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Bis(4,4′-bipyridin-1-ium) *cis*-bis(1,2-dicyano-2-sulfidoethene-1-sulfinato-κ^2S,S')platinate(2−)

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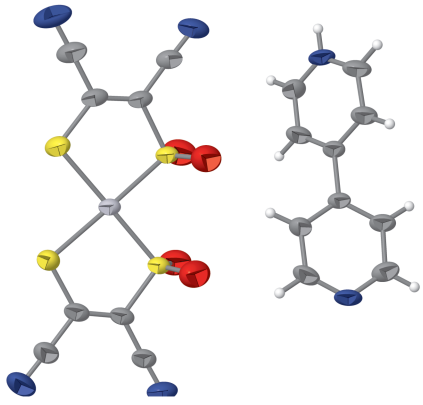
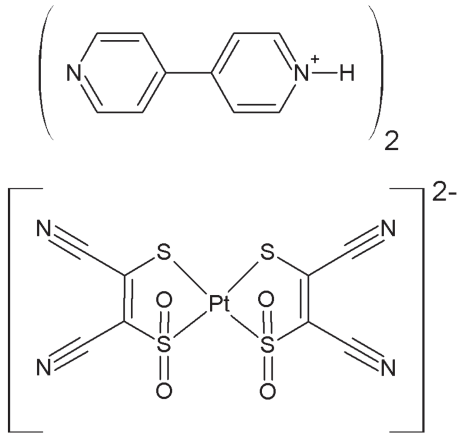
Crystals of the sulfinate-containing platinate salt, $(C_{10}H_9N_2)_2[Pt(C_4N_2O_2S_2)_2]$, were obtained from a solution of $[Pt(4,4'\text{-bpy})_2(mnt)]$ after a long period with minimal light (4,4′-bpy is 4,4′-bipyridine and mnt is maleonitriledithiolate). In the crystals, the cations associate via C—H···O hydrogen bonds with hydrogen bonded (—H···) chains of pyridinium anions. The *cis*-geometry of the sulfinate around the square-planar platinum atom, coupled with a torsion of one of the rings of the pyridinium, engenders multiple hydrogen bonds between the sulfinate oxygen atoms and the pyridinium hydrogen atoms.

3D view



Chemical scheme



Structure description

The asymmetric unit of the title compound contains one-half of the platinum bis-sulfinate moiety with the platinum residing on an inversion centre and a single pyridinium cation. The square-planar platinate anions have the sulfinate moieties in a *cis* arrangement around the platinum atom (Fig. 1). The Pt—S distances between the S2 thiolate and the S1 sulfinate are 2.3120 (13) and 2.2554 (12) Å, respectively. The S═O bond distances [S1═O1 = 1.448 (4) and S1═O2 = 1.439 (4) Å] in this structure match the S═O distances of 1.470 (4) and 1.444 (4) Å observed in platinum(II) sulfinato-thiolato complexes (Ishii *et al.*, 2007). The S—O single-bond distances in sulfenato ligands typically are around 0.1 Å longer at 1.55 Å (Buonomo *et al.*, 1995).

The pyridinium cations form hydrogen-bonded one-dimensional chains along the *c*-axis direction, which surround the platinate anions. These anions are slipped-stacked so as to fit between the pyridinium chains (Fig. 2). This type of packing of the anions is observed in a $[Pt(mnt)_2]^-$ salt with a planar 4-aminopyridinium monocation (Pei *et al.*, 2012), but when $[Pt(mnt)_2]^{2-}$ crystallizes with a planar dicationic $[4,4'\text{-}H_2bpy]^{2+}$ it forms *ABAB* stacks of alternating cations and anions (Crawford *et al.*, 2004). The sulfinate moieties alternate their positions along the slipped stacking of the anions, which corresponds to a rotation between the two rings of the pyridinium cation [torsion angle

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N3^{i}	0.86	1.88	2.730 (5)	171
C7—H7···N2^{ii}	0.93	2.50	3.363 (7)	155
C7—H7···O2^{iii}	0.93	2.57	3.197 (7)	125
C8—H8···O1	0.93	2.40	3.301 (6)	164
C8—H8···O2^{iii}	0.93	2.77	3.287 (7)	116

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

C8—C9—C10—C11 of 130.8 (5)°], that positions the H8 and H7 hydrogen atoms for H-bonding with the O1 and O2($-x+1, y, -z+\frac{3}{2}$) atoms of the sulfinates (Table 1 and Fig. 1).

