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Coordination of bis(pyrazol-1-yl)amine to palladium(II): influence of the co-ligands and counter-ions on the molecular and crystal structures

María de los Angeles Mendoza,[a] Sylvain Bernès[b]*‡ and Guillermo Mendoza-Díaz[a]

[a]Departamento de Ingenierías Química Electrónica y Biomédica, División de Ciencias e Ingenierías, Campus León, Universidad de Guanajuato, Loma del Bosque 103, Lomas del Campestre, León, Guanajuato 37150, Mexico, and [b]DEP Facultad de Ciencias Químicas, UANL, Guerrero y Progreso S/N, Col. Treviño, 64570 Monterrey, N.L., Mexico. *Correspondence e-mail: sylvain_bernes@Hotmail.com

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‡ Currently unaffiliated to UANL.

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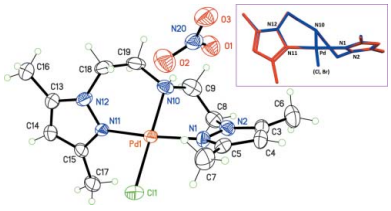
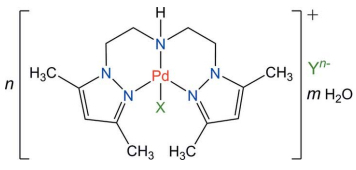
The structures of a series of complexes with general formula n[Pd(pza)X]Y·mH$_2$O (n = 1, 2; X = Cl, Br, I, N$_3$, NCS; Y = NO$_3$, I, N$_3$, [Pd(SCN)$_4$]; m = 0, 0.5, 1) have been determined, where pza is the tridentate ligand bis[2-(3,5-dimethylpyrazol-1-yl)ethyl]amine, C$_{14}$H$_{23}$N$_5$. In all complexes, {bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}chloridopalladium nitrate, [Pd(pza)Cl]NO$_3$, (1), {bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}bromidopalladium nitrate, [Pd(pza)Br]NO$_3$, (2), {bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]-amine-κN}iodidopalladium iodide hemihydrate, [Pd(pza)I]I·0.5H$_2$O, (3), azido-{bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}palladium azide monohydrate, [Pd(pza)N$_3$]N$_3$·H$_2$O, (4), and bis[{bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}(thiocyanato-κN)palladium] tetrakis(thiocyanato-κS)-palladate, [Pd(pza)NCS]$_2$[Pd(SCN)$_4$], (5), the [Pd(pza)X]$^+$ complex cation displays a square-planar coordination geometry, and the pza ligand is twisted, approximating twofold rotation symmetry. Although the pza ligand is found with the same conformation along the series, the dihedral angle between pyrazole rings depends on the co-ligand X. This angle span the range 79.0 (3)–88.6 (1)° for the studied complexes. In (3), two complex cations, two I$^-$ anions and one water molecule of crystallization are present in the asymmetric unit. In (5), the central amine group of pza is disordered over two positions [occupancy ratio 0.770 (18):0.230 (18)]. The complex [Pd(SCN)$_4$]$^{2-}$ anion of this compound exhibits inversion symmetry and shows the Pd^{2+} transition metal cation likewise in a square-planar coordination environment. Compound (5) is also a rare occurrence of a non-polymeric compound in which the pseudohalide ligand NCS$^-$ behaves both as thiocyanate and isothiocyanate, *i.e.* is coordinating either through the N atom (in the cation) or the S atom (in the anion).

1. Chemical context

The coordination chemistry of transition metals having a d^8 shell is clearly dominated by the square-planar geometry, which gives strong crystal field stabilization, because filled orbitals d_{z2} and degenerated orbitals (d_{xz} d_{yz}) do not interact directly with orbitals of the ligands. This holds true for group 10 metal complexes, for which the tetrahedral geometry is considered as an oddity (Alvarez *et al.*, 2005).





Complex	n	X	Y	m
(1)	1	Cl	NO$_3$	0
(2)	1	Br	NO$_3$	0
(3)	1	I	I	0.5
(4)	1	N$_3$	N$_3$	1
(5)	2	NCS	[Pd(SCN)$_4$]	0

We synthesized a series of such square-planar complexes, with general formula n[Pd(pza)X]Y·mH$_2$O, in which pza is the

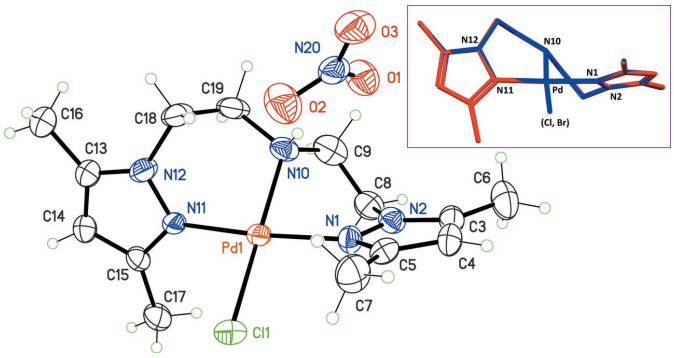


Figure 1
View of the molecular structure of complex (1), corresponding to $X = Cl^-$ and $Y = NO_3^-$, with displacement ellipsoids for non-H atoms drawn at the 30% probability level. The inset is an overlay (*Mercury*; Macrae *et al.*, 2008) of the cations in (1) and (2), in which $X = Br^-$.

tridentate ligand bis-[2-(3,5-dimethylpyrazol-1-yl)ethyl]amine, and *X*, *Y* are halide, pseudohalide, nitrate, or a complex anion. This series was first considered within a larger project related to a systematic study of modifications of *cis*-platin, obtained through the substitution of NH_3 ligands by *N*-heterocyclic systems, like imidazole- and pyrazole-based ligands. The Pd^{II} synthetic chemistry may be easily transferred to Pt^{II}, with the advantage that Pd^{II} starting materials are somewhat cheaper than their Pt^{II} analogues. On the other hand, regarding the chemical crystallography, Pd^{II} complexes are almost always isostructural to their Pt^{II} analogues. Finally, any new Pd^{II} complex is also of potential interest for studies about the fundamental aspects of the catalysis of the Heck reaction type.

We thus focused our efforts on the crystallographic characterization of the Pd^{II} complexes obtained as single crystals, with the hope of rationalizing the effect of the co-ligand *X* and counter-ion *Y* on the molecular and crystal structures of the complex $[Pd(pza)X]^+$ cations. An earlier report of the crystal structure of the starting material, $[Pd(pza)Cl]Cl{\cdot}2H_2O$ has been given (Mendoza *et al.*, 2006), and we now report on the characterization of $[Pd(pza)Cl]NO_3$ (1), $[Pd(pza)Br]NO_3$ (2), $[Pd(pza)I]I{\cdot}0.5(H_2O)$ (3), $[Pd(pza)N_3]N_3{\cdot}H_2O$ (4), and $2[Pd(pza)NCS][Pd(SCN)_4]$ (5).

2. Structural commentary: molecular and crystal structures

Complex (1) is a result of the substitution of the counter-ion $Y = Cl^-$ in the starting material, *i.e.* in the dihydrate $[Pd(pza)Cl]Cl{\cdot}2H_2O$ by a nitrate, but crystallizes as an anhydrous species, $[Pd(pza)Cl]NO_3$ (Fig. 1). As expected, the square-planar coordination of the metal cation is retained, and the conformation of the pza ligand is not affected by the counter-ion substitution. The cation conformation may be characterized by the dihedral angle between the pyrazole mean planes, 85.1 (3)° *versus* 87.62 (11)° in the chloride salt (Mendoza *et al.*, 2006). A least-squares fit between the $[Pd(pza)Cl]^+$ cations in the chloride and nitrate salts gives an r.m.s. deviation of 0.124 Å. However, the crystal structures are different because the water molecules in the chloride dihydrate are determinant for the supramolecular arrangement through hydrogen-bonding and intermolecular contacts. In (1), the nitrate ion interacts with the central amine group of the pza ligand, with a N10—H10···O1 separation of 1.98 Å. Other inter-ion contacts beyond the asymmetric unit are unexceptional, and the observed crystal structure is basically a consequence of Coulombic interactions rather than hydrogen bonds (Table 1).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···N20^{i}	0.93	2.66	3.510 (10)	153
C7—H7*C*···Cl1	0.96	2.81	3.410 (10)	121
C8—H8*A*···O3^{ii}	0.97	2.28	3.222 (10)	163
N10—H10···N20	0.90	2.57	3.453 (10)	167
N10—H10···O1	0.90	1.98	2.857 (9)	164
N10—H10···O2	0.90	2.45	3.186 (10)	140
C14—H14*A*···Cl1^{iii}	0.93	2.82	3.629 (9)	146
C16—H16*A*···O1^{iv}	0.96	2.64	3.572 (12)	164
C17—H17*A*···O3^{ii}	0.96	2.53	3.491 (12)	175
C17—H17*C*···Cl1	0.96	2.79	3.367 (10)	119
C18—H18*A*···O2	0.97	2.51	3.364 (11)	146
C18—H18*B*···O1^{iv}	0.97	2.61	3.428 (11)	142
C19—H19*A*···O3^{iv}	0.97	2.47	3.112 (11)	124

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

Table 2
Hydrogen-bond geometry (Å, °) for (2).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···N20^{i}	0.93	2.66	3.540 (7)	159
C7—H7*C*···Br1	0.96	3.06	3.500 (8)	110
C8—H8*A*···O3^{ii}	0.97	2.30	3.219 (9)	157
N10—H10···N20	0.90	2.54	3.427 (6)	169
N10—H10···O1	0.90	1.98	2.857 (7)	166
N10—H10···O2	0.90	2.43	3.181 (8)	142
C14—H14*A*···Br1^{iii}	0.93	2.88	3.687 (6)	146
C16—H16*A*···O1^{iv}	0.96	2.65	3.511 (10)	150
C17—H17*A*···O3^{ii}	0.96	2.55	3.485 (10)	164
C17—H17*C*···Br1	0.96	2.98	3.459 (8)	112
C18—H18*A*···O2	0.97	2.52	3.358 (9)	144
C18—H18*B*···O1^{iv}	0.97	2.65	3.468 (8)	142
C19—H19*B*···O3^{iv}	0.97	2.47	3.099 (9)	122

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

Complex (2), with $X = Br^-$ and $Y = NO_3^-$ is isostructural with the $X = Cl^-$ analogue (1). However, a slight relaxation of the folded pza ligand is observed, with a dihedral angle between pyrazole rings of 83.6 (2)°. An overlay between cations in (1) and (2) gives a small deviation of 0.049 Å (Fig. 1, inset). The nitrate anion interacts with the complex cation in (2) with a distance N10—H10···O1 = 1.98 Å (Table 2). Thus, the nature of the halogen co-ligand *X* in $[Pd(pza)X]NO_3$ seems to be unimportant for the resulting crystal structure.

