

# [(1,2,5,6- $\eta$ )-Cycloocta-1,5-diene]bis(thiocyanato- $\kappa$ S)platinum(II)

Kwang Ha\*

Chonnam National University, School of Chemical Engineering, Research Institute of Catalysis, Gwangju, Republic of Korea. \*Correspondence e-mail: hakwang@chonnam.ac.kr

Received 28 January 2019

Accepted 29 January 2019

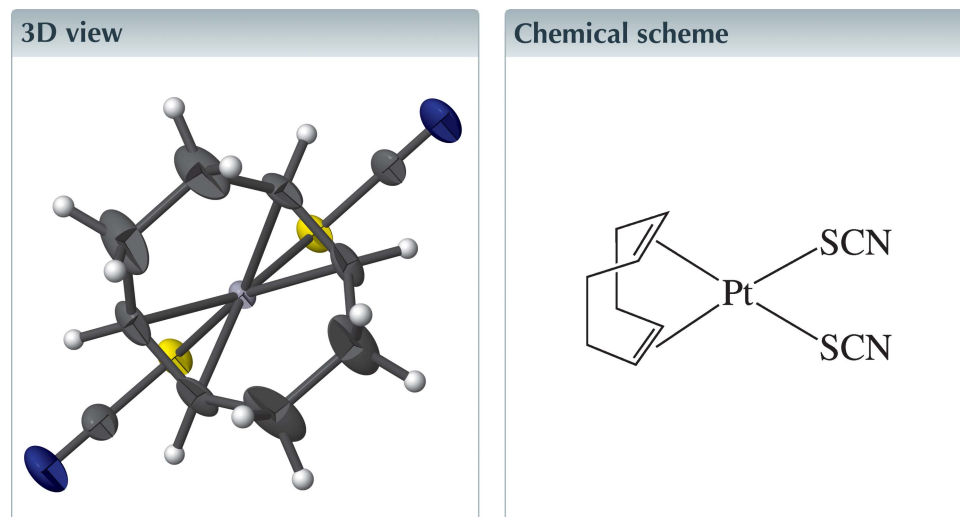
Edited by E. R. T. Tiekink, Sunway University, Malaysia

Keywords: crystal structure; platinum(II) complex; cycloocta-1,5-diene; thiocyanate.

CCDC reference: 1894262

Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

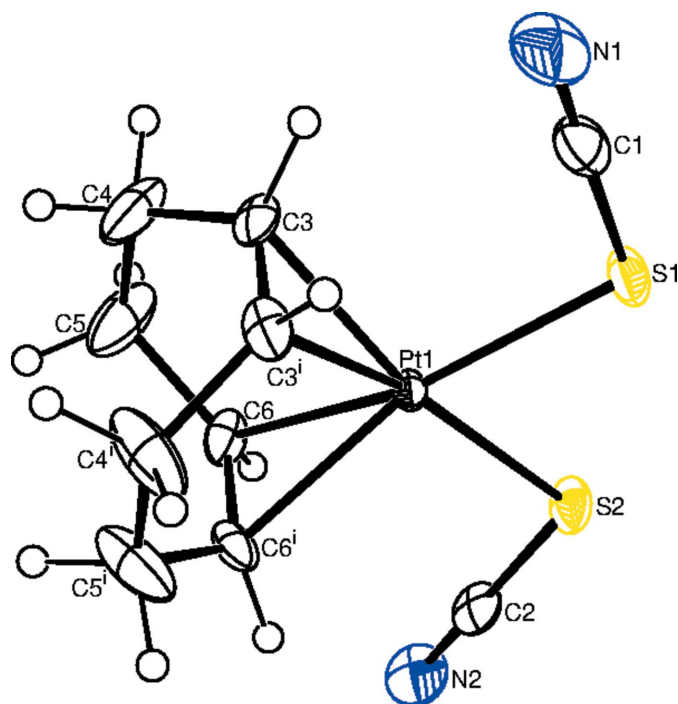
In the title complex,  $[\text{Pt}(\text{SCN})_2(\text{C}_8\text{H}_{12})]$ , the  $\text{Pt}^{\text{II}}$  ion lies in a square-planar coordination geometry defined by the mid-points of the two  $\pi$ -coordinated double bonds of cycloocta-1,5-diene and two S-bound  $\text{SCN}^-$  anions. The complex is disposed about a mirror plane passing through the Pt atom and the  $\text{SCN}^-$  ligands, and bisecting the cycloocta-1,5-diene molecule. The room-temperature crystal structure of the title complex was previously reported in the orthorhombic space group  $Pna2_1$  [Musitu & Garcia-Blanco (1984). *Acta Cryst. A* **40**, C101]. The low-temperature structure presented herein represents a different (higher symmetry) orthorhombic space group  $Pnma$  whereby the  $\text{Pt}^{\text{II}}$  atom lies on a mirror plane, lacking in the earlier study.



