

Bis[tris(pyridin-2-yl)methanol- κ^2N,N']-palladium(II) dinitrate at 150 and 298 K

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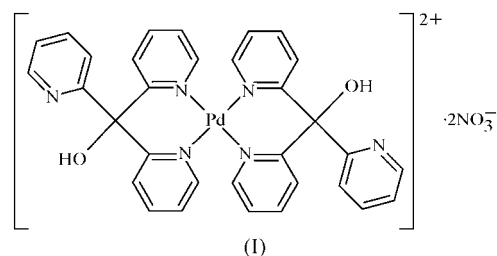
The title complex, $[\text{Pd}\{(\text{py})_3\text{COH}\}_2](\text{NO}_3)_2$, where $(\text{py})_3\text{COH}$ is tris(pyridin-2-yl)methanol ($\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}$), studied at 150 and 298 K, has the potentially tridentate ligands present as bidentate ligands, with the Pd atom at a centre of symmetry. At 150 K, the Pd–N distances are 2.022 (3) and 2.026 (3) Å. The mean planes of the coordinated pyridine groups form dihedral angles of 42.1 (1) and 45.3 (1)° (at 150 K) with the coordination plane; the uncoordinated rings situated either side of the coordination plane form dihedral angles of 42.2 (1)° with it. The nitrate ions are regular and interact weakly with the hydroxyl group.

Comment

Potentially tridentate 'tripodal' ligands such as $(\text{py})_3\text{CH}$ (py is pyridin-2-yl), $(\text{pz})_3\text{CH}$ (pz is pyrazol-1-yl) and $[(\text{pz})_3\text{BH}]^-$, when coordinated to palladium(II) in the complexes $[\text{Pd}\{(\text{py})_3\text{CH}\}_2](\text{NO}_3)_2$, $[\text{Pd}\{(\text{pz})_3\text{CH}\}_2](\text{BF}_4)_2$ (both isomorphous) and $[\text{Pd}\{(\text{pz})_3\text{BH}\}_2]$, may interact as bidentate ligands to give square-planar coordination for the metal atom (Canty *et al.*, 1986). We have isolated a similar complex, the title compound, (I), with stoichiometry $[\text{Pd}\{(\text{py})_3\text{COH}\}_2](\text{NO}_3)_2$, incorporating a ligand with added potential for interaction, and have examined its structure in a search for possible additional interaction at the Pd atom and elsewhere. We report here the single-crystal X-ray studies of (I) at 150 and 298 K.

Complex (I) crystallizes in space group $P2_1/c$, with similar cell dimensions to the earlier complexes. This is surprising in view of the substitution of the methanic H atom by the polar hydroxyl group. The present complex thus provides a third member of this series of isomorphous complexes, in which the metal atom lies on a crystallographic inversion centre, with one half of the formula unit (half of the complex cation and a single nitrate ion) comprising the asymmetric unit of the

structure (Figs. 1 and 2). The hydroxyl H atom and atom N2C aside, the cation symmetry is a good approximation to $2/m$, the Pd–N bonds being effectively equivalent [2.022 (3) and 2.026 (3) Å at 150 K], with the chelate angle within the six-membered 'boat' (atoms Pd and C10 at the prows) being 87.2 (1)°. The torsion angles are given in Table 1. Geometries are generally harmonious with those found in the pair of isomorphous counterparts, with the uncoordinated ring shielding the Pd atom from the approach of other moieties. The hydroxyl group at the cation periphery interacts with the nitrate anion (Table 2), which is perhaps surprising since the uncoordinated pyridine offers, presumably, a more basic site.



As noted in the *Experimental*, the present study was preceded by a room-temperature study on the same specimen. It is of interest to note that for all cation non-H atoms, all U_{eq} values (Å²) are less than 0.054 (3) at 298 K and less than 0.033 (3) at 150 K. For the nitrate ion, however, the U_{eq} values at 298 K are all greater than 0.101 (3), decreasing much more dramatically to be less than 0.049 (2) at 150 K. It is interesting

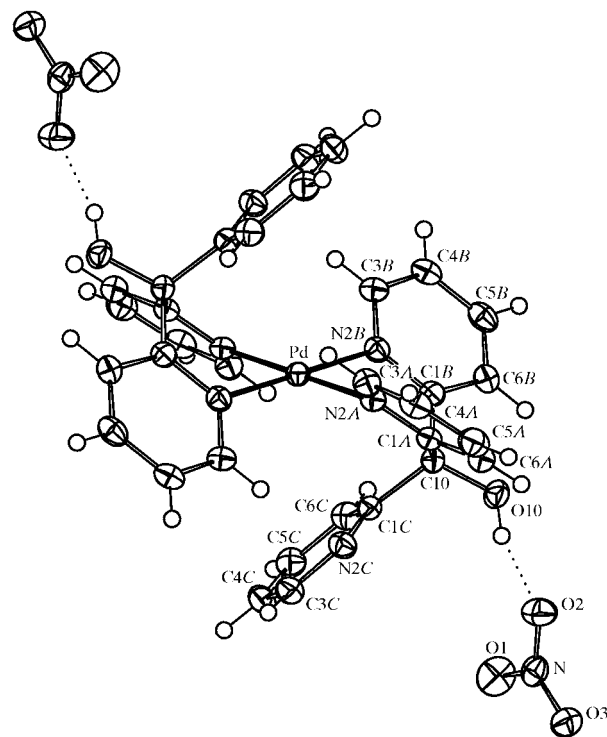


Figure 1
The molecule of (I) at 150 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with arbitrary radii of 0.1 Å.

