IUCrData

ISSN 2414-3146

Received 24 January 2019
Accepted 28 January 2019

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; platinum(II); diimine dithiolate; Pt···Pt interaction; hydrogen bonding.

CCDC reference: 1894191

Structural data: full structural data are available from iucrdata.iucr.org

(2,2′-Bipyridine)(1,2-dicyanoethene-1,2-dithiolato)platinum(II)

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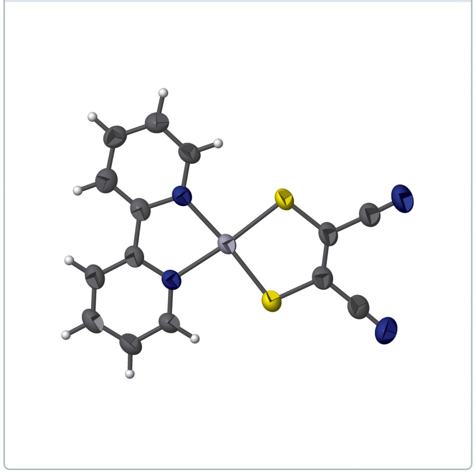
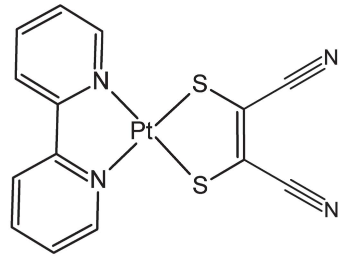
In the crystal structure of the title complex, [Pt($C_4N_2S_2$)($C_{10}H_8N_2$)], the complex molecules pack as head-to-tail/inversion dimers, which are stabilized by HOMO–LUMO interactions and a Pt···Pt distance of 3.6625 (8) Å. The dimers are linked by C—H···N hydrogen bonds, forming layers parallel to the (101) plane.

3D view



Chemical scheme



Structure description

Since Eisenberg's initial report on luminescent platinum(II) diimine dithiolate complexes (Zuleta, *et al.* 1989), this class of compounds has been utilized in areas such as dye-sensitized solar cells (Islam *et al.*, 2001; Geary *et al.*, 2005), photosplitting of water (Zhang *et al.*, 2007, Zarkadoulas *et al.*, 2012) and non-linear optics (Cummings *et al.*, 1997). X-ray structures of platinum(II)dithiolate complexes with modified bipyridine ligands are common in papers such as those describing the photophysical properties (Lazarides *et al.*, 2011), reaction kinetics (Stace *et al.*, 2016), or charge-transfer properties (Smucker *et al.*, 2003; Browning *et al.*, 2014) of these compounds. The crystal structure of one of the initial complexes, Pt(2,2′-bpy)(mnt), which inspired many variations, has heretofore not been published. This paper remedies the absence in the literature.

The title compound crystallized in the centrosymmetric monoclinic space group $P2_1/n$ and contains a single molecule of Pt(2,2′-bpy)(mnt) as the contents of its asymmetric unit (Fig. 1). The platinum(II) atom has a square-pyramidal coordination sphere and the Pt—N and Pt—S bond distances (Table 1) are typical for *M*(diimine)(dithiolate) molecules. Within the complex there are short C—H···S interactions present (Fig. 1 and Table 2).

The structure contains head-to-tail (inversion) dimers of Pt(2,2′-bpy)(mnt), as shown in Fig. 2. Intradimer integrity is maintained *via* HOMO–LUMO interactions whereby the former (of mixed metal/dithiolate molecular orbital character) overlaps with the latter

https://doi.org/10.1107/S2414314619001585

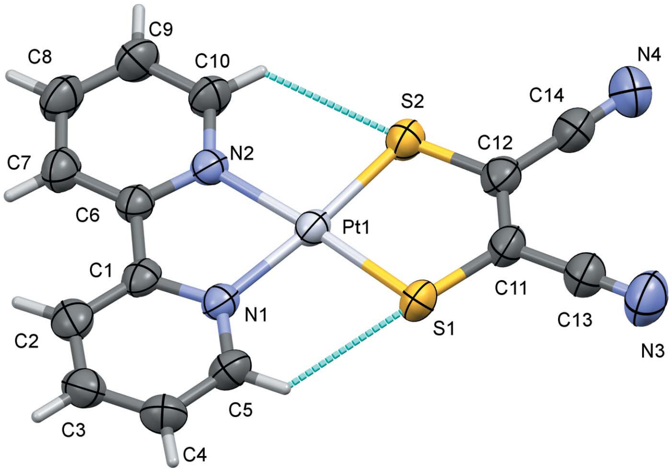


Figure 1
A view of the molecular structure of the title compound, with atom labeling. Displacement ellipsoids are drawn at the 50% probability level. The short intramolecular C—H···S contacts are shown as dashed lines (Table 2).