Complex (3), built up with $X = Y =$ iodide, crystallized as a hemihydrate, with two cation complexes and two free iodide ions in the asymmetric unit (Fig. 2). The square-planar geometry of Pd^{II} is retained, as well as the pza conformation. However, the relaxation of folding, observed with $X = Br^-$ in

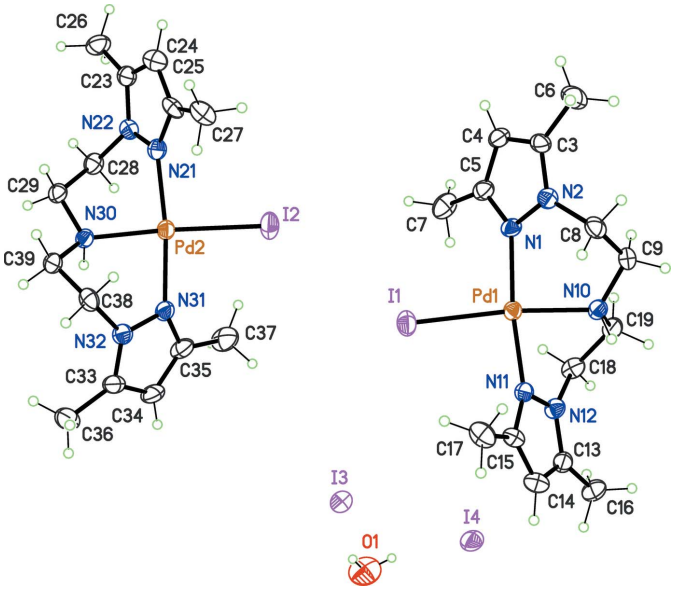


Figure 2
View of the molecular structure of complex (3), corresponding to $X = Y = I^-$, with displacement ellipsoids for non-H atoms drawn at the 30% probability level.

compound (2), is amplified with $X = I^-$: the angle between the pyrazole rings is now 79.0 (3) and 83.3 (3)°, for the Pd1 and Pd2 cations, respectively. There seems to be a regular trend for $[Pd(pza)X]^+$ cations: the smaller the ionic radius of the co-ligand X, the closer the angle between the pyrazole rings is to 90°. A possible rationalization of this observation is that methyl groups substituting pyrazole rings at position 3 interact with the co-ligand X. This destabilizing steric interaction favors the twisting of pza, which in general adopts a non-crystallographic twofold rotation symmetry. However, the large iodide anion forces the separation between methyl groups, compared to the small chloride ion. In order to keep the coordination geometry around Pd^{II} as planar as possible, the heterocycles in pza then make a slight rotation motion,

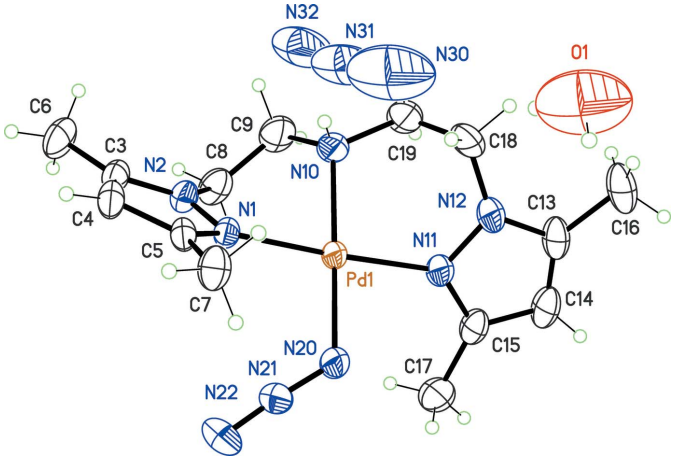


Figure 3
View of the molecular structure of complex (4), corresponding to $X = Y = N_3^-$, with displacement ellipsoids for non-H atoms drawn at the 30% probability level.

Table 3
Hydrogen-bond geometry (Å, °) for (3).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···I3	0.85	2.68	3.497 (7)	161
O1—H2···I4	0.85	2.66	3.443 (10)	155
N10—H10A···I3^{i}	0.90	2.94	3.653 (6)	137
N30—H30A···O1^{ii}	0.90	2.22	3.011 (9)	146
N30—H30A···I4^{ii}	0.90	3.30	3.853 (6)	122

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+1, -z$.

Table 4
Hydrogen-bond geometry (Å, °) for (4).

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10···N32	0.90	1.95	2.838 (11)	171
N10—H10···N31	0.90	2.66	3.460 (13)	148
O1—H11···N32^{i}	0.84	2.67	3.295 (19)	132
O1—H12···N30	0.85	2.38	3.08 (2)	140

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

which is reflected in the deviation from orthogonality of these terminal rings. In other words, the combined twisting and folding motions of the pza ligand lead to as planar as possible a coordination environment for Pd^{II}. Counter-ions Y and lattice water molecules have only slight influences, if any, on the cation conformation. In the case of (3), the water molecule behaves both as a donor and acceptor group for hydrogen bonding. O—H···I bonds are formed with the non-coordinating iodide anions, and the central amine group of pza forms a N—H···O bond with the same water molecule (Table 3). However, as for previous complexes (1) and (2), no extended supramolecular structures are formed in the crystal.

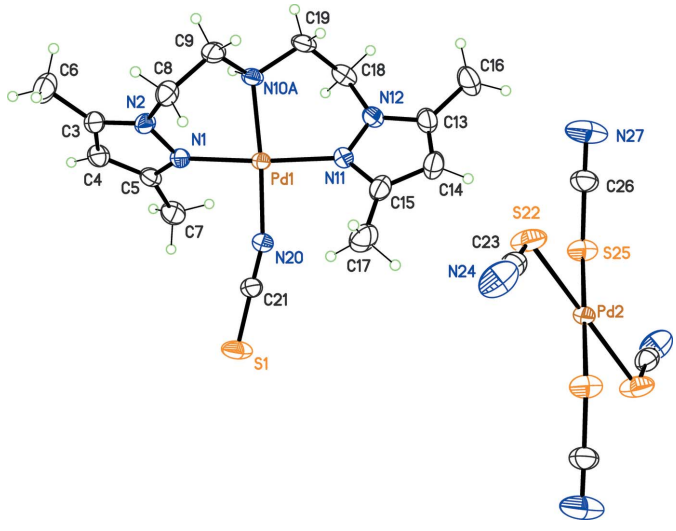


Figure 4
View of the molecular structure of complex (5), corresponding to $X = NCS^-$ and $Y = [Pd(SCN)_4]^{2-}$, with displacement ellipsoids for non-H atoms at the 30% probability level. Only one position for the disordered amine group in the cation has been retained (N10A). In the anion, unlabelled atoms are generated by symmetry code ($-x+1, -y+2, -z+2$).

Table 5
Hydrogen-bond geometry (Å, °) for (5).

D—H···A	D—H	H···A	D···A	D—H···A
N10A—H10A···N24^{i}	0.90	2.01	2.889 (9)	166
N10B—H10B···S1^{ii}	0.90	2.71	3.52 (2)	151

Symmetry codes: (i) $x, y, z-1$; (ii) $x-1, y, z$.

Using the pseudohalide $X = Y$ = azide, compound (4) was crystallized as an hydrate, $[Pd(pza)N_3]N_3{\cdot}H_2O$ (Fig. 3). The nitrogen atoms in the coordinating N_3^- ligand are not sterically demanding as the iodide ion in (3) and, as a consequence, the pyrazole rings come back in a more orthogonal arrangement, identical to that observed in $[Pd(pza)Cl]^+$. The dihedral angle between pyrazole rings is 87.3 (1)° in (4). The strongest hydrogen bond is found between the amine group of pza and the free azide ion, the N10—H10···N32 separation being 1.95 Å and the angle for the contact 171° (Table 4).

