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trans-Diamminebis(1,2-dicyanoethene-1,2-dithiolato)platinum(IV)

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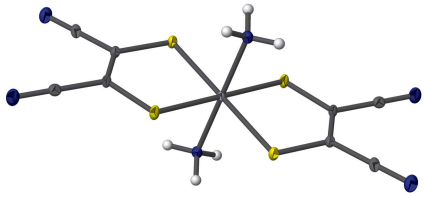
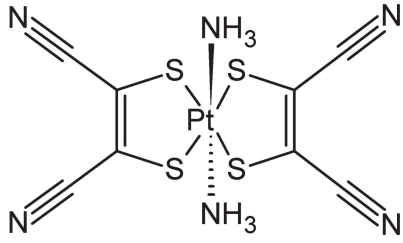
The title compound, $[Pt(C_4N_2S_2)_2(NH_3)_2]$, represents an octahedral platinum(IV) complex with two *trans*-ammine and two mnt (mnt = 1,2-dicyanoethene-1,2-dithiolato) ligands. The Pt—N and Pt—S distances are consistent with those in other platinum(IV) complexes. As a result of a slight canting of the coordination of the mnt ligand to the platinum(IV) atom, the nitrile nitrogen atoms are positioned suitably to hydrogen-bond with adjacent ammines.

3D view



Chemical scheme



Structure description

The neutral title complex contains two ammine and two mnt ligands forming an octahedral platinum(IV) complex. The C—S distances of 1.747 (3) and 1.744 (3) Å and the C═C distance of 1.358 (4) Å support the ene-1,2-dithiolate form of the mnt ligand (Güntner *et al.*, 1989; Chandrasekaran *et al.*, 2014). The two ammine ligands are *trans* with a Pt—N bond length of 2.055 (2) Å, which is consistent with the Pt—N distances in other platinum(IV) complexes of 2.056 (9) (Fanwick & Huckaby, 1982) and 2.053 (5) Å (Brawner *et al.*, 1978). The Pt—S distances of 2.3434 (8) and 2.3461 (7) Å are longer than in square-planar platinum complexes with mnt such as the Pt^{II}—S distances of 2.290 and 2.282 Å in $[Pt(mnt)_2]^{2-}$ (Günter *et al.*, 1989) or the Pt^{III}—S distance of 2.262 Å in $[Pt(mnt)_2]^{-}$ (Mochida *et al.*, 2010). This longer Pt—S bond is comparable, however, with the Pt—S distance of 2.3619 Å found in a similar octahedral platinum(IV) complex with two dithiolene and two *trans* phosphine ligands (Chandrasekaran *et al.*, 2014). The coordination of the mnt ligands is slightly canted from the platinum(IV) atom, which allows for hydrogen bonding between the nitrile nitrogen atoms and adjacent ammines (Fig. 1, Table 1). These interactions lead to the formation of a three-dimensional network.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2^{i}	0.89	2.16	3.016 (3)	160
N3—H3B···S2^{ii}	0.89	2.73	3.610 (3)	171
N3—H3C···N1^{iii}	0.89	2.26	3.011 (3)	142

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

Synthesis and crystallization

A solution of 13.9 mg (7.46×10^{-5}mol) of Na_2mnt dissolved in 10 mL of water was combined with a solution of 25 mg (7.48×10^{-5} mol) of tetraammineplatinum(II) chloride dissolved in 25 mL of water, and stirred for 2 h in air. The solvent was removed using a vacuum oven to give 26.5 mg of a brown product isolated [^{1}H NMR (*d*-DMSO) 4.23ppm]. Light-orange crystals of the title compound were grown by liquid diffusion of diethyl ether into a methanol solution of the synthesized product in a tall, narrow tube that was covered with parafilm. The platinum(II) dithiolene complex is presumed to oxidize to the ammine-stabilized octahedral platinum(IV) dithiolene compound *via* air, demonstrating a synthetic route toward stable neutral Pt^{IV} dithiolene complexes (Geiger *et al.*, 2001).