## Structure description

With reference to the title complex,  $[\text{Pt}(\text{SCN})_2(\text{cod})]$ , the crystal structures of related  $\text{cod-Pt}^{\text{II}}$  complexes  $[\text{Pt}X_2(\text{cod})]$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{cod} = \text{cycloocta-1,5-diene}$ ) have been determined previously. The chlorido complex  $[\text{PtCl}_2(\text{cod})]$  (Goel *et al.*, 1982; Syed *et al.*, 1984; Musitu & Garcia-Blanco, 1984) and the bromido complex  $[\text{PtBr}_2(\text{cod})]$  (Musitu & Garcia-Blanco, 1984) both crystallize in the orthorhombic space group  $P2_12_12_1$ . The iodo complex  $[\text{PtI}_2(\text{cod})]$  crystallizes in the monoclinic space group  $P2_1/n$  (Musitu & Garcia-Blanco, 1984). The room-temperature crystal structure of the title complex was previously reported in the orthorhombic space group  $Pna2_1$  (Musitu & Garcia-Blanco, 1984). The low-temperature structure presented herein represents a different (higher symmetry) orthorhombic space group  $Pnma$  whereby the  $\text{Pt}^{\text{II}}$  atom lies on a mirror plane, lacking in the earlier study (Musitu & Garcia-Blanco, 1984).

In the title complex, the central  $\text{Pt}^{\text{II}}$  ion has a square-planar coordination geometry defined by the mid-points of the two  $\pi$ -coordinated double bonds of cycloocta-1,5-diene and two S atoms derived from two  $\text{SCN}^-$  anions (Fig. 1). The complex is disposed about a



**Figure 1**  
The molecular structure of the title complex showing the atom labelling and displacement ellipsoids drawn at the 40% probability level for non-H atoms [symmetry code: (i)  $x, \frac{1}{2} - y, z$ ].

mirror plane passing through the Pt atom and the SCN<sup>-</sup> ligands, and bisecting cycloocta-1,5-diene. Therefore, the asymmetric unit contains one half of the complex molecule. The cod ligand coordinates to the Pt atom in the boat conformation with the coordinated double-bond lengths of 1.386 (9) and 1.388 (9) Å, and with the cod ring angles lying in the range of 117.6 (4)–124.4 (3)°. The thiocyanato ligands are linear displaying S–C–N bond angles of 179.0 (6) and 180.0 (5)°, and the S atoms are coordinated to the Pt atom with nearly tetrahedral Pt–S–C bond angles of 106.0 (2) and 106.6 (2)°, characteristic of an S-bonded conformation (Ha, 2013).

### Synthesis and crystallization

To a solution of K<sub>2</sub>PtCl<sub>4</sub> (2.0820 g, 5.016 mmol) and KSCN (2.3967 g, 24.662 mmol) in H<sub>2</sub>O (40 ml) and EtOH (10 ml) was added cycloocta-1,5-diene (1.0235 g, 9.461 mmol) and refluxed for 2 h. The formed precipitate was separated by filtration, washed with H<sub>2</sub>O and acetone, and dried at 323 K, to give a light-yellow powder (1.4009 g). Yellow crystals suitable for X-ray analysis were obtained by slow evaporation from an acetone solution at room temperature.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[Pt(SCN) <sub>2</sub> (C <sub>8</sub> H <sub>12</sub> )]
<i>M</i> <sub>r</sub>	419.43
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	223
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.8696 (12), 7.5226 (6), 9.0540 (6)
<i>V</i> (Å <sup>3</sup> )	1148.98 (14)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	12.54
Crystal size (mm)	0.21 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker PHOTON 100 CMOS detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2016)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.363, 0.745
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	27245, 1237, 1178
<i>R</i> <sub>int</sub>	0.082
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.620
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.019, 0.045, 1.11
No. of reflections	1237
No. of parameters	79
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.55, -0.79

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *ORTEP-3 for Windows* (Farrugia, 2012).

