

# Crystal structure of dichlorido[4-[(*E*)-(methoxyimino- $\kappa$ N)methyl]-1,3-thiazol-2-amine- $\kappa$ N<sup>3</sup>]palladium(II)

Viktorita V. Dyakonenko,<sup>a\*</sup> Olga O. Zholob,<sup>b</sup> Svitlana I. Orysyk<sup>b</sup> and Vasily I. Pekhnyo<sup>b</sup>

<sup>a</sup>State Scientific "Institution Institute for Single Crystals", National Academy of Science of Ukraine, 60 Lenina ave., Kharkiv 61001, Ukraine, and <sup>b</sup>V.I. Vernadskii Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, 03680 Kyiv, Ukraine. \*Correspondence e-mail: vika@xray.isc.kharkov.com

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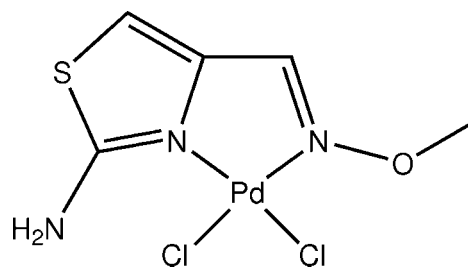
In the title compound, [PdCl<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>OS)], the Pd<sup>II</sup> atom adopts a distorted square-planar coordination sphere defined by two N atoms of the bidentate ligand and two Cl atoms. The mean deviation from the coordination plane is 0.029 Å. The methyl group is not coplanar with the plane of the metallacycle [torsion angle C—O—N—C = 20.2 (4)°]. Steric repulsion between the methyl group and atoms of the metallacycle is manifested by shortened intramolecular H···C contacts of 2.27, 2.38 and 2.64 Å, as compared with the sum of the van der Waals radii of 2.87 Å. The amino group participates *via* one H atom in the formation of an intramolecular N—H···Cl hydrogen bond. In the crystal, the other H atom of the amino group links molecules *via* bifurcated N—H···(Cl,O) hydrogen bonds into chains parallel to [001].

**Keywords:** crystal structure; palladium; multi-functional ligand; 4-[(methoxyimino)methyl]-1,3-thiazol-2-amine (MIMTA).

**CCDC reference:** 1037339

## 1. Related literature

4-[(Methoxyimino)methyl]-1,3-thiazol-2-amine (MIMTA) belongs to the class of polyfunctional oximes that are potential biologically active complexing agents (Dodoff *et al.*, 2009; Elo, 2004; Scaffidi-Domianello *et al.*, 2011; Donde & Patil, 2011; Kuwar *et al.*, 2006). Palladium complexes based on MIMTA are thus interesting in biomedicine (Orysyk *et al.*, 2013). For the structures of related complexes, see: Orysyk *et al.* (2015); Mokhir *et al.* (2002). For van der Waals radii, see: Zefirov (1997).



## 2. Experimental

### 2.1. Crystal data

[PdCl <sub>2</sub> (C <sub>5</sub> H <sub>7</sub> N <sub>3</sub> OS)]	<i>V</i> = 969.0 (7) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 334.50	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Mo <i>K</i> α radiation
<i>a</i> = 4.347 (3) Å	<i>μ</i> = 2.64 mm <sup>-1</sup>
<i>b</i> = 13.583 (2) Å	<i>T</i> = 294 K
<i>c</i> = 16.411 (3) Å	0.4 × 0.3 × 0.2 mm

### 2.2. Data collection

Agilent Xcalibur Sapphire3 diffractometer	4284 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis RED</i> ; Agilent, 2012)	2106 independent reflections
<i>T</i> <sub>min</sub> = 0.742, <i>T</i> <sub>max</sub> = 1.000	2028 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.019