Refinement

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

Funding information

We are grateful of the Welch Foundation (AD-0007) for a department grant supporting undergraduate research and the NSF MRI for a Jeol ECZ-400 NMR at Austin College (CHE-1725651) and a Rigaku XtaLAB Synergy-S X-ray diffractometer at UNT (CHE-1726652).

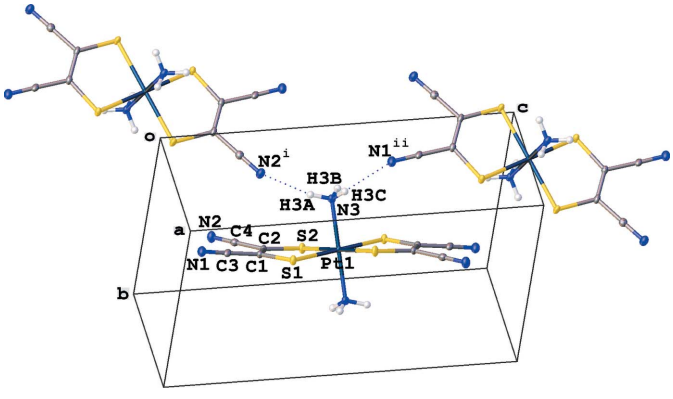


Figure 1
Displacement ellipsoid plot 50% probability of all non-H atoms showing N—H hydrogen bonding between nitrile nitrogen atoms and hydrogen atoms on adjacent ammines. Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Pt(C_4N_2S_2)_2(NH_3)_2]$
M_r	509.52
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	6.1778 (3), 7.7700 (4), 14.8862 (7)
β (°)	95.935 (4)
V (Å^3)	710.73 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	10.45
Crystal size (mm)	0.05 × 0.02 × 0.01
Data collection	
Diffractometer	Rigaku XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019)
T_{min}, T_{max}	0.509, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8027, 1556, 1375
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.038, 1.05
No. of reflections	1556
No. of parameters	89
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, −0.54

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

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Crystal data

$[Pt(C_4N_2S_2)_2(NH_3)_2]$
M_r = 509.52
Monoclinic, $P2_1/c$
a = 6.1778 (3) Å
b = 7.7700 (4) Å
c = 14.8862 (7) Å
β = 95.935 (4)°
V = 710.73 (6) Å^3
Z = 2
$F(000)$ = 476
D_x = 2.381 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5207 reflections
θ = 2.7–29.7°
μ = 10.45 mm^{-1}
T = 100 K
Plate, clear light orange
0.05 × 0.02 × 0.01 mm

Data collection

Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)
T_{min} = 0.509, T_{max} = 1.000
8027 measured reflections
1556 independent reflections
1375 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.1°, θ_{min} = 2.8°
h = −7→7
k = −9→9
l = −18→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.038
S = 1.05
1556 reflections
89 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0154P)^2 + 0.3678P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pt1	0.500000	0.500000	0.500000	0.00819 (6)
S1	0.62740 (13)	0.46855 (9)	0.35800 (5)	0.01208 (16)
S2	0.20123 (12)	0.65846 (10)	0.43437 (5)	0.01294 (16)
N1	0.4195 (5)	0.4964 (3)	0.1195 (2)	0.0179 (6)
N2	−0.0905 (4)	0.7217 (3)	0.20727 (17)	0.0182 (6)
N3	0.3182 (4)	0.2794 (3)	0.47944 (16)	0.0125 (5)
H3A	0.283811	0.263528	0.420476	0.015*
H3B	0.197076	0.289137	0.506596	0.015*
H3C	0.395109	0.189825	0.502333	0.015*
C1	0.4056 (5)	0.5506 (4)	0.2889 (2)	0.0110 (6)
C2	0.2301 (5)	0.6263 (4)	0.32026 (18)	0.0116 (6)
C3	0.4129 (5)	0.5226 (3)	0.1948 (2)	0.0120 (6)
C4	0.0516 (5)	0.6804 (4)	0.25742 (19)	0.0124 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.00671 (9)	0.01158 (10)	0.00598 (9)	0.00083 (6)	−0.00073 (6)	0.00050 (6)
S1	0.0099 (4)	0.0183 (4)	0.0079 (3)	0.0023 (3)	0.0005 (3)	0.0006 (3)
S2	0.0104 (3)	0.0193 (4)	0.0088 (3)	0.0045 (3)	−0.0006 (3)	0.0021 (3)
N1	0.0231 (16)	0.0163 (15)	0.0136 (14)	0.0000 (11)	−0.0009 (12)	0.0000 (10)
N2	0.0171 (14)	0.0228 (15)	0.0143 (13)	0.0030 (12)	−0.0008 (11)	0.0019 (11)
N3	0.0099 (13)	0.0157 (13)	0.0117 (12)	0.0002 (10)	−0.0008 (10)	0.0027 (10)
C1	0.0123 (15)	0.0119 (14)	0.0085 (14)	−0.0017 (12)	−0.0010 (12)	0.0009 (11)
C2	0.0136 (15)	0.0119 (15)	0.0086 (14)	−0.0020 (12)	−0.0028 (11)	0.0024 (11)
C3	0.0149 (16)	0.0076 (15)	0.0124 (16)	0.0001 (11)	−0.0035 (12)	0.0008 (11)
C4	0.0135 (15)	0.0111 (15)	0.0127 (14)	−0.0019 (12)	0.0014 (12)	−0.0002 (12)

