

C36	0.7433 (7)	0.5680 (7)	0.8980 (6)	0.051 (2)
C42	0.7051 (8)	0.8008 (7)	0.5504 (6)	0.059 (2)
C43	0.6553 (9)	0.8778 (8)	0.4383 (7)	0.068 (2)
C44	0.7317 (9)	0.9411 (7)	0.3630 (7)	0.063 (2)
C45	0.8568 (8)	0.9274 (6)	0.3978 (6)	0.057 (2)
C46	0.9095 (7)	0.8514 (6)	0.5107 (6)	0.047 (2)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Os—C	1.795 (10)	Os—Br1	2.5042 (8)
Os—Ow	2.181 (6)	Os—Br3	2.5072 (8)
Os—Br2	2.4692 (8)	C—O	1.164 (9)
Os—Br4	2.4753 (10)		
C—Os—Ow	177.8 (3)	Br2—Os—Br1	88.70 (3)
C—Os—Br2	92.6 (2)	Br4—Os—Br1	174.91 (4)
Ow—Os—Br2	86.08 (14)	C—Os—Br3	93.0 (2)
C—Os—Br4	90.5 (3)	Ow—Os—Br3	88.42 (14)
Ow—Os—Br4	87.87 (15)	Br2—Os—Br3	173.97 (3)
Br2—Os—Br4	90.66 (3)	Br4—Os—Br3	91.60 (3)
C—Os—Br1	94.6 (3)	Br1—Os—Br3	88.55 (3)
Ow—Os—Br1	87.04 (15)	O—C—Os	177.4 (7)

Table 3. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

D—H...A	H...A	D...A	D—H...A
Ow ¹ —HA...Br1	2.53 (5)	3.258 (5)	144 (7)
Ow ¹ —HB...Br3	2.67 (4)	3.452 (6)	156 (7)

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

H atoms of the cation were refined using a riding model with a common displacement parameter. H atoms of the water molecule were found from a Fourier map and refined with a distance restraint of 0.85 (2) $\text{\AA}$ for O—H and a fixed displacement parameter of 0.085 $\text{\AA}^2$.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Financial support from Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaquabis(4-amino-3-methyl-4,5-dihydro-1H-1,2,4-triazole-5-thione)nickel(II) Nitrate: a Sulfur–Nitrogen Chelate

ASHOK K. SEN,^a SURENDRA N. DUBEY^a AND PHILIP J. SQUATTRITO^{b*}

^aDepartment of Chemistry, Kurukshetra University, Kurukshetra 132119, Haryana, India, and ^bDepartment of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA. E-mail: 3clwp5s@cmuvm.csv.cmich.edu

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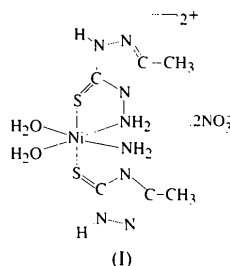
Abstract

The title compound, $[\text{Ni}(\text{C}_3\text{H}_6\text{N}_4\text{S})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, is an octahedral complex of nickel(II) in which two triazole ligands are coordinated in a bidentate fashion through the amine and thione substituents. The coordination sphere has the two S atoms *trans* with respect to each other, while the N atoms and two water molecules are ligated in *cis* positions. The Ni—S and Ni—N bond lengths in the chelate are consistent with those in similar octahedral nickel complexes. The geometry of the

complexed triazole moiety is not substantially different from that of the free molecule.