Finally, in the fifth compound (5), the counter-ion Y is a complex anion, namely $[Pd(SCN)_4]^{2-}$. The formula for (5) is $2[Pd(pza)NCS][Pd(SCN)_4]$, and the anion is located about an inversion centre, while the cation is in a general position (Fig. 4). The pza ligand in $[Pd(pza)NCS]^+$, in contrast to previous compounds, has the amine group N10 disordered over two positions, N10A and N10B, with occupancies 0.770 (18) and 0.230 (18), respectively. The same type of disorder was previously reported for an Au^{III} complex (Segapelo *et al.*, 2011). In spite of this disorder, the general conformation of pza is identical to that observed in compounds (1)–(4), approximating the non-crystallographic twofold rotation symmetry. The co-ligand X = NCS^- coordinates through its N atom, and the local environment of the metal is very similar to that resulting from azide coordination in complex (4). The dihedral angle between pyrazole rings should thus be close to 90°. The actual value is 88.6 (1)°. The anion $[Pd(SCN)_4]^{2-}$ is also square-planar, but with the ligands coordinating in a κS-fashion, while in the cation, the NCS ligand is bound in a κN-fashion to the metal cation. If complexes with bridging thiocyanate ligands are not considered, very few structures are known in which the ambidentate ligand NCS^- is bonded in two modes (κS- and κN-) to the same transition metal. In the case of Pd^{II}, classified as a soft acid in the Pearson's HSAB concept, the soft base SCN^- should have a preference for the κS-coordination. Apparently, only a few non-polymeric crystal structures have been reported including both coordination modes of SCN^- to this metal (*e.g.* Paviglianiti *et al.*, 1989; Chang *et al.*, 2005). In the crystal structure, weak hydrogen bonds between the disordered amino group and the NCS groups of neighbouring cations and anions are observed (Table 5).

3. Database survey

The ligand pza has been widely used in coordination chemistry. The current release of the CSD (Version 5.35 with all updates; Groom & Allen, 2014) affords 39 entries distributed over 18 articles. With Pd^{II}, two structures are reported to date, which are pseudopolymorphs with $X = Y = Cl^-$ (Mendoza *et al.*, 2006; Guzei *et al.*, 2010). Other transition metals have been coordinated by pza and structures are available for Co^{II} (van Berkel *et al.*, 1994; Massoud *et al.*, 2012*a*, 2013), Ni^{II} (Ajellal *et al.*, 2006; Massoud *et al.*, 2012*a*, 2013), Cu^{II} (van Berkel *et al.*, 1994; Martens *et al.*, 1995; Kim *et al.*, 2000; Monzani *et al.*, 2000; Riklin *et al.*, 2001; Massoud *et al.*, 2012*a*,*b*, 2013), Zn^{II} (Burth & Vahrenkamp, 1998; Lian *et al.*, 2007*a*; Lee *et al.*, 2007; Massoud *et al.*, 2013), Cd^{II} (Griffith *et al.*, 1987; Massoud *et al.*, 2013), Re^{I} (Alves *et al.*, 2002) and Au^{III} (Segapelo *et al.*, 2011). The pza ligand generally behaves as a tridentate ligand, with exceptions for some Zn^{II} compounds, in which one pyrazole ring is not coordinating to the metal (Burth & Vahrenkamp, 1998; Lian *et al.*, 2007*a*; Lee *et al.*, 2007). Few complexes have also been prepared with *s*- and *p*-metals, *viz*. Li^{I} (Lian *et al.*, 2007*a*), Mg^{II} (Lian *et al.*, 2007*b*), and Al^{III} (Lian *et al.*, 2007*a*).

The conformation observed for pza is determined by the coordination number of the metal centre. For example, hexacoordinated transition metals like Ni^{II} or Cd^{II} favor the facial coordination of pza, which is then found in a folded conformation, while coordination numbers 5 and 4 promote some defolding. The ligand pza with the dihedral angle between pyrazole rings very close to 0° has been observed in Co^{II} complexes (Massoud *et al.*, 2012*a*, 2013). A conformation for pza close to that observed in (1)–(5) has been reported with Mg^{II} (Lian *et al.*, 2007*b*) and Au^{III} (Segapelo *et al.*, 2011).

4. Synthesis and crystallization

Complexes (1)–(5) were synthesized starting from $[Pd(pza)Cl]Cl{\cdot}2H_2O$ (Mendoza *et al.*, 2006), by substitution of co-ligands and counter-ions, as depicted in Fig. 5.

Synthesis of (1). $[Pd(pza)Cl]Cl{\cdot}2H_2O$ (1 mmol) was dissolved in CH_3CN, and a solution of $AgNO_3$ (1 mmol in CH_3CN) was added slowly. The mixture was stirred for 1 h at room temperature. After elimination by filtration of the white precipitate of AgCl, the mixture was further stirred for 1 h. Evaporation of the solvent afforded complex (1) as a brown–yellow solid, in 82% yield, and crystals were obtained by recrystallization from CH_3CN.

Synthesis of (2). $[Pd(pza)Cl]Cl{\cdot}2H_2O$ (1 mmol) was dissolved in CH_3CN, and a solution of $AgNO_3$ (2 mmol in CH_3CN) was added slowly. The mixture was stirred for 2 h at room temperature, and the precipitated AgCl was removed by filtration. An aqueous solution of NaBr (1 mmol) was then added, and $NaNO_3$ precipitates, which was removed by filtration. The solution was further stirred for 5 h. Evaporation of the solvent afforded complex (2) as a yellow solid, in 76% yield, and crystals were obtained by recrystallization from CH_3CN.

Synthesis of (3). $[Pd(pza)Cl]Cl{\cdot}2H_2O$ (1 mmol) was dissolved in CH_3CN (5 ml) and a solution of 2 mmol of $NaBF_4$ in CH_3CN was added slowly. After elimination of NaCl by filtration, a solution of 2 mmol of NEt_4I in CH_3CN was added slowly, and the mixture, which turned red, was stirred for 6 h at room temperature. Evaporation of the solvent afforded complex (3) as a red solid, in 82% yield, and crystals were

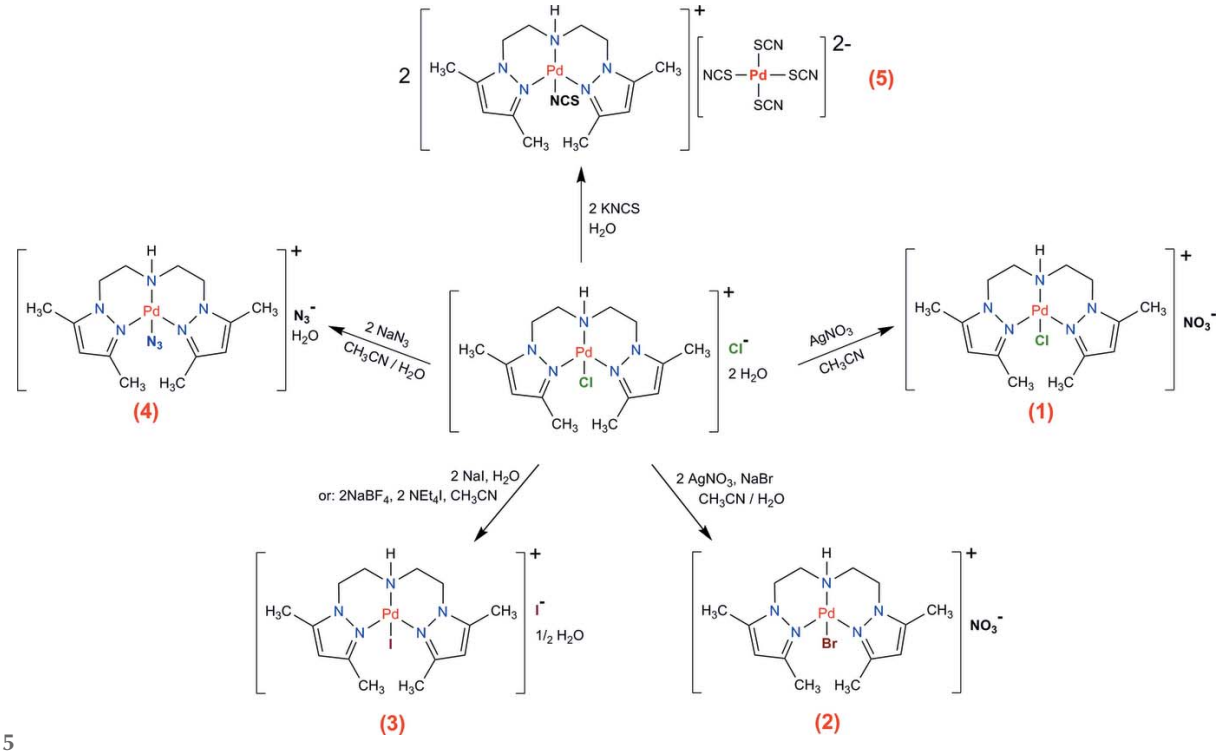


Figure 5
General synthetic scheme for complexes (1)–(5).

obtained by recrystallization from CH_3CN. Alternatively, complex (3) may be obtained in 89% yield by reacting an aqueous solution of [Pd(pza)Cl]Cl·2H_2O (1 mmol) and NaI (2 mmol) for 6 h at room temperature.

Synthesis of (4). [Pd(pza)Cl]Cl·2H_2O (1 mmol) was dissolved in CH_3CN. A solution of NaN_3 (2 mmol, CH_3CN/H_2O mixture 4:1, *v*/*v*) was added slowly. The formed precipitate of NaCl was eliminated by filtration, and the mixture was further stirred at room temperature for 10 h. Evaporation of the solvent afforded complex (4) as a yellow solid, in 61% yield, and crystals were obtained by recrystallization from CH_3CN.

