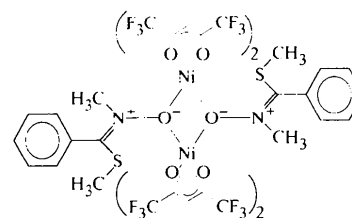


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1989). Magnetic measurements for the latter compound indicated antiferromagnetic coupling between the metal atoms.

In the title compound, (I) (Fig. 1), the thioester nitronone group (O1, N1, C2 and S1) is approximately planar, with an r.m.s. deviation of 0.01 Å. The dihedral angle



(I)

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Bis(μ -{N-[(methylthio)phenylmethylene]-methanamine N-oxide}-O:O)bis[bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-O,O')nickel(II)]

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Abstract

The title compound, $[\text{Ni}_2(\text{C}_5\text{HF}_6\text{O}_2)_4(\text{C}_9\text{H}_{11}\text{NOS})_2]$, crystallizes as a centrosymmetric dimer containing two $\text{Ni}(\text{hfac})_2$ moieties bridged by two nitronone ligands (hfac is the 1,1,1,5,5,5-hexafluoropentane-2,4-dionate anion). The $\text{Ni}\cdots\text{Ni}$ distance is 3.2904 (5) Å, with $\text{Ni}-\text{O}_{\text{nitronone}}$ distances of 2.0776 (12) and 2.0974 (12) Å. The average $\text{Ni}-\text{O}_{\text{hfac}}$ distance is 2.022 (16) Å.

Comment

Although metal adducts of pyridine *N*-oxides are well known, structural reports of complexes of nitronones in which the N atom is not part of an aromatic ring are less common. The present compound was synthesized as part of a study of such complexes. The resulting centrosymmetric dimer contains two $\text{Ni}(\text{hfac})_2$ units (hfac is the 1,1,1,5,5,5-hexafluoropentane-2,4-dionate anion) bridged by two nitronone O atoms. This type of dimeric structure was also found in a series of $M(\text{hfac})_2$ complexes ($M^{2+} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$) of 2,5,5-trimethyl-1-pyrroline *N*-oxide (Villamena *et al.*, 1998) and the $\text{Mn}(\text{hfac})_2$ adduct of 2-phenyl-4,4,5,5-tetramethylimidazoline 3-oxide (Carducci & Doedens,

between the phenyl ring and the plane of the thioester nitronone group is 66.00 (4)°. This is comparable to the value of 65.6° found for the uncomplexed nitronone

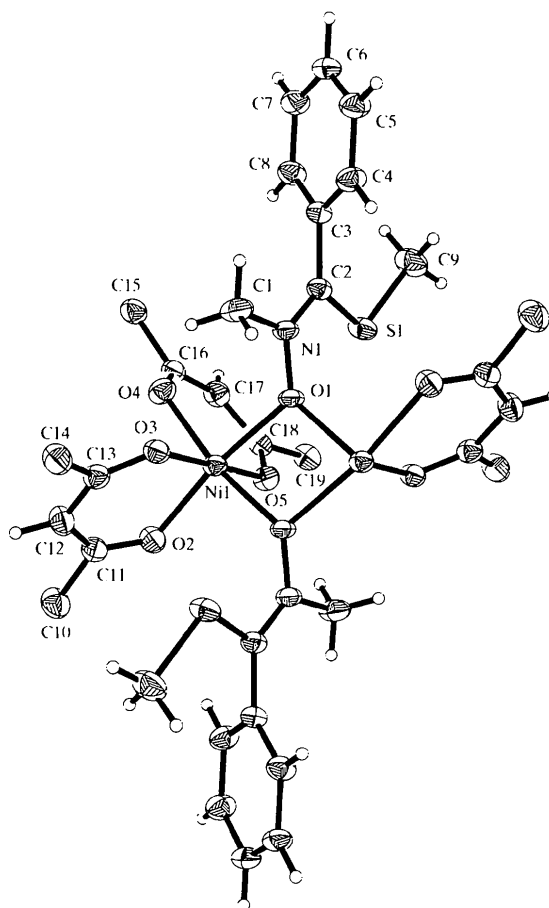


Fig. 1. View of the title compound showing the numbering scheme. Anisotropic displacement ellipsoids are shown at the 50% probability level. F atoms and one hfac ring have been omitted for clarity. H atoms are drawn as circles of arbitrary radii.

(Coates & Firsan, 1986). Other bond distances and angles are also similar to those in the free ligand, with the possible exception of the N—O bond distance reported as 1.313 Å by Coates & Firsan (1986), but observed as 1.357 (2) Å in the present complex. A small but consistent lengthening of the nitron N—O bond on complexation was also seen in *M*(hfac)₂ adducts (*M*²⁺ = Mn²⁺, Co²⁺, Ni²⁺, Fe²⁺, Cu²⁺) of the bidentate chelating ligand *N*-*tert*-butyl- α -(2-pyridyl)nitron (Villamena *et al.*, 1998). However, those adducts additionally showed evidence of a decrease in the C=N bond distance [to an average of 1.279 (9) Å] on complexation, an effect which is not seen here.