Comment

Thiosemicarbazones and related compounds with S—C—N linkages display a wide range of biological activity. Metal complexes of these compounds have been synthesized in order to gauge their activity *versus* that of the free ligand and to determine the coordination behavior of the ligand towards the metal (Offiong, 1995; West, Lockwood, Liberta, Chen & Willett, 1993; Satpathy, Panda, Mishra, Chopdar & Pradhan, 1991). Relatively few complexes of divalent nickel with a chelated S—C—N—N moiety have been structurally characterized. Those that have been characterized include square-planar, trigonal-bipyramidal and octahedral complexes. Square-planar geometries are observed in the sulfate (Gronbek & Rasmussen, 1962) and nitrate (Hazell, 1972) salts of bis(thiosemicarbazide)nickel(II). Both *cis* and *trans* isomers were reported, with no coordination by the anion or water molecules. Acetylpyrazine thiosemicarbazones (West, Lockwood, Liberta, Chen & Willett, 1993) act as tridentate ligands towards Ni, forming square-planar complexes together with a chloro ligand. In all of the square-planar examples, the Ni—S bond distances are in the range 2.16–2.19 Å, while the Ni—N distances are in the range 1.85–1.95 Å. The difference in the Ni—S and Ni—N bond lengths is consistent with the difference in van der Waals radii of S and N atoms (Bondi, 1964). Trigonal-bipyramidal geometries are found in the bis(acetone thiosemicarbazone)-chloronickel(II) and bis(acetone thiosemicarbazone)-nitratonickel(II) complexes (Mathew, Palenik & Clark, 1973). The N atoms occupy the apical positions and the S atoms the equatorial positions of the trigonal bipyramid. The increase in coordination number is accompanied by an increase in Ni—S [2.290 (2)–2.337 (5) Å] and Ni—N [2.098 (11)–2.139 (12) Å] distances. The tris(thiosemicarbazide)nickel(II) complex (Ballard, Powell & Jayasooriya, 1974) is octahedral, with the ligands in a meridional arrangement. The Ni—S bond distances are longer still [2.399 (8)–2.432 (8) Å], while the Ni—N distances [2.087 (11)–2.114 (11) Å] are similar to those in the pentacoordinate complexes. There appears to be a corresponding shortening of the S—C bond length from square planar [1.712 (5)–1.756 (3) Å] through trigonal bipyramidal [1.65 (2)–1.710 (7) Å] to octahedral [1.69 (1) Å], though the changes are small and the errors large in some cases. The metrical data (Table 2) for the title compound, (I), are consistent with this pattern and very similar to those of the other octahedral complex. Though bis(aminomercaptotriazole)-diaquanickel(II) complexes have been reported (Satpathy, Panda, Mishra, Chopdar & Pradhan, 1991), the title compound is the first whose structure has been determined.



As shown in Fig. 1, the nearly planar triazole ligands bond to the Ni atom with the S atoms in *trans* positions and the N atoms in *cis* positions. The remaining two *cis* sites are occupied by water molecules. The Ni atom resides on a twofold rotation axis which bisects the O—Ni—O and N—Ni—N bond angles. The crystal packing (Fig. 2) is reinforced by hydrogen bonds between neighboring complexes (O—H...N) and between the complex cation and nitrate ion (N—H...O). The metrical data for the complexed triazole are very similar to those of the free ligand (Escobar-Valderrama, Garcia-Tapia, Ramirez-Ortiz, Rosales, Toscano & Valdes-Martinez, 1989). The only bond distance that differs by more than three e.s.d.'s is N(1)—N(2) which is longer in the complex [1.419 (4) Å] than in the free triazole [1.397 (3) Å]. As expected, the angles in the S—C—N—N chelate are

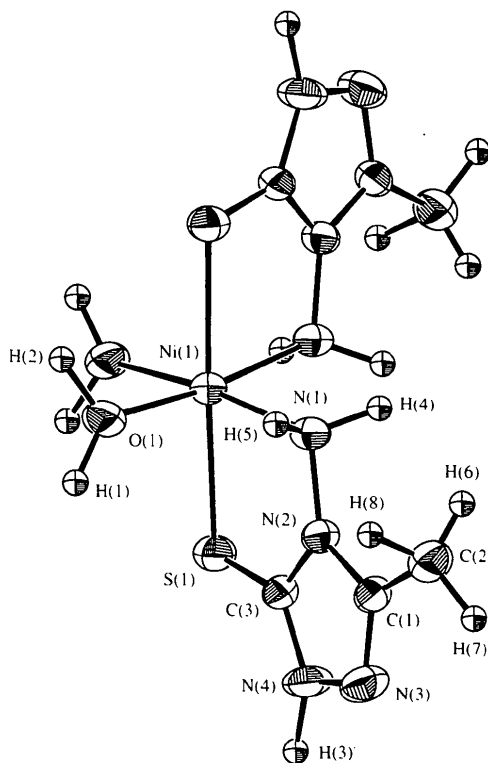


Fig. 1. An ORTEP diagram (Johnson, 1976) of the title complex showing the atomic labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

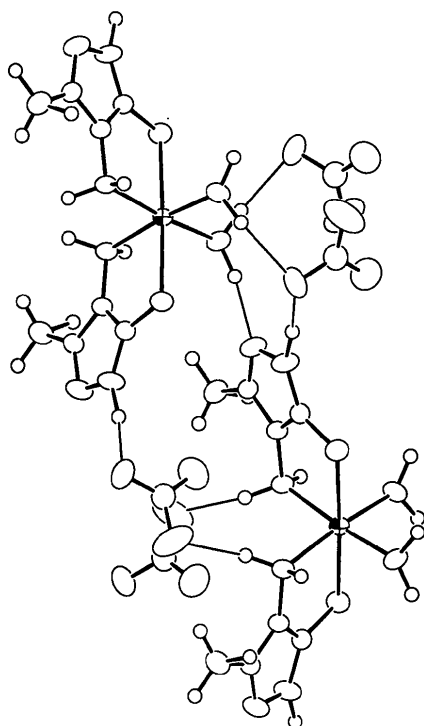


Fig. 2. An ORTEP packing diagram (Johnson, 1976) showing hydrogen bonding (narrow lines) between the complex cations and nitrate anions. The view is along the *c* axis, with the *a* axis vertical.

