also displays normal bond lengths and angles, with mean P—C and C—C distances of 1.80 (2) and 1.38 (2) Å, respectively.

Experimental

All the following operations were carried out under an atmosphere of dry nitrogen. To an NMR tube containing $[PPh_4]_2[WO_2S_2]$ (0.005 g, 0.0052 mmol), 0.8 ml of CD_3CN was added to give a green solution. ^{t}BuBr (10 μl, 0.0867 mmol) was added by syringe and the reaction maintained at room temperature. After 5 h, an orange colour was observed and after 18 h, a red precipitate and red crystals of the title compound had formed in the NMR tube.

Crystal data

$(C_{24}H_{20}P)_2[W_6O_{19}].2C_2D_3N$
$M_r = 2174.04$
Monoclinic
$P2_1/n$
$a = 13.102\,(3)$ Å
$b = 11.570\,(2)$ Å
$c = 19.345\,(3)$ Å
$\beta = 101.126\,(12)°$
$V = 2877.3\,(9)$ Å^3
$Z = 2$
$D_x = 2.509$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.0–15.0°$
$\mu = 12.07$ mm^{-1}
$T = 170$ K
Prism
0.30 × 0.22 × 0.18 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (3 reflections) (North *et al.*, 1968)
$T_{\min} = 0.055$, $T_{\max} = 0.114$
5095 measured reflections
5095 independent reflections

2765 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -23 \rightarrow 22$
3 standard reflections every 200 reflections intensity decay: 1.05%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.022$
$S = 1.31$
5095 reflections
368 parameters
H atoms geometrically idealized with C—H 0.95 Å
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} = 0.024$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -0.93$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $8.0\,(5) \times 10^{-8}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

W(1)—O(1)	2.3198 (6)	W(2)—O(5^i)	1.919 (7)
W(1)—O(2)	1.928 (9)	W(2)—O(8)	1.939 (9)
W(1)—O(3)	1.925 (9)	W(2)—O(9)	1.727 (9)
W(1)—O(5)	1.901 (9)	W(3)—O(1)	2.3189 (6)
W(1)—O(6)	1.697 (8)	W(3)—O(3)	1.896 (8)
W(1)—O(7)	1.901 (9)	W(3)—O(4)	1.944 (9)
W(2)—O(1)	2.3292 (6)	W(3)—O(7^i)	1.930 (8)
W(2)—O(2)	1.907 (7)	W(3)—O(8^i)	1.903 (9)
W(2)—O(4)	1.910 (9)	W(3)—O(10)	1.718 (10)

Symmetry code: (i) $2 - x, -y, -z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1378). Services for accessing these data are described at the back of the journal.

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[Pd(H*L*)Cl$_2$] and [Pd*L*$_2$], where H*L* is 2-(3-Pyrazolyl)pyridine

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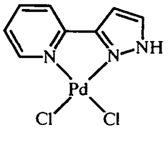
Abstract

The complexes *cis*-[Pd(H*L*)Cl$_2$] {dichloro[2-(3-pyrazolyl-N^2)pyridine-*N*]palladium(II), $[PdCl_2(C_8H_7N_3)]$} and *trans*-[Pd*L*$_2$] {bis[2-(3-pyrazolyl-N^2)pyridinato-

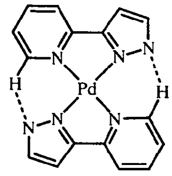
N]palladium(II), $[Pd(C_8H_6N_3)_2]$} were isolated as by-products from preparations of palladium(II) complexes with the podand ligand tris[3-(2-pyridyl)pyrazol-1-yl]-hydroborate, $[HBL_3]^-$. Both have square-planar coordination geometries. In *cis*-$[Pd(HL)Cl_2]$, the ligand H*L* acts as a neutral bidentate chelate. In $[PdL_2]$, which has a *trans* geometry, the pyrazole N^1 position is deprotonated. This has two consequences: (*a*) steric interference with the pyridyl H^6 proton of the alternate ligand is removed, and (*b*) inter-ligand intramolecular hydrogen bonding occurs between the pyridyl H^6 proton and the deprotonated pyrazolyl N^1 atom.