Experimental

Ni(hfac)₂ hydrate (98% purity) was purchased (Aldrich Chemical Company) and stored in a vacuum over P₂O₅. The nitron *N*-[(methylthio)phenylmethylene]methanamine *N*-oxide was synthesized according to the published procedure of Coates & Firsan (1986). The nitron (0.05 g, 0.3 mmol) and Ni(hfac)₂ hydrate (0.05 g, 0.1 mmol) were dissolved in 10 ml CH₂Cl₂, and 3 ml of *n*-heptane was added with stirring. The solution was allowed to evaporate slowly overnight to produce, as the sole product, crystals of the title compound suitable for structural analysis. The product was isolated by filtration from the remaining *n*-hexane. Elemental analysis (National Chemical Consulting Inc., NJ, USA) found (calculated): C 35.05 (34.89), H 1.66 (2.00), N 2.16% (2.14%).

Crystal data

[Ni ₂ (C ₅ HF ₆ O ₂) ₄ -(C ₉ H ₁₁ NOS) ₂]	Mo K α radiation
<i>M_r</i> = 1308.14	λ = 0.71073 Å
Monoclinic	Cell parameters from 8192 reflections
<i>P</i> 2 ₁ / <i>n</i>	θ = 1.98–28.27°
<i>a</i> = 11.1046 (5) Å	μ = 1.04 mm ⁻¹
<i>b</i> = 15.0729 (8) Å	<i>T</i> = 173 (2) K
<i>c</i> = 14.2998 (7) Å	Block
β = 100.205 (1)°	0.30 × 0.24 × 0.16 mm
<i>V</i> = 2355.6 (2) Å ³	Green
<i>Z</i> = 2	
<i>D_x</i> = 1.844 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Siemens SMART CCD diffractometer	4700 reflections with <i>I</i> > 2 σ (<i>I</i>)
ω scans	<i>R</i> _{int} = 0.026
Absorption correction: empirical (Blessing, 1995)	θ_{\max} = 28.27°
<i>T</i> _{min} = 0.644, <i>T</i> _{max} = 0.888	<i>h</i> = -14 → 14
18 423 measured reflections	<i>k</i> = -19 → 18
5547 independent reflections	<i>l</i> = -17 → 18
	Intensity decay: none

Refinement

Refinement on <i>F</i> ²	(Δ/σ) _{max} = 0.002
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.031	$\Delta\rho_{\max}$ = 0.335 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.076	$\Delta\rho_{\min}$ = -0.390 e Å ⁻³

S = 1.030
5547 reflections
405 parameters
All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 1.4P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL93*
Extinction coefficient: 0.0053 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni1...Ni1'	3.2904 (5)	Ni1—O1'	2.0776 (12)
Ni1—O4	2.0134 (13)	Ni1—O1	2.0974 (12)
Ni1—O3	2.0222 (12)	O1—N1	1.357 (2)
Ni1—O5	2.0236 (12)	N1—C2	1.303 (2)
Ni1—O2	2.0277 (13)	N1—C1	1.466 (2)
O4—Ni1—O3	87.48 (5)	O2—Ni1—O1'	96.19 (5)
O4—Ni1—O5	91.16 (5)	O4—Ni1—O1	93.01 (5)
O3—Ni1—O5	178.03 (5)	O3—Ni1—O1	92.82 (5)
O4—Ni1—O2	94.88 (5)	O5—Ni1—O1	88.68 (5)
O3—Ni1—O2	90.62 (5)	O2—Ni1—O1	171.53 (5)
O5—Ni1—O2	88.07 (5)	O1'—Ni1—O1	75.98 (5)
O4—Ni1—O1'	168.92 (5)	N1—O1—Ni1'	122.31 (10)
O3—Ni1—O1'	91.84 (5)	N1—O1—Ni1	127.34 (10)
O5—Ni1—O1'	89.77 (5)	Ni1'—O1—Ni1	104.02 (5)

Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.

The data were corrected for absorption and other systematic errors by comparison of equivalent reflections measured at different φ and ω values (Blessing, 1995). H atoms were refined isotropically without restraint in observed positions. Final C—H distances ranged from 0.92 (2) to 0.99 (3) Å, with a mean of 0.94 [2] Å. H-atom *U* values ranged from 0.036 (6) to 0.069 (9) Å², with a mean of 0.048 [12] Å².

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993a). Molecular graphics: *SHELXTL* (Sheldrick, 1993b). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1094). Services for accessing these data are described at the back of the journal.

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