contracted a few degrees relative to those of the uncomplexed molecule. The amine H atoms are directed towards the S atom in the free ligand, but away from the S atom in the chelate. In both compounds, the triazole exists as the thione tautomer, *i.e.* the ring N atom is protonated rather than the S atom.

Experimental

The triazole ligand was prepared by heating a mixture of thiocarbohydrazide and excess glacial acetic acid under reflux for 4 h. The slightly yellow solid product separated from the clear solution on standing overnight at room temperature. The triazole and nickel nitrate hexahydrate were combined in a 2:1 molar ratio in warm ethanol, yielding a green solution. Deep-green crystals of the title compound grew from this solution on standing. Elemental analysis (C, H and N) of the crystals was in excellent agreement with the formula obtained from the X-ray structure analysis.

Crystal data

$[\text{Ni}(\text{C}_3\text{H}_6\text{N}_4\text{S})_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2$

$M_r = 479.07$

Orthorhombic

Pbcn

$a = 15.683(2) \text{ \AA}$

$b = 8.888(2) \text{ \AA}$

$c = 12.653(3) \text{ \AA}$

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 23 reflections

$\theta = 17.8\text{--}21.7^\circ$

$\mu = 1.390 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Parallelepiped

$V = 1763.8(9) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.804 \text{ Mg m}^{-3}$

$0.30 \times 0.20 \times 0.15 \text{ mm}$
 Emerald green

Data collection

Rigaku AFC-6S diffractometer

$\omega/2\theta$ scans

Absorption correction: none

1796 measured reflections

1796 independent reflections

1052 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\text{max}} = 24.91^\circ$

$h = 0 \rightarrow 18$

$k = 0 \rightarrow 10$

$l = 0 \rightarrow 14$

3 standard reflections

monitored every 150

reflections

intensity decay: 0.7%

Refinement

Refinement on F

$R = 0.035$

$wR = 0.033$

$S = 2.166$

1052 reflections

123 parameters

H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\text{max}} = 0.056$

$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni(1)	1	0.33325 (8)	3/4	0.0289 (2)
S(1)	1.12925 (7)	0.3282 (1)	0.85303 (9)	0.0360 (3)
O(1)	1.0469 (2)	0.4935 (3)	0.6441 (2)	0.0424 (9)
O(2)	0.5907 (2)	0.4160 (4)	0.6894 (3)	0.068 (1)
O(3)	0.5972 (2)	0.2130 (3)	0.5980 (3)	0.058 (1)
O(4)	0.4891 (3)	0.3549 (5)	0.5870 (3)	0.093 (2)
N(1)	1.0617 (2)	0.1713 (4)	0.6503 (3)	0.0327 (10)
N(2)	1.1496 (2)	0.1573 (4)	0.6752 (3)	0.0288 (10)
N(3)	1.2831 (2)	0.0905 (4)	0.6772 (3)	0.041 (1)
N(4)	1.2636 (2)	0.1815 (4)	0.7628 (3)	0.041 (1)
N(5)	0.5585 (2)	0.3289 (5)	0.6263 (3)	0.041 (1)
C(1)	1.2125 (3)	0.0747 (4)	0.6258 (3)	0.032 (1)
C(2)	1.2018 (3)	−0.0181 (5)	0.5297 (4)	0.043 (1)
C(3)	1.1825 (2)	0.2231 (4)	0.7638 (3)	0.031 (1)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Ni(1)—S(1)	2.411 (1)	N(1)—N(2)	1.419 (4)
Ni(1)—O(1)	2.089 (3)	N(2)—C(1)	1.380 (5)
Ni(1)—N(1)	2.144 (3)	N(2)—C(3)	1.365 (5)
S(1)—C(3)	1.686 (4)	N(3)—N(4)	1.386 (5)
O(2)—N(5)	1.223 (4)	N(3)—C(1)	1.292 (5)
O(3)—N(5)	1.248 (4)	N(4)—C(3)	1.325 (5)
O(4)—N(5)	1.218 (5)	C(1)—C(2)	1.479 (6)
S(1)—Ni(1)—S(1')	177.86 (7)	C(1)—N(2)—C(3)	109.2 (3)
S(1)—Ni(1)—O(1)	93.62 (8)	N(4)—N(3)—C(1)	105.5 (3)
S(1)—Ni(1)—O(1')	87.84 (8)	N(3)—N(4)—C(3)	112.4 (3)
S(1)—Ni(1)—N(1)	85.76 (9)	O(2)—N(5)—O(3)	120.6 (4)
S(1)—Ni(1)—N(1')	92.80 (9)	O(2)—N(5)—O(4)	121.1 (5)
O(1)—Ni(1)—O(1')	94.0 (2)	O(3)—N(5)—O(4)	118.3 (4)
O(1)—Ni(1)—N(1)	85.5 (1)	N(2)—C(1)—N(3)	109.1 (4)
O(1)—Ni(1)—N(1')	173.5 (1)	N(2)—C(1)—C(2)	126.0 (4)
N(1)—Ni(1)—N(1')	95.7 (2)	N(3)—C(1)—C(2)	124.9 (4)
Ni(1)—S(1)—C(3)	93.7 (1)	S(1)—C(3)—N(2)	126.8 (3)
Ni(1)—N(1)—N(2)	111.5 (2)	S(1)—C(3)—N(4)	129.5 (4)
N(1)—N(2)—C(1)	129.8 (4)	N(2)—C(3)—N(4)	103.7 (4)
N(1)—N(2)—C(3)	120.8 (3)		

