86}F_{12}MnN_4O_8Si_2$	$V = 4037.4 (13) \text{ \AA}^3$
$M_r = 1642.7$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$
$a = 14.784 (2) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$b = 13.402 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 21.084 (4) \text{ \AA}$	$0.30 \times 0.10 \times 0.10 \text{ mm}$
$\beta = 104.88 (1)^\circ$	

Data collection

Nonius KappaCCD diffractometer	8261 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4786 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.921$, $T_{\max} = 0.973$	$R_{\text{int}} = 0.071$
30037 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	512 parameters
$wR(F^2) = 0.153$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$
8261 reflections	$\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$

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)		

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