### 2.3. Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.022	Δρ <sub>max</sub> = 0.37 e Å <sup>-3</sup>
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.047	Δρ <sub>min</sub> = -0.36 e Å <sup>-3</sup>
<i>S</i> = 1.04	Absolute structure: Flack (1983),
2106 reflections	969 Friedel pairs
120 parameters	Absolute structure parameter:
H-atom parameters constrained	0.39 (4)

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3A···Cl2	0.86	2.34	3.124 (3)	151
N3—H3B···Cl1 <sup>1</sup>	0.86	2.48	3.280 (3)	156
N3—H3B···O1 <sup>1</sup>	0.86	2.45	3.015 (3)	124

Symmetry code: (i)  $-x + \frac{1}{2}, -y + 2, z - \frac{1}{2}$ .

Data collection: *CrysAlis CCD* (Agilent, 2012); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5096).

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## supporting information

*Acta Cryst.* (2015). E71, m10–m11 [https://doi.org/10.1107/S2056989014026619]

## Crystal structure of dichlorido{4-[(*E*)-(methoxyimino- $\kappa$ N)methyl]-1,3-thiazol-2-amine- $\kappa$ N<sup>3</sup>}palladium(II)

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### S1. Experimental

PdCl<sub>2</sub> (0.036 g, 0.2 mmol) was dissolved in 6*N* HCl (3 ml) at 313–323 K, and ethanol (7 ml) was added. To the resulting light-brown solution was added a hot solution of 4-[(methoxyimino)methyl]-1,3-thiazol-2-amine (0.031 g, 0.2 mmol), dissolved in ethanol (10 ml). The reaction mixture was stirred for one hour under reflux and cooled down to room temperature whereupon orange needle-like single crystals were filtered off, washed with ethanol and diethyl ether and dried in a vacuum desiccator over CaCl<sub>2</sub>. Yield: 0.045 g (65%).

### S2. Refinement

All hydrogen atoms were located from difference Fourier maps and constrained to ride on their parent atoms, with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  (except  $U_{\text{iso}} = 1.5U_{\text{eq}}$  for the methyl group). The structure was refined from a crystal twinned by inversion (Flack parameter value 0.39 (4)).