Geometric parameters (Å, º)

Pt1—S1^{i}	2.3434 (8)	N1—C3	1.143 (4)
Pt1—S1	2.3434 (8)	N2—C4	1.138 (4)
Pt1—S2	2.3461 (7)	N3—H3A	0.8900
Pt1—S2^{i}	2.3461 (7)	N3—H3B	0.8900
Pt1—N3^{i}	2.055 (2)	N3—H3C	0.8900
Pt1—N3	2.055 (2)	C1—C2	1.358 (4)
S1—C1	1.747 (3)	C1—C3	1.423 (4)
S2—C2	1.744 (3)	C2—C4	1.433 (4)
S1^{i}—Pt1—S1	180.0	C2—S2—Pt1	100.09 (10)
S1^{i}—Pt1—S2	89.87 (3)	Pt1—N3—H3A	109.5
S1—Pt1—S2^{i}	89.87 (3)	Pt1—N3—H3B	109.5
S1—Pt1—S2	90.13 (3)	Pt1—N3—H3C	109.5
S1^{i}—Pt1—S2^{i}	90.13 (3)	H3A—N3—H3B	109.5
S2^{i}—Pt1—S2	180.0	H3A—N3—H3C	109.5

N3^{i}—Pt1—S1^{i}	90.46 (7)	H3B—N3—H3C	109.5
N3—Pt1—S1^{i}	89.54 (7)	C2—C1—S1	124.1 (2)
N3—Pt1—S1	90.46 (7)	C2—C1—C3	120.8 (3)
N3^{i}—Pt1—S1	89.54 (7)	C3—C1—S1	114.9 (2)
N3^{i}—Pt1—S2	91.06 (7)	C1—C2—S2	124.2 (2)
N3—Pt1—S2^{i}	91.06 (7)	C1—C2—C4	119.4 (3)
N3—Pt1—S2	88.94 (7)	C4—C2—S2	116.4 (2)
N3^{i}—Pt1—S2^{i}	88.94 (7)	N1—C3—C1	178.5 (3)
N3—Pt1—N3^{i}	180.0	N2—C4—C2	179.3 (3)
C1—S1—Pt1	100.20 (11)		
Pt1—S1—C1—C2	6.6 (3)	S1—C1—C2—S2	1.7 (4)
Pt1—S1—C1—C3	−169.3 (2)	S1—C1—C2—C4	−176.5 (2)
Pt1—S2—C2—C1	−8.8 (3)	C3—C1—C2—S2	177.4 (2)
Pt1—S2—C2—C4	169.4 (2)	C3—C1—C2—C4	−0.8 (5)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N2^{ii}	0.89	2.16	3.016 (3)	160
N3—H3*B*···S2^{iii}	0.89	2.73	3.610 (3)	171
N3—H3*C*···N1^{iv}	0.89	2.26	3.011 (3)	142

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