Synthesis of (5). [Pd(pza)Cl]Cl·2H_2O (1 mmol) was dissolved in H_2O, and an aqueous solution of 2 mmol of KNCS was added slowly. The mixture was stirred for 10 h at room temperature. The formed pink solid, (5), was separated by filtration and dried in reduced pressure at 313 K. Yield: 48%. Crystals were obtained by recrystallization from a mixture of CH_3CN and CH_2Cl_2 (2:1, *v*/*v*).

5. Refinement

Crystal data, data collection and structure refinement details for (1)–(5) are summarized in Table 6. Data collection and refinement are routine works, except for a positional disorder found in (5) for sites N10*A*/N10*B*, for which the s.o.f. converged to 0.770 (18) and 0.230 (18), respectively. All H atoms bonded to C and N atoms were placed in calculated positions and refined as riding atoms, with fixed bond lengths of 0.93, 0.96, 0.97, and 0.90 Å for aromatic, methyl, methylene, and amine groups, respectively. In (3) and (4), H atoms for water molecules were found in difference maps, and first refined with free coordinates and restrained distances O—H = 0.85 (2) and H···H = 1.34 (4) Å. In the final cycles, water H atoms were fixed and refined as riding atoms. Isotropic displacement parameters for all H atoms were calculated as U_{iso}(H) = xU_{eq}(carrier atom), with x = 1.2 (methylene, aromatic, and amine groups) or x = 1.5 (methyl and water).

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Table 6
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$[PdCl(C_{14}H_{23}N_5)]NO_3$	$[PdBr(C_{14}H_{23}N_5)]NO_3$	$[PdI(C_{14}H_2N_5)]I\cdot 0.5H_2O$	$[Pd(N_3)(C_{14}H_{23}N_5)]N_3\cdot H_2O$	$[Pd(NCS)(C_{14}H_{23}N_5)]_2[Pd(NCS)_4]$
M_r	465.23	509.69	630.58	469.85	1190.43
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	298	298	299	296	298
a, b, c (Å)	11.046 (2), 12.2941 (15), 14.0978 (16)	10.934 (6), 12.443 (4), 14.112 (6)	12.013 (4), 12.089 (4), 15.162 (5)	8.132 (3), 22.851 (5), 11.372 (3)	9.0286 (17), 10.532 (2), 13.066 (3)
α, β, γ (°)	90, 94.740 (16), 90	90, 94.76 (4), 90	106.17 (2), 97.34 (3), 106.79 (3)	90, 109.03 (2), 90	94.838 (14), 100.947 (12), 103.989 (13)
V (Å^3)	1907.9 (5)	1913.4 (14)	1972.0 (11)	1997.8 (10)	1172.5 (4)
Z	4	4	4	4	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.14	3.08	4.08	0.96	1.45
Crystal size (mm)	0.40 × 0.12 × 0.10	0.60 × 0.40 × 0.18	0.20 × 0.15 × 0.04	0.50 × 0.40 × 0.40	0.40 × 0.40 × 0.12
Data collection					
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4	Siemens P4
Absorption correction	ψ scan (*XSCANS*; Siemens, 1996)	ψ scan (*XSCANS*; Siemens, 1996)	ψ scan (*XSCANS*; Siemens, 1996)	ψ scan (*XSCANS*; Siemens, 1996)	ψ scan (*XSCANS*; Siemens, 1996)
T_{min}, T_{max}	0.469, 0.517	0.206, 0.352	0.446, 0.523	0.266, 0.366	0.256, 0.378
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4513, 3372, 2110	12224, 4962, 3329	8975, 6835, 4559	8431, 4032, 3528	8889, 5367, 4874
R_{int}	0.044	0.080	0.043	0.056	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.596	0.677	0.595	0.623	0.650
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.158, 1.05	0.051, 0.148, 1.05	0.040, 0.101, 1.03	0.036, 0.097, 1.08	0.039, 0.107, 1.06
No. of reflections	3372	4962	6835	4032	5367
No. of parameters	230	231	414	248	282
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.45, −1.11	1.10, −1.01	0.85, −1.04	0.55, −1.04	0.83, −1.06

Computer programs: *XSCANS* (Siemens, 1996), *SHELXS2014*, *SHELXL2014* and *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

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Coordination of bis(pyrazol-1-yl)amine to palladium(II): influence of the co-ligands and counter-ions on the molecular and crystal structures

María de los Angeles Mendoza, Sylvain Bernès and Guillermo Mendoza-Díaz

Computing details

For all compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS* (Siemens, 1996); data reduction: *XSCANS* (Siemens, 1996); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008). Molecular graphics: *SHELXTL* (Sheldrick, 2008) for (1), (3), (4), (5); *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008) for (2). For all compounds, software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(1) {Bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}chloridopalladium nitrate

Crystal data

$[PdCl(C_{14}H_{23}N_5)]NO_3$
M_r = 465.23
Monoclinic, $P2_1/n$
a = 11.046 (2) Å
b = 12.2941 (15) Å
c = 14.0978 (16) Å
β = 94.740 (16)°
V = 1907.9 (5) Å^3
Z = 4
$F(000)$ = 944
D_x = 1.620 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 51 reflections
θ = 4.2–11.4°
μ = 1.14 mm^{-1}
T = 298 K
Irregular, yellow
0.40 × 0.12 × 0.10 mm

Data collection

Siemens P4 diffractometer
Radiation source: fine-focus sealed tube, FN4
Graphite monochromator
ω scans
Absorption correction: ψ scan (XSCANS; Siemens, 1996)
T_{min} = 0.469, T_{max} = 0.517
4513 measured reflections
3372 independent reflections
2110 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 25.1°, θ_{min} = 2.2°
h = −13→2
k = −14→1
l = −16→16
2 standard reflections every 98 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.158
S = 1.05
3372 reflections
230 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 4.1623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.45$ e Å^{-3}
$\Delta\rho_{min} = -1.11$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.72319 (6)	0.71729 (4)	0.48704 (4)	0.0531 (2)
Cl1	0.8178 (2)	0.79157 (19)	0.36252 (16)	0.0787 (7)
N1	0.6837 (6)	0.8628 (5)	0.5434 (4)	0.0526 (15)
N2	0.5729 (6)	0.8737 (5)	0.5775 (4)	0.0590 (17)
C3	0.5644 (8)	0.9712 (7)	0.6217 (6)	0.063 (2)
C4	0.6727 (8)	1.0222 (7)	0.6145 (6)	0.062 (2)
H4A	0.6935	1.0913	0.6372	0.074*
C5	0.7454 (8)	0.9534 (6)	0.5679 (6)	0.057 (2)
C6	0.4531 (9)	1.0055 (9)	0.6675 (8)	0.094 (3)
H6A	0.3833	0.9982	0.6227	0.141*
H6B	0.4614	1.0800	0.6874	0.141*
H6C	0.4433	0.9603	0.7219	0.141*
C7	0.8714 (9)	0.9703 (8)	0.5461 (8)	0.087 (3)
H7A	0.9208	0.9113	0.5717	0.131*
H7B	0.9010	1.0375	0.5740	0.131*
H7C	0.8752	0.9734	0.4784	0.131*
C8	0.4865 (8)	0.7861 (7)	0.5628 (6)	0.071 (2)
H8A	0.4758	0.7689	0.4955	0.086*
H8B	0.4086	0.8094	0.5827	0.086*
C9	0.5280 (9)	0.6844 (8)	0.6183 (7)	0.085 (3)
H9A	0.5163	0.6950	0.6851	0.102*
H9B	0.4782	0.6232	0.5956	0.102*
N10	0.6567 (6)	0.6590 (5)	0.6082 (4)	0.0592 (17)
H10	0.6972	0.6969	0.6553	0.071*
N11	0.7516 (6)	0.5655 (5)	0.4398 (4)	0.0592 (17)
N12	0.8073 (7)	0.4924 (5)	0.5011 (4)	0.0668 (19)
C13	0.8283 (8)	0.3993 (7)	0.4553 (6)	0.066 (2)
C14	0.7855 (8)	0.4148 (6)	0.3638 (6)	0.065 (2)
H14A	0.7896	0.3645	0.3148	0.078*
C15	0.7349 (7)	0.5173 (6)	0.3546 (5)	0.0550 (19)
C16	0.8887 (11)	0.3031 (8)	0.5040 (7)	0.096 (3)
H16A	0.8463	0.2837	0.5583	0.145*
H16B	0.9714	0.3210	0.5244	0.145*
H16C	0.8872	0.2429	0.4605	0.145*
C17	0.6704 (9)	0.5709 (8)	0.2707 (6)	0.081 (3)
H17A	0.5987	0.6063	0.2896	0.121*
H17B	0.6478	0.5173	0.2230	0.121*
H17C	0.7229	0.6238	0.2453	0.121*
C18	0.8104 (10)	0.5127 (7)	0.6030 (5)	0.078 (3)
H18A	0.8676	0.5707	0.6201	0.094*