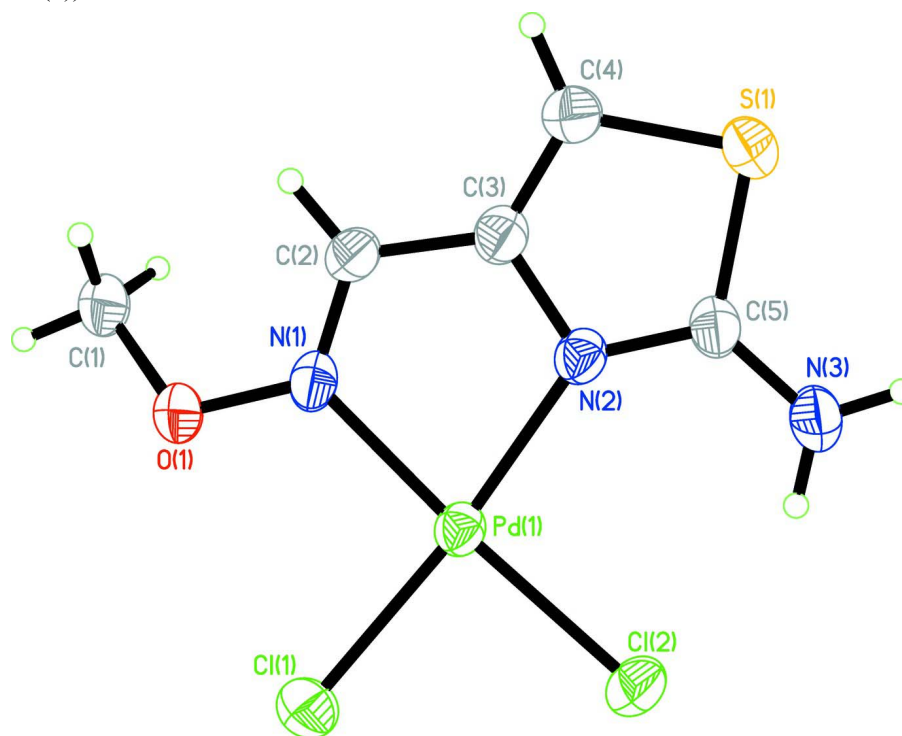


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

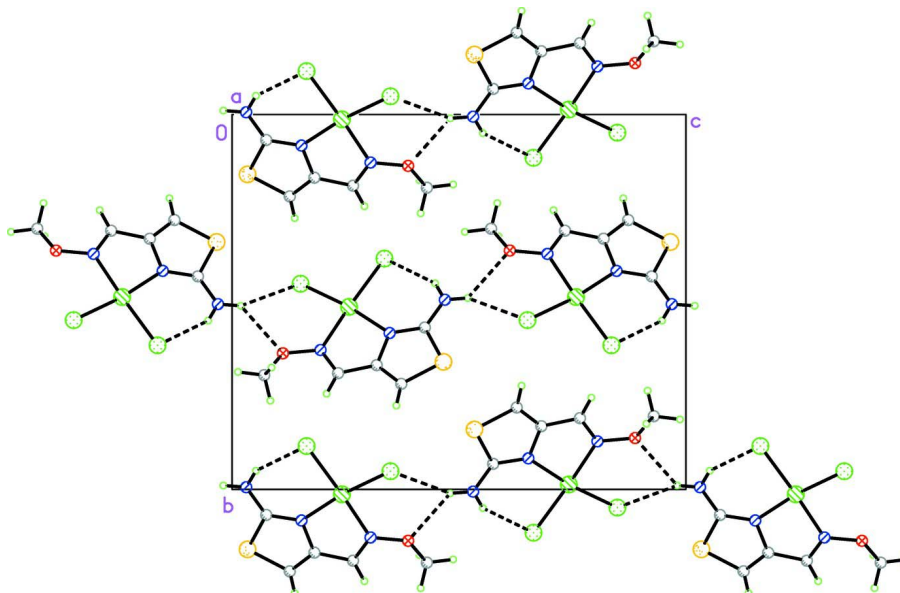


Figure 2

Crystal packing of the title compound with hydrogen bonds shown as dashed lines.

### Dichlorido{4-[(*E*)-(methoxyimino- $\kappa$ N)methyl]-1,3-thiazol-2-amine- $\kappa$ N<sup>3</sup>}palladium(II)

#### Crystal data

[PdCl<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>OS)]

$M_r = 334.50$

Orthorhombic,  $P2_12_12_1$

$a = 4.347$  (3) Å

$b = 13.583$  (2) Å

$c = 16.411$  (3) Å

$V = 969.0$  (7) Å<sup>3</sup>

$Z = 4$

$F(000) = 648$

$D_x = 2.293$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2494 reflections

$\theta = 3.8$ – $31.7^\circ$

$\mu = 2.64$  mm<sup>-1</sup>

$T = 294$  K

, orange

$0.4 \times 0.3 \times 0.2$  mm

#### Data collection

Agilent Xcalibur Sapphire3  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1827 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis RED*; Agilent, 2012)

$T_{\min} = 0.742$ ,  $T_{\max} = 1.000$

4284 measured reflections

2106 independent reflections

2028 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -5 \rightarrow 5$

$k = -17 \rightarrow 16$

$l = -21 \rightarrow 21$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.047$

$S = 1.04$

2106 reflections

120 parameters

0 restraints

Primary atom site location: structure-invariant direct methods  
 Secondary atom site location: difference Fourier map  
 Hydrogen site location: difference Fourier map  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 0.1807P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 969 Friedel pairs

Absolute structure parameter: 0.39 (4)