Comment

In trying to prepare palladium(II) complexes of the podand ligand tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate, $[HBL_3]^-$, using MeOH as solvent, decomposition of the ligand occurred by cleavage of the apical B—N bonds to liberate H*L*. When palladium(II) chloride was the metal salt, the result was $[Pd(HL)Cl_2]$. Likewise reaction of palladium(II) acetate with $[HBL_3]^-$ in MeOH afforded $[PdL_2]$. Such decomposition of $[HBL_3]^-$ to give complexes of H*L* has been observed before (Jones *et al.*, 1997).



$[Pd(HL)Cl_2]$



$[PdL_2]$

$[Pd(HL)Cl_2]$ (Fig. 1) has typical square-planar geometry, very similar to that of $[Pd(bpy)Cl_2]$ (bpy is 2,2′-bipyridine) (Canty *et al.*, 1992; Maekawa *et al.*, 1991). There is a significant pseudo-axial interaction between the Pd atom and a Cl atom of an adjacent complex unit (non-bonded Pd···Cl separation 3.34 Å), and hydrogen bonding between the pyrazolyl NH proton and a Cl atom of an adjacent complex unit (non-bonded H···Cl separation 2.40 Å).

$[PdL_2]$ (Fig. 2) is likewise square planar, with the ligands mutually *trans*, and is centrosymmetric. The most interesting feature of the structure is the loss of the pyrazolyl proton and the involvement of the formally negatively-charged pyrazolyl N^1 atom (N12 according to the crystallographic numbering scheme) in an intramolecular hydrogen bond with the pyridyl H^6 proton of the other ligand (H26 according to the crystallographic numbering scheme). The non-bonded N12···C26^{i} separation is 3.114 (3) Å [symmetry code: (i) $-x, -y, -z$]. In addition, the same pyrazolyl N atom also hydrogen bonds to atom H25 of an adjacent complex unit [C25···N12^{ii} 3.404 (3) Å; symmetry code: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}-z$].

The structural consequence of the ligand deprotonation is that the complex is completely planar, in contrast to $[Pd(bipy)_2]^{2+}$ in which the unfavourable steric interaction between the pyridyl H^6 protons results in significant distortions from planarity; there is either a pseudo-tetrahedral distortion with a significant dihedral angle between the ligand planes, or a 'bow-like' distortion of the ligands themselves, which become markedly non-planar, depending on the anion (Constable, 1989). In $[PdL_2]$, the problem is avoided by loss of the pyrazolyl N^1 proton, which (*a*) allows the metal to have a regular undistorted planar geometry in keeping with its stereoelectronic preferences, and (*b*) allows formation of mutual hydrogen bonding between the two ligands, reminiscent of that which stabilizes planar complexes of dioximes.

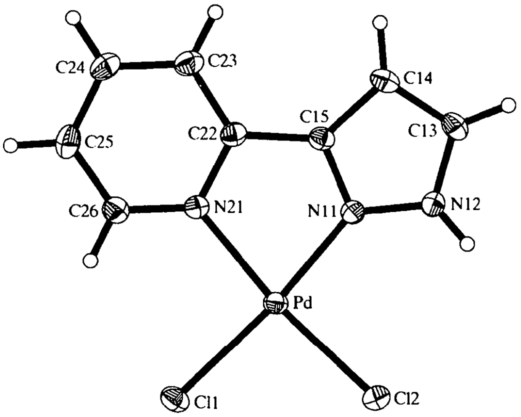


Fig. 1. The molecular structure of $[Pd(HL)Cl_2]$ with atom labels and 40% probability ellipsoids for non-H atoms.

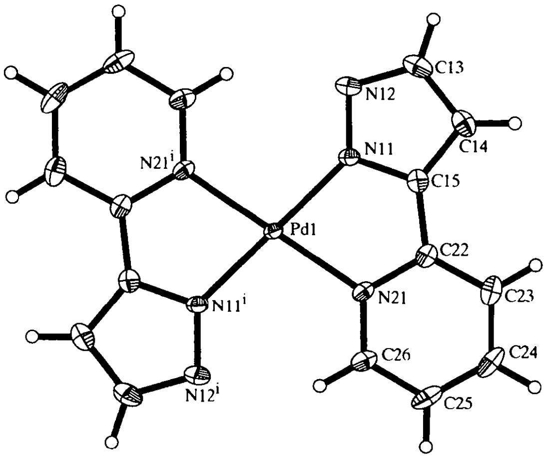


Fig. 2. The molecular structure of $[PdL_2]$ with atom labels and 40% probability ellipsoids for non-H atoms.

