

Dibromidobis(2-methyl-5-phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole- κ N)-nickel(II)

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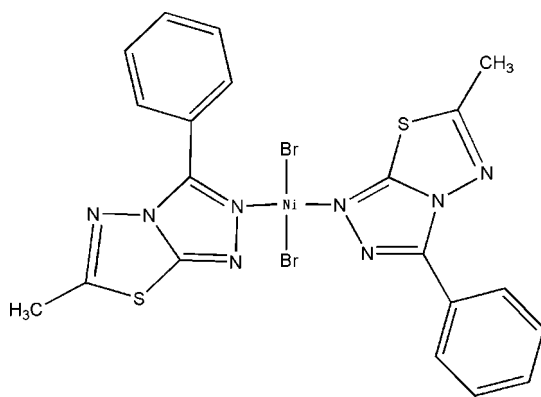
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.044; wR factor = 0.116; data-to-parameter ratio = 15.7.

The title complex, $[\text{NiBr}_2(\text{C}_{10}\text{H}_8\text{N}_4\text{S})_2]$, is a mononuclear molecule consisting of an Ni^{II} ion, two 2-methyl-5-phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole ligands and two bromide ligands. The Ni^{II} atom, located on a center of symmetry, displays a square-planar coordination geometry. Intermolecular $\text{C}-\text{H}\cdots\text{Br}$ hydrogen bonds and $\pi-\pi$ contacts [centroid-centroid distance = 3.58 (6) Å] stabilize the supramolecular structure.

Related literature

For related literature, see: Fornies-Marquina *et al.* (1974); Huang *et al.* (2005); Naveen *et al.* (2006).



Experimental

Crystal data

$[\text{NiBr}_2(\text{C}_{10}\text{H}_8\text{N}_4\text{S})_2]$
 $M_r = 651.06$
 Triclinic, $P\bar{1}$
 $a = 6.8286$ (10) Å
 $b = 8.5231$ (13) Å

$c = 11.3654$ (16) Å
 $\alpha = 98.442$ (2)°
 $\beta = 105.614$ (3)°
 $\gamma = 108.859$ (2)°
 $V = 582.69$ (15) Å³

$Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 4.47$ mm⁻¹

$T = 298$ (2) K
 $0.25 \times 0.20 \times 0.14$ mm

Data collection

Bruker APEXII area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.37$, $T_{\text{max}} = 0.53$

4173 measured reflections
 2383 independent reflections
 1595 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.101$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.116$
 $S = 0.89$
 2383 reflections

152 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.70$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.93$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—Br1	2.3826 (6)	Ni1—N1	1.984 (3)
N1—Ni1—Br1	90.80 (10)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H17C \cdots Br1 ⁱ	0.96	2.90	3.769 (5)	150
C5—H4 \cdots N4	0.93	2.45	3.123 (6)	129

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *S SAINT* (Bruker, 1999); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2086).

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supplementary materials

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Dibromidobis(2-methyl-5-phenyl-s-triazolo[3,4-*b*]-1,3,4-thiadiazole- κ N)nickel(II)

L.-G. Wang

Comment

The molecular structure of 2-methyl-5-phenyl-s-triazolo(3,4-*b*)-1,3,4-thiadiazole (Fornies-Marquina *et al.*, 1974) and its substituted derivatives (Huang *et al.*, 2005; Naveen, *et al.*, 2006) have been reported; however, no example of any metal complex of the ligand are known to date. In this paper, we present the crystal structure of the title compound [NiBr₂(C₁₀H₈N₄S)₂] (I), a Ni complex obtained by the reaction of 2-methyl-5-phenyl-s-triazolo(3,4-*b*)-1,3,4-thiadiazole with nickel sulfate and sodium bromide in a methanol solution.

As illustrated in Fig. 1, the Ni^{II} atom is a neutral mononuclear molecule which lies on a centre of symmetry and displays a square planar coordination geometry, the four coordinating atoms being two N atoms from two 2-methyl-5-phenyl-s-triazolo(3,4-*b*)-1,3,4-thiadiazole, and two bromine atoms (Table 1). The structural components are connected through two types of interactions:

1) C—H \cdots Br hydrogen bonds (involving the C atoms of 2-methyl-5-phenyl-s-triazolo(3,4-*b*)-1,3,4-thiadiazole) as donors and the bromine atoms as acceptors (Table 2), and

2) π - π stacking interactions between the phenyl and triazolo rings, with a centroid-centroid distance of 3.58 (6) Å, forming a supramolecular network structure.

Besides, there is an intramolecular C—H \cdots N hydrogen bond (Table 2) linking the fused ring system and the phenyl plane and promoting their near coplanarity (Dihedral angle: 2.2 (5)°).

Experimental

The title complex was prepared by adding nickel sulfate (0.0155 g, 0.1 mmol) and sodium bromide (0.0205 g, 0.2 mmol) to a CH₃CN solution (12 ml) of 2-methyl-5-phenyl-s-triazolo(3,4-*b*)-1,3,4-thiadiazole (0.045 g, 0.2 mmol). The resulting solution was filtered, and green block crystals were obtained at room temperature on slow evaporation of the solvent over three weeks.