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

### Acknowledgements

The author thanks the KBSI, Seoul Center, for the X-ray data collection.

### Funding information

This study was supported financially by Chonnam National University (grant No. 2017–2777).

### References

- Bruker (2016). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Goel, A. B., Goel, S. & Van Der Veer, D. (1982). *Inorg. Chim. Acta*, **65**, L205–L206.
- Ha, K. (2013). *Z. Kristallogr. New Cryst. Struct.* **228**, 249–250.
- Musitu, F. Mz. & Garcia-Blanco, S. (1984). *Acta Cryst.* **A40**, C101.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Syed, A., Stevens, E. D. & Cruz, S. G. (1984). *Inorg. Chem.* **23**, 3673–3674.

## full crystallographic data

*IUCrData* (2019). 4, x190162 [https://doi.org/10.1107/S2414314619001627]

[(1,2,5,6- $\eta$ )-Cycloocta-1,5-diene]bis(thiocyanato- $\kappa$ S)platinum(II)

Kwang Ha

[(1,2,5,6- $\eta$ )-Cycloocta-1,5-diene]bis(thiocyanato- $\kappa$ S)platinum(II)*Crystal data*

[Pt(SCN)<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)]

$M_r = 419.43$

Orthorhombic, *Pnma*

$a = 16.8696$  (12) Å

$b = 7.5226$  (6) Å

$c = 9.0540$  (6) Å

$V = 1148.98$  (14) Å<sup>3</sup>

$Z = 4$

$F(000) = 784$

$D_x = 2.425$  Mg m<sup>-3</sup>

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

Cell parameters from 9838 reflections

$\theta = 2.4$ – $26.1^\circ$

$\mu = 12.54$  mm<sup>-1</sup>

$T = 223$  K

Block, yellow

$0.21 \times 0.15 \times 0.10$  mm

*Data collection*

Bruker PHOTON 100 CMOS detector  
diffractometer

Radiation source: sealed tube

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2016)

$T_{\min} = 0.363$ ,  $T_{\max} = 0.745$

27245 measured reflections

1237 independent reflections

1178 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.082$

$\theta_{\max} = 26.1^\circ$ ,  $\theta_{\min} = 3.3^\circ$

$h = -20 \rightarrow 20$

$k = -9 \rightarrow 9$

$l = -11 \rightarrow 11$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.045$

$S = 1.11$

1237 reflections

79 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0127P)^2 + 2.853P]$

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

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

$\Delta\rho_{\max} = 0.55$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.79$  e Å<sup>-3</sup>

*Special details*

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

**Refinement.** The hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms: C—H = 0.99 Å (CH) or 0.98 Å (CH<sub>2</sub>) and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.05447 (2)	0.2500	0.10287 (2)	0.01688 (8)
S1	-0.07951 (8)	0.2500	0.16871 (16)	0.0318 (3)
C1	-0.0816 (4)	0.2500	0.3536 (7)	0.0357 (14)
N1	-0.0841 (4)	0.2500	0.4801 (7)	0.0551 (17)
S2	-0.00113 (9)	0.2500	-0.13300 (15)	0.0321 (3)
C2	0.0746 (4)	0.2500	-0.2528 (6)	0.0311 (13)
N2	0.1258 (4)	0.2500	-0.3338 (5)	0.0472 (14)
C3	0.0990 (2)	0.1579 (6)	0.3169 (4)	0.0313 (9)
H3	0.0581	0.1037	0.3812	0.038*
C4	0.1716 (3)	0.0447 (9)	0.2949 (5)	0.0622 (18)
H4A	0.2115	0.0831	0.3669	0.075*
H4B	0.1574	-0.0781	0.3195	0.075*
C5	0.2080 (3)	0.0436 (9)	0.1537 (5)	0.0610 (17)
H5A	0.2086	-0.0793	0.1180	0.073*
H5B	0.2633	0.0805	0.1661	0.073*
C6	0.1717 (2)	0.1577 (6)	0.0354 (4)	0.0293 (8)
H6	0.1732	0.1041	-0.0644	0.035*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Pt1	0.01299 (12)	0.02235 (12)	0.01529 (11)	0.000	-0.00064 (6)	0.000
S1	0.0154 (6)	0.0481 (9)	0.0317 (8)	0.000	0.0019 (5)	0.000
C1	0.026 (3)	0.039 (4)	0.042 (4)	0.000	0.008 (3)	0.000
N1	0.048 (3)	0.078 (5)	0.039 (3)	0.000	0.019 (3)	0.000
S2	0.0240 (7)	0.0505 (9)	0.0217 (6)	0.000	-0.0067 (5)	0.000
C2	0.037 (3)	0.042 (3)	0.015 (2)	0.000	-0.009 (2)	0.000
N2	0.055 (3)	0.067 (4)	0.020 (3)	0.000	-0.002 (3)	0.000
C3	0.0253 (18)	0.055 (2)	0.0132 (15)	0.0058 (18)	-0.0006 (14)	0.0082 (16)
C4	0.046 (3)	0.103 (5)	0.038 (2)	0.042 (3)	0.011 (2)	0.034 (3)
C5	0.056 (3)	0.090 (4)	0.037 (2)	0.048 (3)	0.011 (2)	0.017 (3)
C6	0.0202 (17)	0.049 (2)	0.0189 (16)	0.0121 (17)	0.0042 (14)	-0.0008 (17)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Pt1—C6 <sup>i</sup>	2.183 (3)	C3—C4	1.505 (6)
Pt1—C6	2.183 (3)	C3—H3	0.9900
Pt1—C3 <sup>i</sup>	2.191 (3)	C4—C5	1.418 (6)
Pt1—C3	2.191 (3)	C4—H4A	0.9800
Pt1—S2	2.3324 (13)	C4—H4B	0.9800
Pt1—S1	2.3375 (13)	C5—C6	1.503 (6)
S1—C1	1.674 (7)	C5—H5A	0.9800
C1—N1	1.146 (9)	C5—H5B	0.9800
S2—C2	1.676 (6)	C6—C6 <sup>i</sup>	1.388 (9)
C2—N2	1.133 (8)	C6—H6	0.9900