H18B	0.8380	0.4477	0.6373	0.094*
C19	0.6873 (11)	0.5438 (7)	0.6310 (6)	0.080 (3)
H19A	0.6268	0.4969	0.5982	0.096*
H19B	0.6845	0.5323	0.6989	0.096*
N20	0.8548 (9)	0.7786 (5)	0.7798 (5)	0.069 (2)
O1	0.7422 (7)	0.7795 (6)	0.7736 (5)	0.0859 (19)
O2	0.9057 (8)	0.7441 (7)	0.7123 (6)	0.105 (2)
O3	0.9127 (7)	0.8085 (5)	0.8529 (5)	0.097 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0779 (5)	0.0434 (3)	0.0381 (3)	0.0043 (3)	0.0053 (3)	0.0013 (3)
Cl1	0.0987 (17)	0.0776 (15)	0.0621 (13)	0.0096 (13)	0.0200 (12)	0.0223 (11)
N1	0.056 (4)	0.045 (4)	0.057 (4)	0.001 (3)	0.009 (3)	−0.004 (3)
N2	0.065 (5)	0.060 (4)	0.052 (4)	−0.002 (4)	0.004 (3)	−0.003 (3)
C3	0.072 (6)	0.063 (5)	0.053 (5)	0.019 (5)	−0.003 (4)	−0.006 (4)
C4	0.068 (6)	0.047 (4)	0.070 (5)	0.006 (4)	0.005 (4)	−0.012 (4)
C5	0.065 (6)	0.046 (4)	0.061 (5)	−0.002 (4)	0.006 (4)	0.010 (4)
C6	0.082 (7)	0.102 (8)	0.100 (8)	0.024 (6)	0.010 (6)	−0.029 (6)
C7	0.095 (8)	0.063 (6)	0.105 (8)	−0.015 (5)	0.021 (6)	−0.005 (5)
C8	0.070 (6)	0.083 (6)	0.060 (5)	−0.007 (5)	−0.004 (4)	−0.010 (5)
C9	0.095 (8)	0.088 (7)	0.071 (6)	−0.030 (6)	0.011 (5)	−0.007 (5)
N10	0.083 (5)	0.053 (4)	0.042 (3)	−0.014 (4)	0.006 (3)	−0.003 (3)
N11	0.097 (5)	0.044 (3)	0.036 (3)	0.015 (4)	0.004 (3)	0.000 (3)
N12	0.098 (6)	0.050 (4)	0.050 (4)	0.013 (4)	−0.010 (4)	0.003 (3)
C13	0.081 (6)	0.050 (5)	0.069 (6)	0.010 (4)	0.015 (5)	0.003 (4)
C14	0.080 (6)	0.052 (5)	0.064 (5)	0.009 (5)	0.014 (5)	−0.007 (4)
C15	0.063 (5)	0.061 (5)	0.041 (4)	0.006 (4)	0.002 (4)	−0.008 (4)
C16	0.131 (9)	0.073 (7)	0.089 (7)	0.039 (6)	0.028 (7)	0.012 (5)
C17	0.100 (7)	0.096 (7)	0.045 (5)	0.023 (6)	−0.003 (5)	−0.010 (5)
C18	0.137 (9)	0.047 (5)	0.046 (5)	0.008 (6)	−0.017 (5)	0.004 (4)
C19	0.147 (9)	0.057 (5)	0.037 (4)	−0.013 (6)	0.007 (5)	0.005 (4)
N20	0.102 (7)	0.045 (4)	0.058 (5)	−0.003 (5)	−0.004 (5)	0.003 (4)
O1	0.086 (5)	0.094 (5)	0.077 (4)	−0.004 (4)	0.003 (4)	−0.018 (4)
O2	0.115 (6)	0.110 (6)	0.091 (5)	−0.002 (4)	0.005 (5)	−0.024 (4)
O3	0.136 (6)	0.073 (4)	0.075 (4)	−0.005 (4)	−0.039 (4)	−0.004 (3)

Geometric parameters (Å, º)

Pd1—N11	2.015 (6)	N10—C19	1.485 (10)
Pd1—N1	2.019 (6)	N10—H10	0.9000
Pd1—N10	2.045 (6)	N11—C15	1.339 (9)
Pd1—Cl1	2.305 (2)	N11—N12	1.357 (8)
N1—C5	1.337 (9)	N12—C13	1.344 (10)
N1—N2	1.358 (9)	N12—C18	1.455 (10)
N2—C3	1.358 (10)	C13—C14	1.351 (11)
N2—C8	1.442 (10)	C13—C16	1.496 (12)

C3—C4	1.362 (11)	C14—C15	1.380 (11)
C3—C6	1.495 (12)	C14—H14A	0.9300
C4—C5	1.372 (11)	C15—C17	1.484 (11)
C4—H4A	0.9300	C16—H16A	0.9600
C5—C7	1.465 (12)	C16—H16B	0.9600
C6—H6A	0.9600	C16—H16C	0.9600
C6—H6B	0.9600	C17—H17A	0.9600
C6—H6C	0.9600	C17—H17B	0.9600
C7—H7A	0.9600	C17—H17C	0.9600
C7—H7B	0.9600	C18—C19	1.497 (13)
C7—H7C	0.9600	C18—H18A	0.9700
C8—C9	1.525 (13)	C18—H18B	0.9700
C8—H8A	0.9700	C19—H19A	0.9700
C8—H8B	0.9700	C19—H19B	0.9700
C9—N10	1.473 (11)	N20—O2	1.219 (10)
C9—H9A	0.9700	N20—O3	1.223 (9)
C9—H9B	0.9700	N20—O1	1.239 (9)

N11—Pd1—N1	174.3 (3)	C19—N10—Pd1	115.1 (5)
N11—Pd1—N10	91.6 (3)	C9—N10—H10	104.1
N1—Pd1—N10	83.0 (3)	C19—N10—H10	104.1
N11—Pd1—Cl1	91.30 (19)	Pd1—N10—H10	104.1
N1—Pd1—Cl1	94.30 (19)	C15—N11—N12	107.5 (6)
N10—Pd1—Cl1	172.9 (2)	C15—N11—Pd1	133.8 (5)
C5—N1—N2	106.4 (6)	N12—N11—Pd1	118.5 (4)
C5—N1—Pd1	135.9 (6)	C13—N12—N11	110.2 (6)
N2—N1—Pd1	117.2 (5)	C13—N12—C18	128.9 (7)
C3—N2—N1	110.4 (7)	N11—N12—C18	119.2 (6)
C3—N2—C8	130.9 (8)	N12—C13—C14	106.1 (7)
N1—N2—C8	118.7 (7)	N12—C13—C16	122.8 (8)
N2—C3—C4	106.1 (7)	C14—C13—C16	131.1 (8)
N2—C3—C6	122.5 (9)	C13—C14—C15	109.0 (7)
C4—C3—C6	131.3 (8)	C13—C14—H14A	125.5
C3—C4—C5	107.7 (7)	C15—C14—H14A	125.5
C3—C4—H4A	126.1	N11—C15—C14	107.2 (7)
C5—C4—H4A	126.1	N11—C15—C17	122.7 (7)
N1—C5—C4	109.3 (7)	C14—C15—C17	130.1 (7)
N1—C5—C7	122.6 (8)	C13—C16—H16A	109.5
C4—C5—C7	128.1 (8)	C13—C16—H16B	109.5
C3—C6—H6A	109.5	H16A—C16—H16B	109.5
C3—C6—H6B	109.5	C13—C16—H16C	109.5
H6A—C6—H6B	109.5	H16A—C16—H16C	109.5
C3—C6—H6C	109.5	H16B—C16—H16C	109.5
H6A—C6—H6C	109.5	C15—C17—H17A	109.5
H6B—C6—H6C	109.5	C15—C17—H17B	109.5
C5—C7—H7A	109.5	H17A—C17—H17B	109.5
C5—C7—H7B	109.5	C15—C17—H17C	109.5
H7A—C7—H7B	109.5	H17A—C17—H17C	109.5

C5—C7—H7C	109.5	H17B—C17—H17C	109.5
H7A—C7—H7C	109.5	N12—C18—C19	110.9 (7)
H7B—C7—H7C	109.5	N12—C18—H18A	109.5
N2—C8—C9	111.8 (7)	C19—C18—H18A	109.5
N2—C8—H8A	109.3	N12—C18—H18B	109.5
C9—C8—H8A	109.3	C19—C18—H18B	109.5
N2—C8—H8B	109.3	H18A—C18—H18B	108.1
C9—C8—H8B	109.3	N10—C19—C18	112.5 (7)
H8A—C8—H8B	107.9	N10—C19—H19A	109.1
N10—C9—C8	112.1 (7)	C18—C19—H19A	109.1
N10—C9—H9A	109.2	N10—C19—H19B	109.1
C8—C9—H9A	109.2	C18—C19—H19B	109.1
N10—C9—H9B	109.2	H19A—C19—H19B	107.8
C8—C9—H9B	109.2	O2—N20—O3	121.2 (10)
H9A—C9—H9B	107.9	O2—N20—O1	118.2 (8)
C9—N10—C19	112.7 (7)	O3—N20—O1	120.5 (9)
C9—N10—Pd1	115.0 (5)		