(of primarily chelating diimine ligand character) (Cummings & Eisenberg, 1996) at a distance (C2—C12^i) of 3.408 (9) Å (see Fig. 2). Additional integrity within the dimer is also maintained *via* contacts between the divalent platinum atoms at a distance of 3.6625 (8) Å.

Neighboring dimers of Pt(2,2′-bpy)(mnt) are linked by C—H···N hydrogen bonds (Table 2), forming layers parallel to the (101) plane, as shown in Fig. 3. Given the displacement of the two molecules from the different dimers relative to one another (~2.8 Å), interdimer structural integrity is not maintained by secondary Pt···Pt interactions. Rather, interactions between the π-electron density of the 2,2′-bipyridine ligand from one molecule and the empty d_{z^2} orbital from a platinum atom of the second are more likely. Weak π–π interactions may also be providing additional stability as the centroid-to-centroid distance between neighboring pyridyl rings was measured at 4.247 (4) Å, a distance close to the upper limit typical of such interactions (4.2 Å; Browning *et al.*, 2014).

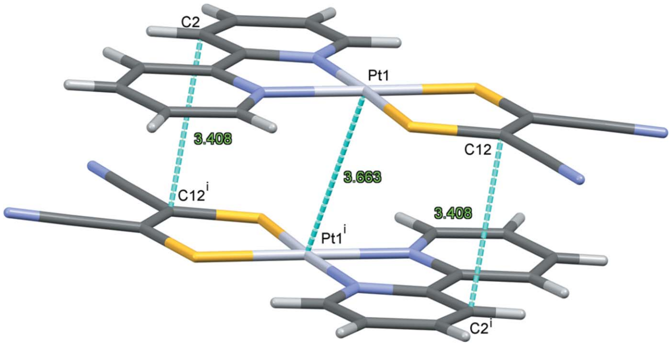


Figure 2
A view of the inversion dimer of the title compound with select Pt1···Pt1^i and C2···C12^i/C12···C2^i distances in Å [symmetry code: (i) = −x + 1, −y + 1, −z + 1].

Table 1
Selected Pt—N and Pt—S bond lengths (Å).

Bond	Bond length
Pt1—S1	2.2487 (16)
Pt1—S2	2.2425 (17)
Pt1—N1	2.035 (5)
Pt1—N2	2.048 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···S1	0.94	2.67	3.260 (8)	121
C10—H10···S2	0.94	2.65	3.245 (6)	121
C2—H2···N3^i	0.94	2.58	3.346 (10)	139

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Synthesis and crystallization

The title compound was synthesized according to published procedures (Zuleta *et al.*, 1990). Orange needles of Pt(2,2′-bpy)(mnt) resulted from the ambient cooling of a narrow glass tube containing a warm saturated DMF solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Acknowledgements

X-ray data were collected at the University of North Texas using a Bruker APEXII CCD diffractometer.

Funding information

Funding for this research was provided by: Welch Foundation (grant No. AD-0007).

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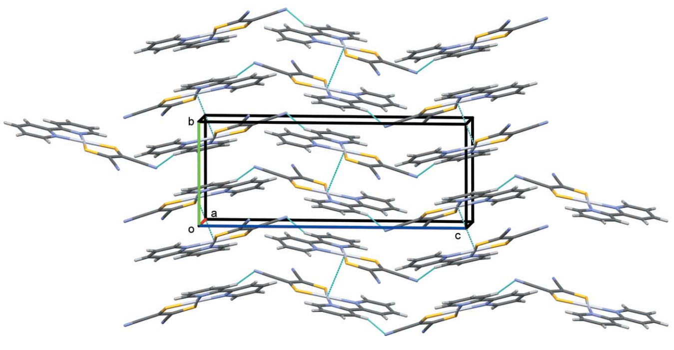

Figure 3
A view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds (Table 2) and Pt···Pt interactions are shown as dashed lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Pt(C_4N_2S_2)(C_{10}H_8N_2)]$
M_r	491.45
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	220
a, b, c (Å)	10.087 (3), 7.349 (2), 19.442 (6)
β (°)	101.276 (6)
V (Å^3)	1413.4 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	10.22
Crystal size (mm)	0.12 × 0.05 × 0.01
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.007, 0.029
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18409, 3118, 2556
R_{int}	0.063
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.642
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.081, 1.05
No. of reflections	3118
No. of parameters	190
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.09, −1.19

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

IUCrData (2019). **4**, x190158 [https://doi.org/10.1107/S2414314619001585]

(2,2′-Bipyridine)(1,2-dicyanoethene-1,2-dithiolato)platinum(II)