$D-H \cdots A$	$D \cdots A$	$D-H \cdots A$	$D \cdots A$
O(1)—H(1) $\cdots$ N(3 ⁱⁱ)	2.832 (4)	N(4)—H(3) $\cdots$ O(3 ⁱ)	2.819 (5)
O(1)—H(2) $\cdots$ O(3 ⁱⁱⁱ)	3.042 (4)	N(1)—H(4) $\cdots$ O(4 ^{iv})	3.031 (5)

Symmetry codes: (i) $2-x, y, \frac{3}{2}-z$; (ii) $\frac{2}{3}-x, \frac{1}{2}+y, z$; (iii) $\frac{2}{3}-x, \frac{1}{2}+y, z$; (iv) $\frac{2}{3}-x, y-\frac{1}{2}, z$.

All H atoms were located on difference electron density maps and included as fixed isotropic scatterers (O—H 0.98–1.08, N—H 1.02–1.11 and C—H 0.91–1.15 Å), with *B* values 1.2 times those of the attached atoms at the time of their inclusion.

Data collection: *MSCI/AFSC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFSC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including intermolecular distances involving both H and non-H atoms, and special angles involving H atoms, and least-squares-planes data have been deposited with the IUCr (Reference: BK1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Second Polymorph of 2,2'-Bipyridyl-(methyl)(phenyl)palladium(II)

ANTHONY L. SPEK,^a MAURITS D. JANSSEN,^b BERTUS A. MARKIES^b AND GERARD VAN KOTEN^b

^a*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and*
^b*Debye Research Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: spea@xray.chem.ruu.nl*

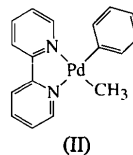
(Received 17 October 1995; accepted 30 October 1995)

Abstract

The crystal structure of a second polymorph of [Pd(CH₃)(C₆H₅)(C₁₀H₈N₂)], containing four crystallographically independent molecules, is presented and compared with the structure of the previously reported polymorph [Markies *et al.* (1994). *J. Organomet. Chem.* **482**, 191–199] containing only one crystallographically independent molecule. In both polymorphs molecules lie in infinite stacks, surrounded by six similar stacks; the main difference between the two polymorphs is about 23° in the tilt angle of the coordination plane with reference to the stacking direction.

Comment

Preliminary attempts to obtain crystals of the title compound yielded needles [modification (II)] with a large monoclinic unit cell and four molecules per asymmetric unit. Subsequent attempts under essentially the same crystallization conditions yielded better quality monoclinic plates [modification (I)] with one molecule in the asymmetric unit (Markies *et al.*, 1991, 1994). Although less accurate than the previously reported structure [modification (I)], the crystal structure of modification (II) is relevant in view of the current interest in polymorphs (Gavezzotti, 1994; Dunitz & Bernstein, 1995). Polymorphs provide information on conformational flexibility and are relevant for *ab initio* crystal structure predictions (Gavezzotti, 1994).



The four crystallographically independent molecules in (II) (Fig. 1) have very similar conformations that closely resemble the conformation found in (I). The main difference between the five molecules may be