C5—N1—N2—C3	1.1 (8)	C15—N11—N12—C13	1.2 (10)
Pd1—N1—N2—C3	173.7 (5)	Pd1—N11—N12—C13	−174.5 (6)
C5—N1—N2—C8	−179.0 (7)	C15—N11—N12—C18	−165.2 (8)
Pd1—N1—N2—C8	−6.4 (8)	Pd1—N11—N12—C18	19.0 (10)
N1—N2—C3—C4	0.1 (9)	N11—N12—C13—C14	0.4 (10)
C8—N2—C3—C4	−179.8 (8)	C18—N12—C13—C14	165.2 (9)
N1—N2—C3—C6	−179.2 (8)	N11—N12—C13—C16	180.0 (9)
C8—N2—C3—C6	0.9 (13)	C18—N12—C13—C16	−15.3 (15)
N2—C3—C4—C5	−1.2 (9)	N12—C13—C14—C15	−1.8 (10)
C6—C3—C4—C5	178.0 (9)	C16—C13—C14—C15	178.6 (10)
N2—N1—C5—C4	−1.8 (8)	N12—N11—C15—C14	−2.3 (9)
Pd1—N1—C5—C4	−172.4 (6)	Pd1—N11—C15—C14	172.5 (6)
N2—N1—C5—C7	177.9 (7)	N12—N11—C15—C17	176.7 (8)
Pd1—N1—C5—C7	7.3 (12)	Pd1—N11—C15—C17	−8.5 (13)
C3—C4—C5—N1	2.0 (9)	C13—C14—C15—N11	2.6 (10)
C3—C4—C5—C7	−177.8 (8)	C13—C14—C15—C17	−176.4 (9)
C3—N2—C8—C9	−113.1 (9)	C13—N12—C18—C19	−115.9 (10)
N1—N2—C8—C9	67.0 (9)	N11—N12—C18—C19	47.7 (10)
N2—C8—C9—N10	−45.8 (10)	C9—N10—C19—C18	168.9 (7)
C8—C9—N10—C19	−159.6 (7)	Pd1—N10—C19—C18	34.4 (8)
C8—C9—N10—Pd1	−25.0 (9)	N12—C18—C19—N10	−78.4 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···N20^{i}	0.93	2.66	3.510 (10)	153
C7—H7*C*···Cl1	0.96	2.81	3.410 (10)	121
C8—H8*A*···O3^{ii}	0.97	2.28	3.222 (10)	163
N10—H10···N20	0.90	2.57	3.453 (10)	167
N10—H10···O1	0.90	1.98	2.857 (9)	164

N10—H10···O2	0.90	2.45	3.186 (10)	140
C14—H14*A*···Cl1^{iii}	0.93	2.82	3.629 (9)	146
C16—H16*A*···O1^{iv}	0.96	2.64	3.572 (12)	164
C17—H17*A*···O3^{ii}	0.96	2.53	3.491 (12)	175
C17—H17*C*···Cl1	0.96	2.79	3.367 (10)	119
C18—H18*A*···O2	0.97	2.51	3.364 (11)	146
C18—H18*B*···O1^{iv}	0.97	2.61	3.428 (11)	142
C19—H19*A*···O3^{iv}	0.97	2.47	3.112 (11)	124

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

(2) {Bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}bromidopalladium nitrate

Crystal data

$[PdBr(C_{14}H_{23}N_5)]NO_3$
M_r = 509.69
Monoclinic, $P2_1/n$
a = 10.934 (6) Å
b = 12.443 (4) Å
c = 14.112 (6) Å
β = 94.76 (4)°
V = 1913.4 (14) Å^3
Z = 4
$F(000)$ = 1016
D_x = 1.769 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 70 reflections
θ = 5.0–12.5°
μ = 3.08 mm^{-1}
T = 298 K
Prism, yellow
0.60 × 0.40 × 0.18 mm

Data collection

Siemens P4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: ψ scan (XSCANS; Siemens, 1996)
T_{min} = 0.206, T_{max} = 0.352
12224 measured reflections
4962 independent reflections
3329 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
θ_{max} = 28.8°, θ_{min} = 2.2°
h = −14→14
k = −16→16
l = −19→19
3 standard reflections every 97 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.148
S = 1.05
4962 reflections
231 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 3.056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.10 e Å^{-3}
$\Delta\rho_{min}$ = −1.01 e Å^{-3}
Extinction correction: SHELXL2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0042 (5)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.72527 (4)	0.72194 (3)	0.49024 (3)	0.04869 (16)

Br1	0.82828 (6)	0.79805 (6)	0.36061 (5)	0.0713 (2)
N1	0.6855 (4)	0.8654 (4)	0.5458 (3)	0.0527 (10)
N2	0.5720 (4)	0.8754 (4)	0.5774 (3)	0.0559 (11)
C3	0.5614 (6)	0.9701 (5)	0.6223 (4)	0.0653 (15)
C4	0.6697 (6)	1.0215 (5)	0.6178 (5)	0.0683 (16)
H4A	0.6890	1.0898	0.6412	0.082*
C5	0.7463 (6)	0.9545 (4)	0.5723 (4)	0.0590 (14)
C6	0.4475 (7)	1.0010 (7)	0.6655 (6)	0.095 (3)
H6A	0.3795	0.9988	0.6179	0.143*
H6B	0.4561	1.0724	0.6908	0.143*
H6C	0.4330	0.9517	0.7157	0.143*
C7	0.8768 (6)	0.9714 (6)	0.5555 (6)	0.089 (2)
H7A	0.9217	0.9060	0.5686	0.134*
H7B	0.9105	1.0273	0.5966	0.134*
H7C	0.8827	0.9917	0.4904	0.134*
C8	0.4863 (6)	0.7883 (5)	0.5612 (5)	0.0694 (17)
H8A	0.4791	0.7704	0.4940	0.083*
H8B	0.4062	0.8114	0.5781	0.083*
C9	0.5245 (6)	0.6902 (6)	0.6176 (5)	0.0741 (18)
H9A	0.5108	0.7022	0.6838	0.089*
H9B	0.4740	0.6299	0.5949	0.089*
N10	0.6556 (4)	0.6634 (4)	0.6103 (3)	0.0566 (11)
H10	0.6956	0.7007	0.6579	0.068*
N11	0.7515 (5)	0.5725 (4)	0.4438 (3)	0.0590 (12)
N12	0.8088 (5)	0.5000 (4)	0.5054 (3)	0.0607 (12)
C13	0.8290 (6)	0.4082 (4)	0.4598 (4)	0.0596 (14)
C14	0.7837 (6)	0.4222 (5)	0.3675 (4)	0.0617 (14)
H14A	0.7853	0.3720	0.3188	0.074*
C15	0.7353 (5)	0.5240 (5)	0.3597 (4)	0.0577 (13)
C16	0.8890 (8)	0.3118 (6)	0.5076 (6)	0.091 (2)
H16A	0.8366	0.2833	0.5529	0.137*
H16B	0.9662	0.3325	0.5398	0.137*
H16C	0.9024	0.2581	0.4608	0.137*
C17	0.6657 (7)	0.5744 (6)	0.2765 (4)	0.081 (2)
H17A	0.6015	0.6186	0.2979	0.121*
H17B	0.6305	0.5194	0.2351	0.121*
H17C	0.7201	0.6179	0.2427	0.121*
C18	0.8102 (7)	0.5208 (5)	0.6062 (4)	0.0715 (18)
H18A	0.8671	0.5787	0.6233	0.086*
H18B	0.8384	0.4571	0.6412	0.086*
C19	0.6851 (7)	0.5506 (5)	0.6330 (4)	0.0704 (18)
H19A	0.6811	0.5390	0.7006	0.084*
H19B	0.6246	0.5045	0.5994	0.084*
N20	0.8449 (4)	0.7830 (3)	0.7852 (3)	0.0351 (8)
O1	0.7422 (7)	0.7835 (4)	0.7749 (4)	0.1053 (19)
O2	0.9013 (7)	0.7448 (6)	0.7245 (6)	0.125 (2)
O3	0.9009 (7)	0.8139 (5)	0.8568 (5)	0.113 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0552 (3)	0.0486 (2)	0.0429 (2)	0.00212 (18)	0.00814 (16)	0.00166 (16)
Br1	0.0761 (4)	0.0797 (4)	0.0608 (4)	0.0144 (3)	0.0225 (3)	0.0231 (3)
N1	0.048 (2)	0.057 (3)	0.054 (2)	0.002 (2)	0.012 (2)	−0.002 (2)
N2	0.048 (2)	0.069 (3)	0.051 (2)	0.006 (2)	0.008 (2)	−0.004 (2)
C3	0.070 (4)	0.067 (4)	0.058 (3)	0.018 (3)	0.002 (3)	−0.011 (3)
C4	0.082 (4)	0.057 (3)	0.065 (4)	0.005 (3)	0.005 (3)	−0.012 (3)
C5	0.068 (3)	0.048 (3)	0.061 (3)	−0.004 (3)	0.004 (3)	0.003 (3)
C6	0.078 (5)	0.120 (6)	0.089 (5)	0.034 (5)	0.013 (4)	−0.034 (5)
C7	0.071 (4)	0.079 (4)	0.120 (6)	−0.021 (4)	0.022 (4)	−0.013 (5)
C8	0.050 (3)	0.088 (5)	0.072 (4)	−0.002 (3)	0.014 (3)	−0.007 (3)
C9	0.069 (4)	0.081 (4)	0.075 (4)	−0.024 (4)	0.024 (3)	−0.009 (4)
N10	0.066 (3)	0.061 (3)	0.044 (2)	−0.011 (2)	0.010 (2)	−0.003 (2)
N11	0.077 (3)	0.055 (2)	0.045 (2)	0.011 (2)	0.005 (2)	0.002 (2)
N12	0.080 (3)	0.049 (2)	0.052 (3)	0.008 (2)	−0.003 (2)	0.001 (2)
C13	0.064 (3)	0.049 (3)	0.066 (3)	0.009 (3)	0.010 (3)	0.002 (3)
C14	0.069 (3)	0.058 (3)	0.059 (3)	0.010 (3)	0.008 (3)	−0.010 (3)
C15	0.057 (3)	0.062 (3)	0.054 (3)	0.009 (3)	0.004 (3)	−0.008 (3)
C16	0.110 (6)	0.067 (4)	0.096 (5)	0.032 (4)	0.010 (5)	0.008 (4)
C17	0.095 (5)	0.093 (5)	0.052 (3)	0.032 (4)	−0.009 (3)	−0.009 (3)
C18	0.107 (5)	0.050 (3)	0.055 (3)	0.006 (4)	−0.011 (3)	0.007 (3)
C19	0.109 (5)	0.057 (3)	0.046 (3)	−0.011 (4)	0.017 (3)	0.007 (3)
N20	0.051 (2)	0.0202 (15)	0.0322 (17)	−0.0047 (17)	−0.0085 (16)	−0.0046 (13)
O1	0.145 (6)	0.093 (4)	0.079 (4)	−0.003 (4)	0.014 (4)	−0.016 (3)
O2	0.115 (5)	0.117 (5)	0.139 (6)	−0.022 (4)	−0.021 (5)	−0.010 (5)
O3	0.140 (5)	0.090 (4)	0.103 (4)	−0.014 (4)	−0.027 (4)	0.006 (3)