Refinement

The diffraction was weak, but in spite of the rather low completeness (92% at $\theta = 25^\circ$) the ratio of "observed" data to total number of parameters was reasonable (10.5). Carbon-bound H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93–0.97 and with $U_{\text{iso}}(\text{H}) = 1.2$.

Figures

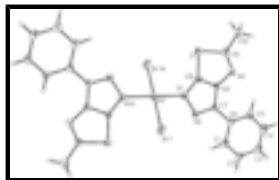


Fig. 1. The molecular structure of (I), showing the atomic numbering scheme. Probability displacement ellipsoids are drawn at the 30% level. In the centrosymmetric molecule, unlabelled atoms are related to labelled ones by the symmetry operator $1 - x, 1 - y, -z$.

Dibromidobis(2-methyl-5-phenyl-s-triazolo[3,4-*b*][1,3,4]thiadiazole- κ N)nickel(II)

Crystal data

[NiBr₂(C₁₀H₈N₄S)₂]

$M_r = 651.06$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.8286$ (10) Å

$b = 8.5231$ (13) Å

$c = 11.3654$ (16) Å

$\alpha = 98.442$ (2)°

$\beta = 105.614$ (3)°

$\gamma = 108.859$ (2)°

$V = 582.69$ (15) Å³

$Z = 1$

$F_{000} = 322$

$D_x = 1.855$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2383 reflections

$\theta = 1.9$ – 27.5 °

$\mu = 4.47$ mm⁻¹

$T = 298$ (2) K

Block, green

$0.25 \times 0.20 \times 0.14$ mm

Data collection

Bruker APEX II area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.37$, $T_{\max} = 0.53$

4173 measured reflections

2383 independent reflections

1595 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.101$

$\theta_{\text{max}} = 27.5$ °

$\theta_{\text{min}} = 1.9$ °

$h = -8 \rightarrow 8$

$k = -11 \rightarrow 10$

$l = -13 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.116$

$S = 0.89$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

2383 reflections $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$
 152 parameters $\Delta\rho_{\min} = -0.93 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.85222 (9)	0.72697 (7)	0.06809 (5)	0.0707 (2)
Ni1	0.5000	0.5000	0.0000	0.0321 (2)
S1	0.3986 (2)	0.08844 (13)	0.13109 (10)	0.0434 (3)
N1	0.5616 (6)	0.4522 (4)	0.1689 (3)	0.0392 (8)
N2	0.6704 (6)	0.5816 (4)	0.2827 (3)	0.0392 (8)
N3	0.6002 (6)	0.3343 (4)	0.3279 (3)	0.0330 (7)
N4	0.5781 (6)	0.1933 (4)	0.3771 (3)	0.0383 (8)
C1	0.8738 (8)	0.7807 (6)	0.5409 (4)	0.0435 (10)
H1	0.8615	0.8379	0.4772	0.052*
C2	0.9710 (8)	0.8729 (6)	0.6677 (4)	0.0504 (12)
H2	1.0233	0.9921	0.6892	0.060*
C3	0.9889 (8)	0.7861 (6)	0.7604 (4)	0.0497 (12)
H3	1.0536	0.8479	0.8447	0.060*
C5	0.8172 (8)	0.5181 (6)	0.6055 (4)	0.0424 (10)
H4	0.7674	0.3990	0.5852	0.051*
C6	0.7950 (7)	0.6011 (5)	0.5107 (4)	0.0340 (9)
C4	0.9134 (8)	0.6106 (6)	0.7314 (4)	0.0511 (12)
H6	0.9264	0.5541	0.7954	0.061*
C8	0.5192 (7)	0.3049 (5)	0.2004 (4)	0.0358 (9)
C9	0.4777 (8)	0.0564 (5)	0.2839 (4)	0.0425 (10)
C10	0.4262 (9)	-0.1189 (6)	0.3024 (5)	0.0629 (15)
H17A	0.4750	-0.1124	0.3911	0.094*
H17B	0.4999	-0.1755	0.2613	0.094*
H17C	0.2703	-0.1826	0.2667	0.094*
C7	0.6932 (7)	0.5085 (5)	0.3759 (4)	0.0327 (9)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0605 (4)	0.0744 (4)	0.0384 (3)	-0.0131 (3)	0.0004 (2)	0.0214 (3)
Ni1	0.0408 (4)	0.0294 (4)	0.0194 (3)	0.0069 (3)	0.0077 (3)	0.0064 (3)
S1	0.0519 (7)	0.0362 (6)	0.0349 (5)	0.0125 (5)	0.0104 (5)	0.0061 (5)
N1	0.047 (2)	0.0380 (19)	0.0244 (16)	0.0099 (17)	0.0081 (16)	0.0064 (14)
N2	0.047 (2)	0.0352 (18)	0.0271 (17)	0.0096 (16)	0.0096 (17)	0.0046 (14)
N3	0.040 (2)	0.0342 (18)	0.0280 (16)	0.0153 (15)	0.0126 (16)	0.0114 (14)
N4	0.043 (2)	0.043 (2)	0.0358 (19)	0.0202 (17)	0.0140 (17)	0.0176 (16)
C1	0.048 (3)	0.046 (3)	0.032 (2)	0.016 (2)	0.011 (2)	0.0063 (19)
C2	0.047 (3)	0.053 (3)	0.037 (2)	0.012 (2)	0.009 (2)	-0.003 (2)
C3	0.043 (3)	0.071 (3)	0.029 (2)	0.020 (2)	0.011 (2)	0.000 (2)
C5	0.049 (3)	0.044 (2)	0.032 (2)	0.016 (2)	0.014 (2)	0.0079 (18)
C6	0.035 (2)	0.042 (2)	0.0276 (19)	0.0158 (19)	0.0139 (19)	0.0076 (17)
C4	0.057 (3)	0.070 (3)	0.028 (2)	0.022 (3)	0.016 (2)	0.016 (2)
C8	0.038 (2)	0.039 (2)	0.029 (2)	0.0118 (19)	0.0128 (19)	0.0084 (17)
C9	0.043 (3)	0.042 (2)	0.045 (2)	0.019 (2)	0.013 (2)	0.015 (2)
C10	0.073 (4)	0.047 (3)	0.062 (3)	0.024 (3)	0.006 (3)	0.021 (3)
C7	0.033 (2)	0.037 (2)	0.0283 (19)	0.0124 (18)	0.0100 (18)	0.0096 (17)