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Crystal data

$[Pt(C_4N_2S_2)(C_{10}H_8N_2)]$
$M_r = 491.45$
Monoclinic, $P2_1/n$
$a = 10.087$ (3) Å
$b = 7.349$ (2) Å
$c = 19.442$ (6) Å
$\beta = 101.276$ (6)°
$V = 1413.4$ (8) Å^3
$Z = 4$
$F(000) = 920$
$D_x = 2.310$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8369 reflections
$\theta = 2.5–27.1°$
$\mu = 10.22$ mm^{-1}
$T = 220$ K
Needle, orange
0.12 × 0.05 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
$T_{min} = 0.007$, $T_{max} = 0.029$
18409 measured reflections
3118 independent reflections
2556 reflections with $I > 2\sigma(I)$
$R_{int} = 0.063$
$\theta_{max} = 27.1°$, $\theta_{min} = 2.1°$
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 9$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 1.05$
3118 reflections
190 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
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 2.09$ e Å^{-3}
$\Delta\rho_{min} = -1.19$ e Å^{-3}

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.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Pt1	0.43643 (2)	0.70734 (3)	0.53458 (2)	0.03903 (10)
S1	0.51148 (16)	0.6436 (2)	0.64868 (8)	0.0470 (3)
S2	0.22499 (16)	0.6416 (2)	0.54649 (8)	0.0469 (3)
N1	0.6216 (5)	0.7728 (7)	0.5150 (3)	0.0396 (10)
N2	0.3858 (5)	0.7650 (6)	0.4297 (3)	0.0392 (10)
C7	0.4693 (7)	0.8661 (10)	0.3301 (3)	0.0522 (15)
H7	0.542164	0.904905	0.310168	0.063*
C9	0.2366 (8)	0.7948 (10)	0.3194 (4)	0.0572 (17)
H9	0.149274	0.782025	0.292112	0.069*
C1	0.6228 (7)	0.8192 (7)	0.4475 (3)	0.0420 (13)
C4	0.8613 (7)	0.8111 (10)	0.5421 (4)	0.0558 (17)
H4	0.942142	0.808236	0.575644	0.067*
C5	0.7390 (7)	0.7732 (9)	0.5608 (4)	0.0492 (14)
H5	0.738405	0.746376	0.608044	0.059*
C2	0.7416 (7)	0.8605 (9)	0.4255 (4)	0.0522 (15)
H2	0.740318	0.893202	0.378586	0.063*
C10	0.2615 (7)	0.7526 (10)	0.3897 (3)	0.0499 (15)
H10	0.189427	0.714035	0.410351	0.060*
C6	0.4905 (7)	0.8193 (8)	0.4000 (3)	0.0421 (13)
C8	0.3413 (8)	0.8561 (11)	0.2894 (3)	0.0587 (17)
H8	0.325677	0.890471	0.241974	0.070*
C14	0.1239 (7)	0.5176 (11)	0.6564 (3)	0.0565 (17)
N3	0.4007 (7)	0.4658 (11)	0.8047 (3)	0.0749 (19)
N4	0.0271 (7)	0.4718 (11)	0.6732 (3)	0.0722 (18)
C11	0.3675 (7)	0.5754 (9)	0.6776 (3)	0.0501 (15)
C12	0.2442 (7)	0.5745 (9)	0.6334 (3)	0.0494 (15)
C13	0.3842 (7)	0.5158 (10)	0.7483 (3)	0.0550 (16)
C3	0.8621 (7)	0.8531 (10)	0.4734 (4)	0.0537 (15)
H3	0.944232	0.876651	0.459047	0.064*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.04558 (14)	0.04030 (14)	0.03045 (13)	−0.00093 (10)	0.00560 (9)	−0.00120 (9)
S1	0.0534 (8)	0.0553 (9)	0.0311 (7)	−0.0029 (7)	0.0052 (6)	0.0021 (6)
S2	0.0495 (8)	0.0539 (9)	0.0372 (7)	−0.0007 (7)	0.0080 (6)	0.0017 (7)
N1	0.045 (3)	0.038 (2)	0.034 (2)	−0.001 (2)	0.005 (2)	−0.0028 (19)
N2	0.045 (3)	0.036 (2)	0.035 (2)	−0.002 (2)	0.004 (2)	−0.0001 (19)
C7	0.067 (4)	0.049 (3)	0.041 (3)	−0.004 (3)	0.011 (3)	0.006 (3)
C9	0.057 (4)	0.068 (5)	0.042 (4)	−0.003 (3)	−0.002 (3)	0.007 (3)
C1	0.057 (3)	0.032 (3)	0.037 (3)	−0.001 (2)	0.009 (3)	−0.005 (2)
C4	0.047 (4)	0.063 (5)	0.054 (4)	−0.008 (3)	0.003 (3)	−0.003 (3)
C5	0.051 (3)	0.056 (4)	0.038 (3)	−0.001 (3)	0.001 (3)	−0.003 (3)
C2	0.061 (4)	0.046 (3)	0.053 (4)	−0.004 (3)	0.019 (3)	−0.010 (3)
C10	0.047 (3)	0.062 (4)	0.039 (3)	0.000 (3)	0.002 (3)	0.003 (3)