Geometric parameters (Å, º)

Pd1—N11	2.000 (5)	N10—C19	1.470 (8)
Pd1—N1	2.012 (4)	N10—H10	0.9000
Pd1—N10	2.048 (4)	N11—C15	1.330 (7)
Pd1—Br1	2.4194 (11)	N11—N12	1.368 (6)
N1—C5	1.330 (7)	N12—C13	1.339 (7)
N1—N2	1.359 (6)	N12—C18	1.444 (7)
N2—C3	1.347 (7)	C13—C14	1.366 (8)
N2—C8	1.438 (7)	C13—C16	1.500 (8)
C3—C4	1.352 (9)	C14—C15	1.373 (8)
C3—C6	1.482 (9)	C14—H14A	0.9300
C4—C5	1.378 (8)	C15—C17	1.484 (8)
C4—H4A	0.9300	C16—H16A	0.9600
C5—C7	1.480 (9)	C16—H16B	0.9600
C6—H6A	0.9600	C16—H16C	0.9600
C6—H6B	0.9600	C17—H17A	0.9600
C6—H6C	0.9600	C17—H17B	0.9600
C7—H7A	0.9600	C17—H17C	0.9600

C7—H7B	0.9600	C18—C19	1.496 (10)
C7—H7C	0.9600	C18—H18A	0.9700
C8—C9	1.498 (9)	C18—H18B	0.9700
C8—H8A	0.9700	C19—H19A	0.9700
C8—H8B	0.9700	C19—H19B	0.9700
C9—N10	1.484 (8)	N20—O2	1.195 (8)
C9—H9A	0.9700	N20—O3	1.200 (7)
C9—H9B	0.9700	N20—O1	1.121 (8)

N11—Pd1—N1	173.81 (19)	C19—N10—Pd1	115.5 (4)
N11—Pd1—N10	90.80 (19)	C9—N10—H10	104.1
N1—Pd1—N10	83.45 (19)	C19—N10—H10	104.1
N11—Pd1—Br1	91.58 (14)	Pd1—N10—H10	104.1
N1—Pd1—Br1	94.40 (13)	C15—N11—N12	106.7 (4)
N10—Pd1—Br1	173.21 (14)	C15—N11—Pd1	134.7 (4)
C5—N1—N2	106.3 (5)	N12—N11—Pd1	118.4 (3)
C5—N1—Pd1	136.9 (4)	C13—N12—N11	110.0 (4)
N2—N1—Pd1	116.2 (4)	C13—N12—C18	129.6 (5)
N1—N2—C3	110.5 (5)	N11—N12—C18	118.4 (5)
N1—N2—C8	118.7 (5)	C14—C13—N12	106.8 (5)
C3—N2—C8	130.8 (5)	C14—C13—C16	129.9 (6)
C4—C3—N2	106.4 (5)	N12—C13—C16	123.3 (6)
C4—C3—C6	131.8 (6)	C13—C14—C15	107.5 (5)
N2—C3—C6	121.9 (6)	C13—C14—H14A	126.2
C3—C4—C5	107.7 (5)	C15—C14—H14A	126.2
C3—C4—H4A	126.1	N11—C15—C14	109.0 (5)
C5—C4—H4A	126.1	N11—C15—C17	122.3 (5)
N1—C5—C4	109.0 (6)	C14—C15—C17	128.5 (5)
N1—C5—C7	122.6 (6)	C13—C16—H16A	109.5
C4—C5—C7	128.3 (6)	C13—C16—H16B	109.5
C3—C6—H6A	109.5	H16A—C16—H16B	109.5
C3—C6—H6B	109.5	C13—C16—H16C	109.5
H6A—C6—H6B	109.5	H16A—C16—H16C	109.5
C3—C6—H6C	109.5	H16B—C16—H16C	109.5
H6A—C6—H6C	109.5	C15—C17—H17A	109.5
H6B—C6—H6C	109.5	C15—C17—H17B	109.5
C5—C7—H7A	109.5	H17A—C17—H17B	109.5
C5—C7—H7B	109.5	C15—C17—H17C	109.5
H7A—C7—H7B	109.5	H17A—C17—H17C	109.5
C5—C7—H7C	109.5	H17B—C17—H17C	109.5
H7A—C7—H7C	109.5	N12—C18—C19	111.0 (5)
H7B—C7—H7C	109.5	N12—C18—H18A	109.4
N2—C8—C9	112.3 (5)	C19—C18—H18A	109.4
N2—C8—H8A	109.1	N12—C18—H18B	109.4
C9—C8—H8A	109.1	C19—C18—H18B	109.4
N2—C8—H8B	109.1	H18A—C18—H18B	108.0
C9—C8—H8B	109.1	C18—C19—N10	111.8 (5)
H8A—C8—H8B	107.9	C18—C19—H19A	109.3

N10—C9—C8	112.0 (5)	N10—C19—H19A	109.3
N10—C9—H9A	109.2	C18—C19—H19B	109.3
C8—C9—H9A	109.2	N10—C19—H19B	109.3
N10—C9—H9B	109.2	H19A—C19—H19B	107.9
C8—C9—H9B	109.2	O2—N20—O3	118.3 (6)
H9A—C9—H9B	107.9	O2—N20—O1	118.7 (5)
C9—N10—C19	113.3 (5)	O3—N20—O1	122.9 (6)
C9—N10—Pd1	113.9 (4)		

C5—N1—N2—C3	0.7 (6)	C15—N11—N12—C13	0.7 (7)
Pd1—N1—N2—C3	173.2 (4)	Pd1—N11—N12—C13	−174.0 (4)
C5—N1—N2—C8	−178.2 (5)	C15—N11—N12—C18	−164.6 (6)
Pd1—N1—N2—C8	−5.6 (6)	Pd1—N11—N12—C18	20.7 (7)
N1—N2—C3—C4	0.8 (7)	N11—N12—C13—C14	−0.1 (7)
C8—N2—C3—C4	179.5 (6)	C18—N12—C13—C14	163.1 (7)
N1—N2—C3—C6	−178.8 (6)	N11—N12—C13—C16	−179.2 (6)
C8—N2—C3—C6	−0.2 (10)	C18—N12—C13—C16	−16.0 (11)
N2—C3—C4—C5	−1.9 (7)	N12—C13—C14—C15	−0.5 (7)
C6—C3—C4—C5	177.6 (7)	C16—C13—C14—C15	178.5 (7)
N2—N1—C5—C4	−1.9 (6)	N12—N11—C15—C14	−1.0 (7)
Pd1—N1—C5—C4	−172.0 (4)	Pd1—N11—C15—C14	172.4 (5)
N2—N1—C5—C7	176.5 (6)	N12—N11—C15—C17	174.4 (6)
Pd1—N1—C5—C7	6.3 (10)	Pd1—N11—C15—C17	−12.1 (10)
C3—C4—C5—N1	2.4 (7)	C13—C14—C15—N11	0.9 (7)
C3—C4—C5—C7	−175.8 (7)	C13—C14—C15—C17	−174.1 (7)
N1—N2—C8—C9	68.0 (7)	C13—N12—C18—C19	−114.3 (7)
C3—N2—C8—C9	−110.6 (7)	N11—N12—C18—C19	47.7 (7)
N2—C8—C9—N10	−47.3 (7)	N12—C18—C19—N10	−79.3 (6)
C8—C9—N10—C19	−158.6 (5)	C9—N10—C19—C18	168.4 (5)
C8—C9—N10—Pd1	−23.9 (7)	Pd1—N10—C19—C18	34.5 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···N20^{i}	0.93	2.66	3.540 (7)	159
C7—H7*C*···Br1	0.96	3.06	3.500 (8)	110
C8—H8*A*···O3^{ii}	0.97	2.30	3.219 (9)	157
N10—H10···N20	0.90	2.54	3.427 (6)	169
N10—H10···O1	0.90	1.98	2.857 (7)	166
N10—H10···O2	0.90	2.43	3.181 (8)	142
C14—H14*A*···Br1^{iii}	0.93	2.88	3.687 (6)	146
C16—H16*A*···O1^{iv}	0.96	2.65	3.511 (10)	150
C17—H17*A*···O3^{ii}	0.96	2.55	3.485 (10)	164
C17—H17*C*···Br1	0.96	2.98	3.459 (8)	112
C18—H18*A*···O2	0.97	2.52	3.358 (9)	144

C18—H18*B*···O1^{iv}	0.97	2.65	3.468 (8)	142
C19—H19*B*···O3^{iv}	0.97	2.47	3.099 (9)	122

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

(3) {Bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}iodidopalladium iodide hemihydrate