Synthesis and crystallization

A methanol/water (1:1) solution containing [Pt(4,4′-bpy)$_2$-(mnt)] (Smith *et al.* 2019; 4,4′-bpy is 4,4′-bipyridine and mnt is maleonitriledithiolate) was combined with excess 4,4′-bpy due to the observed exchangeability of the 4,4′-bpy ligand. This solution was layered with THF in a thin tube. Small orange prisms were harvested from the bottom of the tube after a long period with minimal light. This conversion of a dithiolate ligand to its monosulfinate derivative has been achieved through multiple modes including: photooxidation in the presence of water (Connick & Gray, 1997), chemical oxidation (Sugimoto *et al.*, 2000; Ishii *et al.*, 2007), or after a prolonged period in minimal light (Stace *et al.*, 2016). Protons for the pyridinium likely originated from the solvents.

Refinement

Crystal data, data collection, and refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_{10}H_9N_2)_2[Pt(C_4N_2O_2S_2)_2]$
M_r	853.83
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	293
a, *b*, *c* (Å)	14.5669 (8), 10.8981 (6), 19.4595 (9)
β (°)	98.782 (5)
V (Å^3)	3053.0 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.92
Crystal size (mm)	0.09 × 0.07 × 0.03
Data collection	
Diffractometer	XtaLAB Mini II
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2024)
T_{min}, T_{max}	0.712, 0.851
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21005, 3124, 2503
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.066, 1.04
No. of reflections	3124
No. of parameters	204
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.71, −0.52

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

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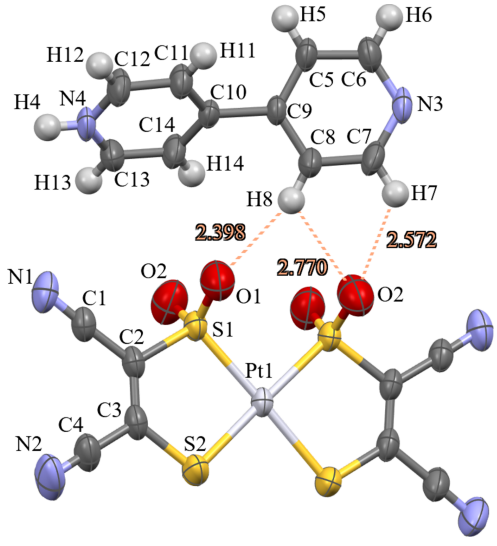

Figure 1
Ellipsoid representation (50% probability) of the title compound showing O···H distances for hydrogen bonds between O1 and H8 and O2($-x+1, y, -z+\frac{3}{2}$) and H8 and H7.

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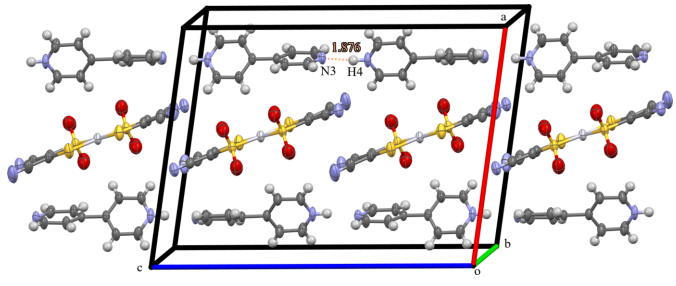

Figure 2
Ellipsoid representation (50% probability) of the packing of the title compound with pyridinium chains connected by hydrogen bonds between N3 of one pyridinium and the H4 of an adjacent pyridinium. The H-bond distance between N3($-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$) and H4($-x+\frac{3}{2}, -y+\frac{1}{2}, -z+1$) is shown. Some symmetry-related cell contents were removed for clarity.