### 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.15497 (6)	0.986930 (16)	0.742144 (12)	0.02751 (7)
Cl1	-0.1238 (2)	1.04846 (7)	0.84901 (5)	0.0396 (2)
Cl2	-0.0192 (2)	1.11559 (6)	0.66418 (5)	0.0411 (2)
S1	0.6968 (2)	0.84020 (7)	0.53414 (5)	0.0394 (2)
O1	0.2794 (6)	0.86291 (19)	0.88793 (12)	0.0379 (6)
N1	0.3271 (7)	0.87185 (19)	0.80514 (14)	0.0306 (6)
N2	0.3996 (6)	0.91712 (19)	0.65287 (15)	0.0291 (6)
N3	0.3636 (8)	1.0058 (2)	0.53113 (15)	0.0489 (8)
H3A	0.2466	1.0498	0.5526	0.059*
H3B	0.4153	1.0104	0.4807	0.059*
C1	0.5024 (9)	0.8046 (3)	0.92925 (18)	0.0389 (8)
H1A	0.4798	0.8132	0.9870	0.058*
H1B	0.7050	0.8249	0.9130	0.058*
H1C	0.4729	0.7366	0.9156	0.058*
C2	0.4954 (8)	0.8100 (2)	0.76650 (18)	0.0328 (7)
H2	0.5819	0.7552	0.7916	0.039*
C3	0.5408 (8)	0.8314 (2)	0.68133 (18)	0.0315 (7)
C4	0.7074 (9)	0.7815 (3)	0.62715 (19)	0.0375 (8)
H4	0.8138	0.7236	0.6379	0.045*
C5	0.4632 (8)	0.9318 (2)	0.57529 (18)	0.0317 (7)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Pd1	0.03240 (12)	0.02459 (11)	0.02555 (10)	-0.00010 (10)	-0.00195 (9)	0.00015 (8)
Cl1	0.0450 (5)	0.0412 (5)	0.0327 (4)	0.0059 (4)	0.0021 (4)	-0.0055 (3)
Cl2	0.0511 (5)	0.0326 (4)	0.0394 (4)	0.0092 (4)	-0.0021 (4)	0.0062 (4)
S1	0.0506 (6)	0.0390 (5)	0.0286 (4)	0.0037 (5)	0.0042 (4)	-0.0028 (3)

O1	0.0456 (14)	0.0444 (14)	0.0237 (9)	0.0096 (12)	0.0026 (10)	0.0059 (9)
N1	0.0373 (15)	0.0304 (14)	0.0240 (11)	-0.0015 (15)	-0.0013 (12)	0.0048 (10)
N2	0.0361 (16)	0.0239 (13)	0.0273 (12)	-0.0007 (12)	-0.0025 (11)	0.0012 (10)
N3	0.077 (2)	0.0424 (17)	0.0276 (12)	0.014 (2)	0.0087 (14)	0.0054 (12)
C1	0.045 (2)	0.045 (2)	0.0260 (14)	0.006 (2)	-0.0007 (16)	0.0053 (14)
C2	0.0409 (18)	0.0273 (15)	0.0303 (15)	0.0048 (15)	-0.0018 (15)	0.0024 (13)
C3	0.0388 (18)	0.0277 (17)	0.0282 (14)	-0.0013 (15)	-0.0032 (14)	-0.0001 (13)
C4	0.045 (2)	0.0342 (18)	0.0333 (15)	0.0069 (17)	-0.0021 (16)	-0.0014 (13)
C5	0.0385 (18)	0.0316 (18)	0.0251 (14)	-0.0029 (16)	0.0012 (14)	0.0012 (13)