C3—C3 <sup>i</sup>	1.386 (9)		
C6 <sup>i</sup> —Pt1—C6	37.1 (2)	C3 <sup>i</sup> —C3—H3	114.3
C6 <sup>i</sup> —Pt1—C3 <sup>i</sup>	80.59 (14)	C4—C3—H3	114.3
C6—Pt1—C3 <sup>i</sup>	92.15 (14)	Pt1—C3—H3	114.3
C6 <sup>i</sup> —Pt1—C3	92.15 (14)	C5—C4—C3	118.3 (4)
C6—Pt1—C3	80.58 (14)	C5—C4—H4A	107.7
C3 <sup>i</sup> —Pt1—C3	36.9 (2)	C3—C4—H4A	107.7
C6 <sup>i</sup> —Pt1—S2	96.21 (10)	C5—C4—H4B	107.7
C6—Pt1—S2	96.21 (10)	C3—C4—H4B	107.7
C3 <sup>i</sup> —Pt1—S2	161.39 (12)	H4A—C4—H4B	107.1
C3—Pt1—S2	161.39 (12)	C4—C5—C6	117.6 (4)
C6 <sup>i</sup> —Pt1—S1	161.32 (11)	C4—C5—H5A	107.9
C6—Pt1—S1	161.32 (11)	C6—C5—H5A	107.9
C3 <sup>i</sup> —Pt1—S1	96.07 (10)	C4—C5—H5B	107.9
C3—Pt1—S1	96.07 (10)	C6—C5—H5B	107.9
S2—Pt1—S1	81.06 (5)	H5A—C5—H5B	107.2
C1—S1—Pt1	106.0 (2)	C6 <sup>i</sup> —C6—C5	124.8 (3)
N1—C1—S1	179.0 (6)	C6 <sup>i</sup> —C6—Pt1	71.47 (11)
C2—S2—Pt1	106.63 (19)	C5—C6—Pt1	110.6 (3)
N2—C2—S2	180.0 (5)	C6 <sup>i</sup> —C6—H6	114.1
C3 <sup>i</sup> —C3—C4	124.4 (3)	C5—C6—H6	114.1
C3 <sup>i</sup> —C3—Pt1	71.56 (12)	Pt1—C6—H6	114.1
C4—C3—Pt1	109.9 (3)		
C3 <sup>i</sup> —C3—C4—C5	-68.8 (7)	C4—C5—C6—C6 <sup>i</sup>	68.2 (7)
Pt1—C3—C4—C5	12.0 (7)	C4—C5—C6—Pt1	-13.0 (7)
C3—C4—C5—C6	0.6 (9)		

Symmetry code: (i)  $x, -y+1/2, z$ .