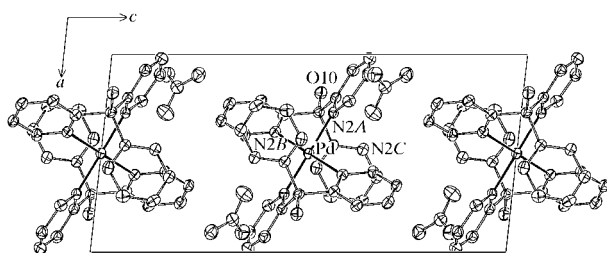


Figure 2
The unit-cell contents of (I) at 150 K, projected down *b*.

to find that, at 150 K, the longest N—O distance in the anion, N—O2, is 1.261 (5) Å, perhaps consequent on the interaction with the hydroxyl H atom. The interplanar dihedral angles (°) at 150 K (298 K) are rings *A/B* 56.9 (1) [58.1 (2)], rings *A/C* 75.0 (1) [76.8 (3)] and rings *B/C* 81.7 (1) [83.2 (2)]. The deviations of the Pd atom from the planes of rings *A* and *B* are 0.097 (5) and 0.039 (5) Å [0.092 (10) and 0.012 (9) Å], respectively. Rings *A*, *B* and *C* form dihedral angles (°) of 42.1 (1) [43.0 (2)], 45.3 (1) [44.9 (2)] and 42.2 (1) [44.1 (2)], respectively, with the coordination plane.

Experimental

The white powder obtained from the reaction of PdMe₂(py)₂COH with water in acetone in the presence of pyridazine (Canty *et al.*, 1994) was dissolved in methanol-water containing a few drops of dilute nitric acid. Colourless crystals of (I) formed over several days and these were found to be suitable for structural studies. An initial determination, executed with a single-counter instrument at room temperature on a capillary-mounted specimen, did not convincingly locate all H atoms. A fragment of the same specimen was used for a second determination using a CCD instrument, as reported here.

Compound (I) at 150 K

Crystal data

[Pd(C₁₆H₁₃N₃O)₂](NO₃)₂
M_r = 757.03
 Monoclinic, *P*2₁/*c*
a = 8.4280 (10) Å
b = 10.284 (2) Å
c = 17.669 (3) Å
 β = 96.294 (2)°
V = 1522.2 (4) Å³
Z = 2

D_x = 1.652 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 4042 reflections
 θ = 2.6–27.5°
 μ = 0.68 mm⁻¹
T = 150 (2) K
 Block, colourless
 0.20 × 0.20 × 0.15 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.73, *T_{max}* = 0.93
 17 629 measured reflections

3681 independent reflections
 2726 reflections with *I* > 2σ(*I*)
R_{int} = 0.045
 θ_{max} = 28.1°
h = -11 → 11
k = -13 → 13
l = -23 → 23

Refinement

Refinement on *F*²
R(*F*) = 0.048
wR(*F*²) = 0.117
S = 1.04
 2726 reflections
 223 parameters

H-atom parameters constrained
w = 1/[σ²(*F*) + 0.54*F*²]
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 2.45 e Å⁻³
 Δρ_{min} = -0.88 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I) at 150 K.

Pd—N2A	2.022 (3)	Pd—N2B	2.026 (3)
N2A—Pd—N2B	87.20 (12)		
N2B—Pd—N2A—C1A	-44.5 (3)	C1A—C10—C1B—N2B	-57.4 (4)
N2A—Pd—N2B—C1B	45.5 (3)	C10—C1A—N2A—Pd	0.7 (4)
C1B—C10—C1A—N2A	58.3 (4)	C10—C1B—N2B—Pd	-2.0 (4)

Compound (I) at 298 K

Crystal data

[Pd(C₁₆H₁₃N₃O)₂](NO₃)₂
M_r = 757.03
 Monoclinic, *P*2₁/*c*
a = 8.430 (3) Å
b = 10.431 (4) Å
c = 17.67 (2) Å
 β = 95.54 (6)°
V = 1546.5 (19) Å³
Z = 2

D_x = 1.626 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6 reflections
 θ = 12.2–16.3°
 μ = 0.67 mm⁻¹
T = 298 (2) K
 Block, colourless
 0.25 × 0.22 × 0.19 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 2θ-ω scans
 Absorption correction: Gaussian *ABSORB* in *Xtal3.5* (Hall *et al.*, 1995)
T_{min} = 0.85, *T_{max}* = 0.88
 4422 measured reflections
 4414 independent reflections

2323 reflections with *I* > 2σ(*I*)
R_{int} = 0.086
 θ_{max} = 30.0°
h = 0 → 10
k = 0 → 14
l = -24 → 24
 8 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.056
wR(*F*²) = 0.145
S = 1.03
 2323 reflections
 223 parameters

H-atom parameters constrained
w = 1/[σ²(*F*) + 0.84*F*²]
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.38 e Å⁻³
 Δρ_{min} = -0.79 e Å⁻³

Table 2

Hydrogen-bonding geometry (Å, °) for (I) at 150 K.

<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>
O10—H10...O2	0.89	1.81	2.666 (5)	163

The H atoms were located in difference Fourier maps and placed at idealized positions (C—H = 0.95 Å), with *U*_{iso}(H) = 1.25*U*_{eq}(C). The largest peaks in the difference maps were 0.87 Å from Pd (at 150 K) and at the site of Pd (at 298 K).

For compound (I), data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*. For compound (II), data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*. For compounds (I) and (II), program(s) used to solve structure: *Xtal3.5* (Hall *et al.*, 1995); program(s) used to refine structure: *CRYLSQ* in *Xtal3.5*; molecular graphics: *Xtal3.5*; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal3.5*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1448). Services for accessing these data are described at the back of the journal.

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