*Geometric parameters (Å, °)*

Pd1—C11	2.2897 (10)	N3—H3A	0.8600
Pd1—C12	2.2943 (9)	N3—H3B	0.8600
Pd1—N1	2.018 (3)	N3—C5	1.313 (4)
Pd1—N2	2.044 (3)	C1—H1A	0.9600
S1—C4	1.723 (3)	C1—H1B	0.9600
S1—C5	1.742 (3)	C1—H1C	0.9600
O1—N1	1.380 (3)	C2—H2	0.9300
O1—C1	1.423 (4)	C2—C3	1.441 (4)
N1—C2	1.282 (4)	C3—C4	1.332 (5)
N2—C3	1.397 (4)	C4—H4	0.9300
N2—C5	1.318 (4)		
C11—Pd1—C12	88.54 (4)	O1—C1—H1B	109.5
N1—Pd1—C11	94.96 (8)	O1—C1—H1C	109.5
N1—Pd1—C12	176.43 (8)	H1A—C1—H1B	109.5
N1—Pd1—N2	79.34 (10)	H1A—C1—H1C	109.5
N2—Pd1—C11	173.65 (8)	H1B—C1—H1C	109.5
N2—Pd1—C12	97.20 (8)	N1—C2—H2	122.4
C4—S1—C5	90.16 (16)	N1—C2—C3	115.2 (3)
N1—O1—C1	114.6 (2)	C3—C2—H2	122.4
O1—N1—Pd1	121.1 (2)	N2—C3—C2	115.6 (3)
C2—N1—Pd1	117.8 (2)	C4—C3—N2	116.1 (3)
C2—N1—O1	121.0 (3)	C4—C3—C2	128.3 (3)
C3—N2—Pd1	112.1 (2)	S1—C4—H4	125.0
C5—N2—Pd1	137.0 (2)	C3—C4—S1	110.0 (3)
C5—N2—C3	110.9 (3)	C3—C4—H4	125.0
H3A—N3—H3B	120.0	N2—C5—S1	112.9 (2)
C5—N3—H3A	120.0	N3—C5—S1	121.7 (2)
C5—N3—H3B	120.0	N3—C5—N2	125.4 (3)
O1—C1—H1A	109.5		
Pd1—N1—C2—C3	0.1 (4)	N1—C2—C3—N2	0.9 (5)
Pd1—N2—C3—C2	-1.4 (4)	N1—C2—C3—C4	178.7 (4)
Pd1—N2—C3—C4	-179.5 (3)	N2—Pd1—N1—O1	175.8 (3)
Pd1—N2—C5—S1	179.58 (19)	N2—Pd1—N1—C2	-0.7 (3)
Pd1—N2—C5—N3	-1.1 (6)	N2—C3—C4—S1	-0.2 (4)

Cl1—Pd1—N1—O1	-7.0 (2)	C1—O1—N1—Pd1	-156.2 (2)
Cl1—Pd1—N1—C2	176.4 (3)	C1—O1—N1—C2	20.2 (4)
Cl1—Pd1—N2—C3	-25.3 (9)	C2—C3—C4—S1	-178.0 (3)
Cl1—Pd1—N2—C5	155.6 (5)	C3—N2—C5—S1	0.5 (4)
Cl2—Pd1—N1—O1	161.6 (12)	C3—N2—C5—N3	179.8 (3)
Cl2—Pd1—N1—C2	-14.9 (15)	C4—S1—C5—N2	-0.5 (3)
Cl2—Pd1—N2—C3	-179.7 (2)	C4—S1—C5—N3	-179.8 (3)
Cl2—Pd1—N2—C5	1.2 (3)	C5—S1—C4—C3	0.4 (3)
O1—N1—C2—C3	-176.4 (3)	C5—N2—C3—C2	177.9 (3)
N1—Pd1—N2—C3	1.1 (2)	C5—N2—C3—C4	-0.2 (4)
N1—Pd1—N2—C5	-178.0 (4)		

*Hydrogen-bond geometry (Å, °)*

<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>
N3—H3 <i>A</i> $\cdots$ Cl2	0.86	2.34	3.124 (3)	151
N3—H3 <i>B</i> $\cdots$ Cl1 <sup>i</sup>	0.86	2.48	3.280 (3)	156
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