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full crystallographic data

IUCrData (2025). **10**, x250383 [https://doi.org/10.1107/S2414314625003839]

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Crystal data

$(C_{10}H_9N_2)_2[Pt(C_4N_2O_2S_2)_2]$
M_r = 853.83
Monoclinic, $C2/c$
a = 14.5669 (8) Å
b = 10.8981 (6) Å
c = 19.4595 (9) Å
β = 98.782 (5)°
V = 3053.0 (3) Å^3
Z = 4
$F(000)$ = 1664
D_x = 1.858 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2218 reflections
θ = 2.4–25.0°
μ = 4.92 mm^{-1}
T = 293 K
Irregular, orange
0.09 × 0.07 × 0.03 mm

Data collection

XtaLAB Mini II diffractometer
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2024)
T_{min} = 0.712, T_{max} = 0.851
21005 measured reflections
3124 independent reflections
2503 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 26.4°, θ_{min} = 2.5°
h = −18→18
k = −13→13
l = −22→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.066
S = 1.04
3124 reflections
204 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 5.2814P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Special details

Refinement. H atoms bound to C and N atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.86 Å) and constrained to ride on the parent atom. U_{iso}(H) values were fixed at multiples of U_{eq}(C) [1.2 for C(H) and N(H) groups].

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pt1	0.5000	0.54391 (3)	0.7500	0.03897 (10)
S1	0.53256 (8)	0.39852 (12)	0.67484 (5)	0.0419 (3)
S2	0.53745 (10)	0.69516 (13)	0.67571 (6)	0.0578 (4)
O1	0.6114 (3)	0.3230 (4)	0.7024 (2)	0.0851 (13)
O2	0.4521 (3)	0.3318 (4)	0.6426 (2)	0.0870 (13)
N1	0.6220 (3)	0.3574 (5)	0.5069 (2)	0.0660 (13)
N2	0.6297 (4)	0.7379 (5)	0.5134 (2)	0.0909 (18)
C1	0.5992 (3)	0.4160 (5)	0.5502 (2)	0.0463 (13)
C2	0.5716 (3)	0.4857 (5)	0.6059 (2)	0.0422 (12)
C3	0.5720 (3)	0.6082 (5)	0.6092 (2)	0.0463 (12)
C4	0.6036 (4)	0.6797 (5)	0.5551 (3)	0.0607 (15)
N3	0.6676 (3)	−0.0315 (4)	0.91351 (18)	0.0501 (10)
N4	0.6763 (3)	0.0238 (4)	0.55456 (18)	0.0539 (11)
H4	0.6777	0.0327	0.5108	0.065*
C5	0.6851 (3)	−0.1265 (5)	0.8051 (2)	0.0490 (12)
H5	0.6972	−0.1970	0.7811	0.059*
C6	0.6820 (3)	−0.1305 (6)	0.8767 (2)	0.0530 (13)
H6	0.6904	−0.2057	0.8994	0.064*
C7	0.6538 (4)	0.0747 (5)	0.8800 (2)	0.0566 (15)
H7	0.6444	0.1445	0.9055	0.068*
C8	0.6526 (4)	0.0866 (5)	0.8087 (2)	0.0513 (13)
H8	0.6403	0.1621	0.7870	0.062*
C9	0.6698 (3)	−0.0150 (4)	0.7708 (2)	0.0371 (11)
C10	0.6723 (3)	−0.0038 (4)	0.6942 (2)	0.0390 (11)
C11	0.7447 (3)	−0.0520 (5)	0.6645 (2)	0.0512 (13)
H11	0.7928	−0.0941	0.6915	0.061*
C12	0.7449 (4)	−0.0366 (5)	0.5939 (2)	0.0578 (14)
H12	0.7934	−0.0689	0.5735	0.069*
C13	0.6066 (4)	0.0702 (5)	0.5822 (2)	0.0557 (14)
H13	0.5595	0.1119	0.5539	0.067*
C14	0.6023 (4)	0.0579 (5)	0.6520 (2)	0.0537 (13)
H14	0.5526	0.0908	0.6706	0.064*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.04944 (16)	0.04359 (17)	0.02506 (13)	0.000	0.00946 (10)	0.000
S1	0.0532 (7)	0.0454 (7)	0.0290 (6)	−0.0023 (6)	0.0125 (5)	0.0011 (5)
S2	0.0908 (10)	0.0468 (8)	0.0387 (7)	−0.0084 (7)	0.0192 (7)	0.0017 (6)
O1	0.106 (3)	0.090 (3)	0.061 (2)	0.019 (3)	0.017 (2)	0.006 (2)
O2	0.096 (3)	0.098 (4)	0.070 (3)	−0.023 (3)	0.023 (2)	−0.016 (3)
N1	0.074 (3)	0.089 (4)	0.039 (2)	0.001 (3)	0.019 (2)	−0.009 (3)
N2	0.133 (5)	0.095 (4)	0.048 (3)	−0.041 (4)	0.024 (3)	0.010 (3)
C1	0.048 (3)	0.060 (4)	0.030 (2)	−0.005 (2)	0.005 (2)	0.002 (2)
C2	0.046 (3)	0.055 (4)	0.027 (2)	−0.001 (2)	0.008 (2)	0.006 (2)

