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Key indicators

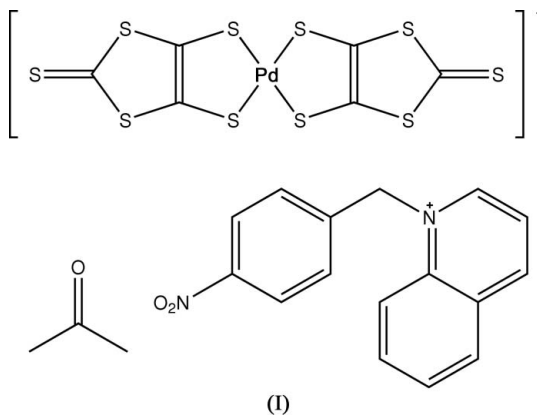
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.044
 wR factor = 0.086
Data-to-parameter ratio = 16.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.***N*-(4-Nitrobenzyl)quinolinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)palladium(III) acetone solvate**

In the title ion-pair compound, $(\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_2)[\text{Pd}(\text{C}_3\text{S}_5)_2] \cdot \text{C}_3\text{H}_6\text{O}$, the Pd^{III} atom exhibits square-planar coordination geometry involving four S atoms of two 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligands. Some weak $\text{S} \cdots \text{S}$ interactions and hydrogen bonds are found, resulting in a three-dimensional supramolecular network structure.

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Comment

Extensive research has been focused on the syntheses and characterization of bis-dithiolate metal complexes and their analogs due to their properties and potential applications, for example as conducting/magnetic materials and in non-linear optics (NLO) (Cassoux, 1999). Among these, 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) metal complexes are well known as molecular conductors. Ni^{III} complexes are commonly employed in those studies, but Pd^{III} complexes are not. In order to extend this knowledge to the Pd^{III} analogs, the title compound, (I), was synthesized.



The crystal structure of (I) shows that there are three separate components in the structure (Fig. 1), namely the $[\text{Pd}^{\text{III}}(\text{dmit})_2]^-$ anion, the *N*-(4-nitrobenzyl)quinolinium cation and the acetone solvent molecule. The Pd^{III} ion adopts square-planar coordination involving the four S atoms of two dmit ligands [$\text{Pd}-\text{S} = 2.2693(10)$ – $2.2757(11)$ Å]. The $[\text{Pd}^{\text{III}}(\text{dmit})_2]^-$ anion plane is almost parallel to the quinoline ring system [dihedral angle = $7.6(1)^\circ$]. Weak π – π interactions exist in the crystal structure; the centroid-to-centroid distance between the C10–C15 and Pd1/S8/S9/C5/C6 rings is $3.6592(2)$ Å, while the interplanar distance is $3.578(2)$ Å.

The anions are dimerized through inter-anion $\text{S} \cdots \text{S}$ weak interactions [$\text{S8} \cdots \text{S8}^i = 3.538(2)$ Å; symmetry code: (i) $-x, -y, -z$]. The three components are stacked in separate columns (Fig. 2); these columns are interlinked through some

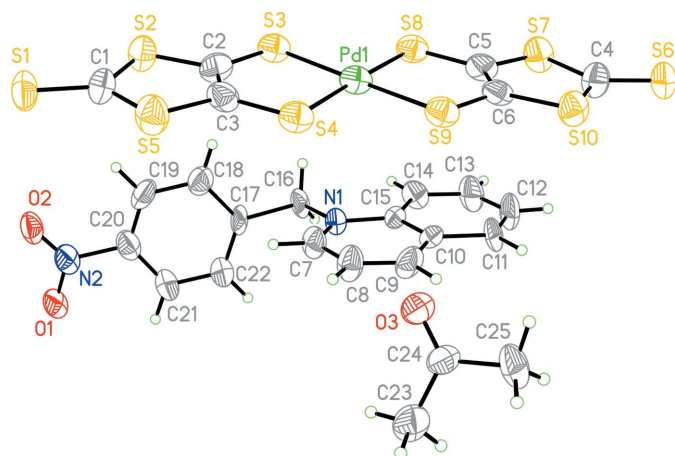


Figure 1
The asymmetric unit of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii.

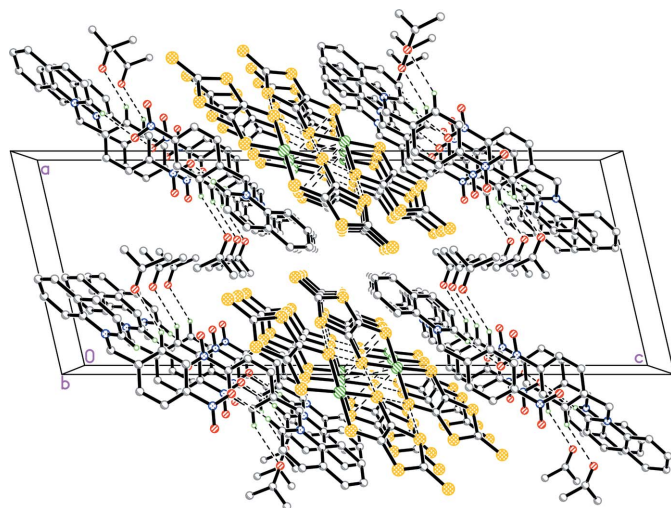


Figure 2
The packing of (I), viewed along the *b* axis. Dashed lines indicate the hydrogen-bonding interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

hydrogen bonds (Table 1) into a three-dimensional supramolecular network.

Experimental

4,5-Bis(thiobenzoyl)-1,3-dithiole-2-thione (812 mg, 2.0 mmol) (Wang *et al.*, 1998) was suspended in dry methanol (20 ml). Under nitrogen, sodium (92 mg, 4.0 mmol) was added to the above mixture at room temperature to give a bright red solution. To this solution, PdCl₂ (177 mg, 1 mmol) was added. After 20 min, a solution of I₂ (127 mg, 0.5 mmol) was added, and after another 20 min, a solution of *N*-(4-nitrobenzyl)quinolinium bromide (2 mmol, 0.380 g) (Bulgarevich *et al.*, 1994) in methanol was added to the reaction mixture, and the solution was stirred further for 30 min. The resulting powder was collected by filtration. Evaporation of a dilute acetone solution of this powder sample at room temperature gave single crystals of (I) in 1–2 weeks.

Crystal data

(C₁₆H₁₃N₂O₂)[Pd(C₃S₅)₂]·C₃H₆O
M_r = 822.54
 Monoclinic, *P*2₁/*c*
a = 12.224 (2) Å
b = 8.0880 (16) Å
c = 32.711 (6) Å
 β = 103.015 (6)°
V = 3151.0 (10) Å³

Z = 4
D_x = 1.734 Mg m⁻³
 Mo *K*α radiation
 μ = 1.28 mm⁻¹
T = 293 (2) K
 Block, black
 0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.745, *T_{max}* = 0.778

16294 measured reflections
 6128 independent reflections
 4753 reflections with *I* > 2σ(*I*)
R_{int} = 0.028
 θ_{\max} = 26.0°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.044
wR(*F*²) = 0.087
S = 1.13
 6128 reflections
 372 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.1449P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.64 \text{ e \AA}^{-3}$

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>
C22—H22...O3 ⁱ	0.93	2.56	3.409 (5)	152
C7—H7...O1 ⁱⁱ	0.93	2.35	3.226 (4)	157

Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) −*x*, *y* + ½, −*z* + ½.

All H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding on their parent atoms, with *U*_{iso}(H) = 1.2 or 1.5 times *U*_{eq}(C).

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXL97.

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