Geometric parameters (\AA , $^\circ$)

Ni1—Br1	2.3826 (6)	C1—H1	0.9300
Ni1—N1	1.984 (3)	C2—C3	1.375 (6)
Ni1—N1 ⁱ	1.984 (3)	C2—H2	0.9300
Ni1—Br1 ⁱ	2.3826 (6)	C3—C4	1.369 (7)
S1—C8	1.716 (4)	C3—H3	0.9300
S1—C9	1.765 (4)	C5—C6	1.375 (6)
N1—C8	1.319 (5)	C5—C4	1.389 (6)
N1—N2	1.405 (4)	C5—H4	0.9300
N2—C7	1.305 (5)	C6—C7	1.473 (5)
N3—C8	1.358 (5)	C4—H6	0.9300
N3—C7	1.368 (5)	C9—C10	1.481 (6)
N3—N4	1.380 (4)	C10—H17A	0.9600
N4—C9	1.297 (6)	C10—H17B	0.9600
C1—C2	1.396 (6)	C10—H17C	0.9600
C1—C6	1.402 (6)		
N1—Ni1—N1 ⁱ	180.00 (19)	C6—C5—C4	120.5 (4)
N1—Ni1—Br1	90.80 (10)	C6—C5—H4	119.7
N1 ⁱ —Ni1—Br1	89.20 (10)	C4—C5—H4	119.7
N1—Ni1—Br1 ⁱ	89.20 (10)	C5—C6—C1	119.9 (4)
N1 ⁱ —Ni1—Br1 ⁱ	90.80 (10)	C5—C6—C7	122.5 (4)
Br1—Ni1—Br1 ⁱ	180.0	C1—C6—C7	117.6 (4)
C8—S1—C9	87.73 (19)	C3—C4—C5	119.3 (4)
C8—N1—N2	106.4 (3)	C3—C4—H6	120.3

C8—N1—Ni1	130.3 (3)	C5—C4—H6	120.3
N2—N1—Ni1	123.3 (2)	N1—C8—N3	109.8 (3)
C7—N2—N1	108.2 (3)	N1—C8—S1	140.1 (3)
C8—N3—C7	106.6 (3)	N3—C8—S1	110.1 (3)
C8—N3—N4	117.5 (3)	N4—C9—C10	122.8 (4)
C7—N3—N4	135.9 (3)	N4—C9—S1	116.4 (3)
C9—N4—N3	108.2 (3)	C10—C9—S1	120.8 (4)
C2—C1—C6	119.2 (4)	C9—C10—H17A	109.5
C2—C1—H1	120.4	C9—C10—H17B	109.5
C6—C1—H1	120.4	H17A—C10—H17B	109.5
C3—C2—C1	119.5 (4)	C9—C10—H17C	109.5
C3—C2—H2	120.3	H17A—C10—H17C	109.5
C1—C2—H2	120.3	H17B—C10—H17C	109.5
C4—C3—C2	121.5 (4)	N2—C7—N3	109.0 (3)
C4—C3—H3	119.2	N2—C7—C6	124.7 (4)
C2—C3—H3	119.2	N3—C7—C6	126.3 (3)

Symmetry codes: (i) $-x+1, -y+1, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C10—H17C \cdots Br1 ⁱⁱ	0.96	2.90	3.769 (5)	150
C5—H4 \cdots N4	0.93	2.45	3.123 (6)	129

Symmetry codes: (ii) $x-1, y-1, z$.

Fig. 1