Experimental

A mixture of K[HBL_3] and either [PdCl$_2$(PhCN)$_2$] or palladium(II) acetate (1 equivalent) in MeOH was stirred at room temperature to give a precipitate, which was filtered off and dried in each case. Recrystallization by diffusion of diethyl ether vapour into concentrated MeCN solutions afforded X-ray quality crystals of [Pd(HL)Cl$_2$] and [PdL_2], respectively, which were initially identified by their elemental analyses. The chosen crystals were coated with a hydrocarbon oil and mounted on a glass fibre.

[Pd(H*L*)Cl$_2$]

Crystal data

[PdCl$_2$(C$_8$H$_7$N$_3$)]
M_r = 322.47
Orthorhombic
Pbca
a = 7.8069 (12) Å
b = 15.768 (4) Å
c = 16.398 (3) Å
V = 2018.6 (6) Å^3
Z = 8
D_x = 2.122 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 250 reflections
θ = 3.0–27.5°
μ = 2.327 mm^{-1}
T = 173 (2) K
Prism
0.2 × 0.1 × 0.1 mm
Clear light orange

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.61, $T_{\max}$ = 0.81
12 288 measured reflections

2314 independent reflections
2012 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 27.48°
$h = -10 \rightarrow 9$
$k = -20 \rightarrow 20$
$l = -19 \rightarrow 21$

Refinement

Refinement on F^2
$R(F)$ = 0.024
$wR(F^2)$ = 0.062
S = 1.169
2314 reflections
127 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 1.5697P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.522 e Å^{-3}
$\Delta\rho_{\min}$ = −0.818 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for [Pd(HL)Cl$_2$]*

Pd1—N11	1.991 (2)	Pd1—Cl2	2.2888 (8)
Pd1—N21	2.055 (2)	Pd1—Cl1	2.2900 (8)
N11—Pd1—N21	79.82 (9)	N11—Pd1—Cl1	174.58 (7)
N11—Pd1—Cl2	92.99 (7)	N21—Pd1—Cl1	94.84 (7)
N21—Pd1—Cl2	172.49 (7)	Cl2—Pd1—Cl1	92.30 (3)

[Pd*L*$_2$]

Crystal data

[Pd(C$_8$H$_6$N$_3$)$_2$]
M_r = 394.72
Monoclinic
$P2_1/n$
a = 11.752 (3) Å
b = 5.1373 (8) Å
c = 12.288 (2) Å
β = 104.62 (2)°
V = 717.9 (2) Å^3
Z = 2
D_x = 1.826 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 102 reflections
θ = 3.0–27.5°
μ = 1.301 mm^{-1}
T = 173 (2) K
Prism
0.3 × 0.2 × 0.1 mm
Yellow

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.66, $T_{\max}$ = 0.89
4332 measured reflections

1638 independent reflections
1331 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 27.47°
$h = -12 \rightarrow 15$
$k = -6 \rightarrow 6$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R(F)$ = 0.018
$wR(F^2)$ = 0.050
S = 1.152
1638 reflections
106 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ < 0.001
$\Delta\rho_{\max}$ = 0.349 e Å^{-3}
$\Delta\rho_{\min}$ = −0.494 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for [PdL$_2$]*

Pd1—N11	2.002 (2)	Pd1—N21	2.039 (2)
N11—Pd1—N21	79.71 (7)		

For both data sets, unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω), each at 20 s exposure. Slightly more than a full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 90 and 180°, with the area detector held at $2\theta = -29°$ and each frame exposed for 30 s. The crystal-to-detector distance was 4.94 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed in either data set. H atoms were constrained to idealized geometries and assigned isotropic displacement parameters of 1.2 times the $U_{\rm iso}$ value of their attached atom.