C6	0.052 (3)	0.037 (3)	0.037 (3)	−0.005 (2)	0.008 (2)	−0.001 (2)
C8	0.073 (4)	0.063 (4)	0.037 (3)	0.001 (4)	0.002 (3)	0.007 (3)
C14	0.063 (4)	0.065 (5)	0.042 (3)	−0.004 (3)	0.012 (3)	−0.007 (3)
N3	0.087 (5)	0.092 (5)	0.047 (3)	0.002 (4)	0.016 (3)	0.008 (3)
N4	0.070 (4)	0.090 (5)	0.062 (4)	−0.016 (4)	0.026 (3)	−0.003 (4)
C11	0.062 (4)	0.055 (4)	0.034 (3)	−0.004 (3)	0.012 (3)	−0.003 (3)
C12	0.059 (4)	0.048 (4)	0.041 (3)	−0.004 (3)	0.011 (3)	−0.005 (3)
C13	0.061 (4)	0.059 (4)	0.045 (4)	−0.002 (3)	0.012 (3)	0.000 (3)
C3	0.049 (3)	0.055 (4)	0.058 (4)	−0.010 (3)	0.013 (3)	−0.010 (3)

Geometric parameters (Å, º)

Pt1—S1	2.2487 (16)	C1—C2	1.383 (9)
Pt1—S2	2.2425 (17)	C1—C6	1.467 (9)
Pt1—N1	2.035 (5)	C4—H4	0.9400
Pt1—N2	2.048 (5)	C4—C5	1.381 (10)
S1—C11	1.731 (7)	C4—C3	1.373 (10)
S2—C12	1.734 (6)	C5—H5	0.9400
N1—C1	1.359 (8)	C2—H2	0.9400
N1—C5	1.335 (8)	C2—C3	1.381 (10)
N2—C10	1.343 (8)	C10—H10	0.9400
N2—C6	1.358 (8)	C8—H8	0.9400
C7—H7	0.9400	C14—N4	1.139 (9)
C7—C6	1.378 (9)	C14—C12	1.436 (9)
C7—C8	1.378 (10)	N3—C13	1.137 (9)
C9—H9	0.9400	C11—C12	1.367 (9)
C9—C10	1.377 (9)	C11—C13	1.421 (9)
C9—C8	1.377 (10)	C3—H3	0.9400

S2—Pt1—S1	89.82 (6)	N1—C5—C4	123.1 (6)
N1—Pt1—S1	95.12 (15)	N1—C5—H5	118.5
N1—Pt1—S2	175.05 (14)	C4—C5—H5	118.5
N1—Pt1—N2	79.9 (2)	C1—C2—H2	120.5
N2—Pt1—S1	174.88 (14)	C3—C2—C1	119.0 (6)
N2—Pt1—S2	95.18 (15)	C3—C2—H2	120.5
C11—S1—Pt1	103.8 (2)	N2—C10—C9	121.8 (7)
C12—S2—Pt1	103.6 (2)	N2—C10—H10	119.1
C1—N1—Pt1	114.9 (4)	C9—C10—H10	119.1
C5—N1—Pt1	127.0 (4)	N2—C6—C7	120.6 (6)
C5—N1—C1	118.0 (6)	N2—C6—C1	114.9 (5)
C10—N2—Pt1	125.8 (4)	C7—C6—C1	124.5 (6)
C10—N2—C6	119.3 (5)	C7—C8—H8	120.5
C6—N2—Pt1	114.9 (4)	C9—C8—C7	119.0 (6)
C6—C7—H7	120.0	C9—C8—H8	120.5
C6—C7—C8	120.0 (6)	N4—C14—C12	178.4 (7)
C8—C7—H7	120.0	C12—C11—S1	121.0 (5)
C10—C9—H9	120.4	C12—C11—C13	121.9 (6)
C10—C9—C8	119.2 (7)	C13—C11—S1	117.1 (5)

C8—C9—H9	120.4	C14—C12—S2	116.5 (5)
N1—C1—C2	121.8 (6)	C11—C12—S2	121.7 (5)
N1—C1—C6	115.4 (5)	C11—C12—C14	121.7 (6)
C2—C1—C6	122.9 (6)	N3—C13—C11	178.1 (9)
C5—C4—H4	120.7	C4—C3—C2	119.6 (6)
C3—C4—H4	120.7	C4—C3—H3	120.2
C3—C4—C5	118.6 (7)	C2—C3—H3	120.2

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···S1	0.94	2.67	3.260 (8)	121
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C2—H2···N3^{i}	0.94	2.58	3.346 (10)	139

Symmetry code: (i) $x+1/2, -y+3/2, z-1/2$.