C3	0.050 (3)	0.061 (4)	0.027 (2)	−0.004 (3)	0.006 (2)	0.006 (2)
C4	0.080 (4)	0.067 (4)	0.036 (3)	−0.020 (3)	0.010 (3)	0.003 (3)
N3	0.060 (2)	0.071 (3)	0.0202 (17)	0.005 (2)	0.0091 (17)	0.000 (2)
N4	0.086 (3)	0.058 (3)	0.0185 (17)	−0.007 (3)	0.010 (2)	0.0003 (19)
C5	0.066 (3)	0.057 (3)	0.024 (2)	−0.005 (3)	0.008 (2)	−0.004 (2)
C6	0.065 (3)	0.064 (4)	0.029 (2)	−0.004 (3)	0.003 (2)	0.007 (3)
C7	0.073 (4)	0.068 (4)	0.029 (2)	0.014 (3)	0.010 (2)	−0.013 (2)
C8	0.076 (4)	0.051 (3)	0.028 (2)	0.015 (3)	0.010 (2)	0.000 (2)
C9	0.045 (2)	0.045 (3)	0.021 (2)	−0.002 (2)	0.0061 (18)	−0.0001 (19)
C10	0.053 (3)	0.041 (3)	0.023 (2)	−0.004 (2)	0.007 (2)	−0.0033 (18)
C11	0.060 (3)	0.066 (4)	0.028 (2)	0.006 (3)	0.010 (2)	0.000 (3)
C12	0.070 (3)	0.077 (4)	0.030 (2)	0.005 (3)	0.019 (2)	−0.001 (3)
C13	0.080 (4)	0.057 (4)	0.029 (2)	0.012 (3)	0.004 (2)	0.004 (2)
C14	0.067 (3)	0.067 (4)	0.029 (2)	0.011 (3)	0.013 (2)	−0.004 (2)

Geometric parameters (Å, º)

Pt1—S1^{i}	2.2554 (12)	C5—H5	0.9300
Pt1—S1	2.2554 (12)	C5—C6	1.402 (6)
Pt1—S2^{i}	2.3120 (13)	C5—C9	1.387 (7)
Pt1—S2	2.3120 (13)	C6—H6	0.9300
S1—O1	1.448 (4)	C7—H7	0.9300
S1—O2	1.439 (4)	C7—C8	1.392 (6)
S1—C2	1.805 (5)	C8—H8	0.9300
S2—C3	1.740 (5)	C8—C9	1.375 (6)
N1—C1	1.147 (6)	C9—C10	1.501 (5)
N2—C4	1.139 (6)	C10—C11	1.382 (6)
C1—C2	1.431 (7)	C10—C14	1.383 (7)
C2—C3	1.337 (7)	C11—H11	0.9300
C3—C4	1.440 (7)	C11—C12	1.384 (6)
N3—C6	1.330 (6)	C12—H12	0.9300
N3—C7	1.328 (6)	C13—H13	0.9300
N4—H4	0.8600	C13—C14	1.376 (6)
N4—C12	1.335 (7)	C14—H14	0.9300
N4—C13	1.321 (6)		
S1^{i}—Pt1—S1	90.74 (6)	N3—C6—C5	122.8 (5)
S1—Pt1—S2	90.13 (4)	N3—C6—H6	118.6
S1^{i}—Pt1—S2	178.08 (5)	C5—C6—H6	118.6
S1^{i}—Pt1—S2^{i}	90.13 (4)	N3—C7—H7	118.4
S1—Pt1—S2^{i}	178.08 (5)	N3—C7—C8	123.3 (5)
S2^{i}—Pt1—S2	89.05 (7)	C8—C7—H7	118.4
O1—S1—Pt1	113.09 (17)	C7—C8—H8	120.5
O1—S1—C2	104.6 (2)	C9—C8—C7	119.0 (5)
O2—S1—Pt1	113.54 (18)	C9—C8—H8	120.5
O2—S1—C2	105.7 (2)	C5—C9—C10	121.5 (4)
C2—S1—Pt1	103.49 (17)	C8—C9—C5	118.4 (4)
C3—S2—Pt1	101.52 (18)	C8—C9—C10	120.1 (4)