For both compounds, data collection: *SMART* (Siemens, 1995*b*); cell refinement: *SAINT* (Siemens, 1995*b*); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Siemens, 1995*a*); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1365). Services for accessing these data are described at the back of the journal.

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Bis[*N*-methylphenazinium(1+)] Tetranitropalladate(II)

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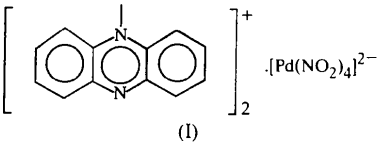
Abstract

In the crystal structure of the title compound, $(C_{13}H_{11}N_2)_2[Pd(NO_2)_4]$, the anions are located between two very slightly bent cations, but the least-squares planes of the anions are nearly perpendicular to those of the cations. These triads are stacked along two different directions, [101] and [10$\bar{1}$], with a mean interplanar distance of 3.325 (4) Å between adjacent triads.

Comment

The title compound, (I), forms a mixed stack according to the terminology for structures of charge-transfer complexes (Soos & Keller, 1977). The donor–acceptor sequence is DAD–DAD, in which the planar ions are greatly overlapped either within a triad or between adjacent triads. The packing arrangement in the unit cell of compound (I) is shown in Fig. 1.



(I)

The triad stacks are arranged alternately along the [101] and [10$\bar{1}$] directions. Bond distances and angles of both ions are normal compared with those of corresponding NMP compounds (NMP is *N*-methyl-

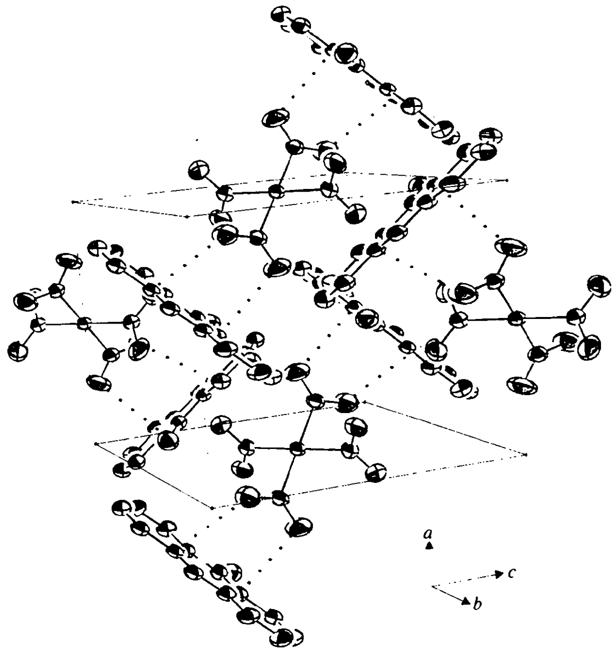


Fig. 1. View of the packing in the unit cell. Dotted lines represent O· · ·C contacts of less than 3.10 Å. Displacement ellipsoids are drawn at the 50% probability level.

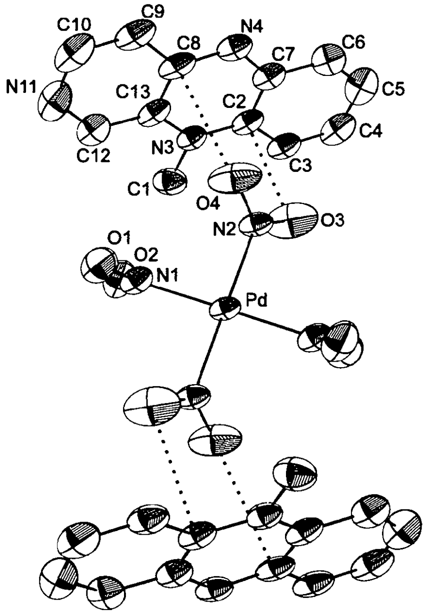


Fig. 2. The formula unit of the title compound showing O· · ·C contacts of less than 3.10 Å as dotted lines and the atomic numbering. H atoms have been omitted. Displacement ellipsoids are drawn at the 50% probability level.