N1—C1—C2	178.0 (6)	C11—C10—C9	121.4 (4)
C1—C2—S1	116.2 (4)	C11—C10—C14	118.5 (4)
C3—C2—S1	119.4 (4)	C14—C10—C9	120.1 (4)
C3—C2—C1	124.5 (4)	C10—C11—H11	120.4
C2—C3—S2	125.4 (4)	C10—C11—C12	119.1 (5)
C2—C3—C4	120.4 (5)	C12—C11—H11	120.4
C4—C3—S2	114.2 (4)	N4—C12—C11	120.9 (5)
N2—C4—C3	178.6 (6)	N4—C12—H12	119.5
C7—N3—C6	117.9 (4)	C11—C12—H12	119.5
C12—N4—H4	119.7	N4—C13—H13	119.4
C13—N4—H4	119.7	N4—C13—C14	121.2 (5)
C13—N4—C12	120.7 (4)	C14—C13—H13	119.4
C6—C5—H5	120.7	C10—C14—H14	120.2
C9—C5—H5	120.7	C13—C14—C10	119.5 (5)
C9—C5—C6	118.6 (5)	C13—C14—H14	120.2
Pt1—S1—C2—C1	178.9 (3)	C6—N3—C7—C8	0.7 (8)
Pt1—S1—C2—C3	−1.9 (4)	C6—C5—C9—C8	0.3 (7)
Pt1—S2—C3—C2	1.7 (5)	C6—C5—C9—C10	179.8 (4)
Pt1—S2—C3—C4	−177.6 (3)	C7—N3—C6—C5	1.5 (7)
S1—C2—C3—S2	0.1 (6)	C7—C8—C9—C5	1.7 (7)
S1—C2—C3—C4	179.4 (4)	C7—C8—C9—C10	−177.8 (5)
O1—S1—C2—C1	60.3 (4)	C8—C9—C10—C11	130.8 (5)
O1—S1—C2—C3	−120.6 (4)	C8—C9—C10—C14	−47.9 (7)
O2—S1—C2—C1	−61.5 (4)	C9—C5—C6—N3	−2.0 (7)
O2—S1—C2—C3	117.7 (4)	C9—C10—C11—C12	−178.5 (5)
C1—C2—C3—S2	179.2 (3)	C9—C10—C14—C13	178.4 (5)
C1—C2—C3—C4	−1.5 (8)	C10—C11—C12—N4	0.1 (9)
N3—C7—C8—C9	−2.4 (8)	C11—C10—C14—C13	−0.3 (8)
N4—C13—C14—C10	0.2 (8)	C12—N4—C13—C14	0.1 (8)
C5—C9—C10—C11	−48.7 (7)	C13—N4—C12—C11	−0.2 (8)
C5—C9—C10—C14	132.6 (5)	C14—C10—C11—C12	0.2 (8)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N3^{ii}	0.86	1.88	2.730 (5)	171
C7—H7···N2^{iii}	0.93	2.50	3.363 (7)	155
C7—H7···O2^{i}	0.93	2.57	3.197 (7)	125
C8—H8···O1	0.93	2.40	3.301 (6)	164
C8—H8···O2^{i}	0.93	2.77	3.287 (7)	116

Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2; (ii) *x*, −*y*, *z*−1/2; (iii) *x*, −*y*+1, *z*+1/2.