Crystal data

$[PdI(C_{14}H_2N_5)]I\cdot 0.5H_2O$
M_r = 630.58
Triclinic, $P\overline{1}$
a = 12.013 (4) Å
b = 12.089 (4) Å
c = 15.162 (5) Å
α = 106.17 (2)°
β = 97.34 (3)°
γ = 106.79 (3)°
V = 1972.0 (11) Å^3
Z = 4
F(000) = 1196
D_x = 2.124 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 68 reflections
θ = 4.2–12.0°
μ = 4.08 mm^{-1}
T = 299 K
Plate, orange
0.20 × 0.15 × 0.04 mm

Data collection

Siemens P4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: *ψ* scan (XSCANS; Siemens, 1996)
T_{min} = 0.446, T_{max} = 0.523
8975 measured reflections
6835 independent reflections
4559 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.0°, θ_{min} = 1.8°
h = −14→3
k = −13→13
l = −18→18
3 standard reflections every 97 reflections
intensity decay: 1.5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.101
S = 1.03
6835 reflections
414 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 6.3989P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −1.04 e Å^{-3}

Special details

Refinement. Geometry of the water molecule first regularized with soft restraints: *DFIX* 0.85 0.02 O1 H1 O1 H2 DANG 1.34 0.04 H1 H2 then fixed in last l.s. cycles.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.64608 (5)	0.84173 (5)	0.70510 (4)	0.03566 (15)
I1	0.75703 (5)	0.76282 (6)	0.57898 (4)	0.05531 (17)
N1	0.6227 (5)	0.7009 (6)	0.7556 (4)	0.0393 (15)
N2	0.6504 (5)	0.7285 (6)	0.8519 (4)	0.0405 (15)

C3	0.6317 (7)	0.6248 (8)	0.8731 (6)	0.045 (2)
C4	0.5940 (7)	0.5293 (8)	0.7912 (6)	0.047 (2)
H4A	0.5768	0.4468	0.7844	0.057*
C5	0.5864 (7)	0.5794 (7)	0.7195 (6)	0.045 (2)
C6	0.6539 (9)	0.6222 (10)	0.9712 (6)	0.067 (3)
H6A	0.7355	0.6698	1.0025	0.101*
H6B	0.6382	0.5391	0.9697	0.101*
H6C	0.6022	0.6560	1.0047	0.101*
C7	0.5422 (8)	0.5142 (8)	0.6166 (6)	0.062 (3)
H7A	0.5253	0.5693	0.5863	0.093*
H7B	0.4707	0.4460	0.6052	0.093*
H7C	0.6019	0.4852	0.5917	0.093*
C8	0.6637 (7)	0.8494 (7)	0.9118 (5)	0.046 (2)
H8A	0.7347	0.9082	0.9063	0.055*
H8B	0.6738	0.8519	0.9769	0.055*
C9	0.5567 (7)	0.8842 (8)	0.8854 (6)	0.049 (2)
H9A	0.4845	0.8156	0.8749	0.058*
H9B	0.5558	0.9523	0.9371	0.058*
N10	0.5581 (5)	0.9190 (6)	0.7995 (4)	0.0389 (15)
H10A	0.6005	0.9996	0.8206	0.047*
N11	0.6523 (5)	0.9860 (5)	0.6634 (4)	0.0355 (14)
N12	0.5449 (5)	1.0022 (6)	0.6428 (4)	0.0417 (15)
C13	0.5610 (7)	1.1056 (7)	0.6222 (5)	0.0433 (19)
C14	0.6808 (7)	1.1565 (8)	0.6286 (6)	0.051 (2)
H14A	0.7183	1.2276	0.6161	0.061*
C15	0.7350 (7)	1.0819 (7)	0.6569 (5)	0.0405 (18)
C16	0.4620 (8)	1.1495 (8)	0.5978 (7)	0.059 (2)
H16A	0.3928	1.0808	0.5603	0.089*
H16B	0.4854	1.2038	0.5626	0.089*
H16C	0.4438	1.1922	0.6545	0.089*
C17	0.8642 (7)	1.0992 (9)	0.6824 (6)	0.057 (2)
H17A	0.8845	1.0992	0.7457	0.085*
H17B	0.9107	1.1760	0.6780	0.085*
H17C	0.8806	1.0337	0.6398	0.085*
C18	0.4389 (6)	0.9129 (7)	0.6494 (6)	0.047 (2)
H18A	0.4311	0.8324	0.6081	0.056*
H18B	0.3694	0.9319	0.6276	0.056*
C19	0.4409 (7)	0.9094 (7)	0.7490 (6)	0.047 (2)
H19A	0.4181	0.9763	0.7843	0.057*
H19B	0.3821	0.8334	0.7461	0.057*
Pd2	0.89057 (5)	0.31577 (5)	0.31013 (4)	0.03801 (16)
I2	0.78206 (5)	0.41030 (5)	0.43265 (4)	0.06044 (19)
N21	0.8807 (5)	0.1716 (6)	0.3554 (4)	0.0408 (15)
N22	0.8361 (5)	0.0562 (6)	0.2895 (4)	0.0413 (15)
C23	0.8361 (7)	−0.0288 (8)	0.3313 (6)	0.0441 (19)
C24	0.8777 (7)	0.0336 (8)	0.4249 (6)	0.053 (2)
H24A	0.8851	−0.0005	0.4723	0.064*
C25	0.9072 (6)	0.1582 (8)	0.4373 (5)	0.0428 (19)

C26	0.7980 (8)	−0.1613 (8)	0.2781 (7)	0.061 (2)
H26A	0.7264	−0.1845	0.2309	0.091*
H26B	0.7830	−0.2070	0.3205	0.091*
H26C	0.8598	−0.1783	0.2482	0.091*
C27	0.9661 (8)	0.2630 (8)	0.5245 (6)	0.059 (2)
H27A	1.0039	0.3345	0.5090	0.089*
H27B	1.0251	0.2453	0.5618	0.089*
H27C	0.9078	0.2777	0.5597	0.089*
C28	0.8342 (7)	0.0419 (7)	0.1900 (5)	0.045 (2)
H28A	0.7730	0.0697	0.1648	0.055*
H28B	0.8152	−0.0439	0.1541	0.055*
C29	0.9540 (7)	0.1153 (7)	0.1807 (5)	0.0435 (19)
H29A	1.0163	0.1051	0.2217	0.052*
H29B	0.9618	0.0845	0.1163	0.052*
N30	0.9695 (5)	0.2441 (5)	0.2048 (4)	0.0380 (15)
H30A	0.9298	0.2498	0.1527	0.046*
N31	0.9132 (5)	0.4530 (6)	0.2548 (5)	0.0436 (16)
N32	1.0221 (5)	0.4929 (6)	0.2337 (5)	0.0437 (16)
C33	1.0186 (7)	0.5512 (8)	0.1718 (6)	0.051 (2)
C34	0.9048 (8)	0.5537 (8)	0.1536 (7)	0.061 (2)
H34A	0.8753	0.5902	0.1139	0.073*
C35	0.8427 (7)	0.4922 (8)	0.2053 (7)	0.054 (2)
C36	1.1245 (8)	0.5984 (9)	0.1333 (7)	0.070 (3)
H36A	1.1892	0.6565	0.1841	0.104*
H36B	1.1040	0.6375	0.0897	0.104*
H36C	1.1482	0.5314	0.1014	0.104*
C37	0.7122 (8)	0.4641 (10)	0.2050 (8)	0.079 (3)
H37A	0.6921	0.4198	0.2476	0.118*
H37B	0.6656	0.4153	0.1425	0.118*
H37C	0.6957	0.5392	0.2245	0.118*
C38	1.1151 (6)	0.4525 (7)	0.2691 (5)	0.044 (2)
H38A	1.1185	0.4627	0.3352	0.053*
H38B	1.1914	0.5033	0.2641	0.053*
C39	1.0946 (6)	0.3211 (7)	0.2160 (6)	0.0430 (19)
H39A	1.1120	0.3141	0.1544	0.052*
H39B	1.1481	0.2923	0.2497	0.052*
I3	0.44634 (6)	0.76946 (6)	0.10827 (4)	0.06206 (19)
I4	−0.00003 (8)	0.83190 (7)	0.05319 (5)	0.0843 (2)
O1	0.2414 (8)	0.8235 (8)	−0.0455 (6)	0.112 (3)
H1	0.3020	0.8127	−0.0184	0.168*
H2	0.1967	0.8227	−0.0063	0.168*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0346 (3)	0.0398 (3)	0.0366 (3)	0.0169 (3)	0.0098 (3)	0.0139 (3)
I1	0.0580 (4)	0.0757 (4)	0.0464 (3)	0.0390 (3)	0.0199 (3)	0.0212 (3)
N1	0.046 (4)	0.040 (4)	0.036 (4)	0.021 (3)	0.004 (3)	0.015 (3)

N2	0.041 (4)	0.041 (4)	0.039 (4)	0.014 (3)	0.008 (3)	0.013 (3)
C3	0.039 (4)	0.056 (5)	0.060 (5)	0.024 (4)	0.026 (4)	0.035 (5)
C4	0.051 (5)	0.041 (5)	0.059 (6)	0.023 (4)	0.018 (4)	0.022 (4)
C5	0.041 (4)	0.041 (5)	0.058 (5)	0.017 (4)	0.014 (4)	0.020 (4)
C6	0.078 (7)	0.090 (8)	0.058 (6)	0.040 (6)	0.027 (5)	0.045 (6)
C7	0.065 (6)	0.044 (5)	0.057 (6)	0.017 (5)	−0.004 (5)	−0.002 (4)
C8	0.054 (5)	0.050 (5)	0.030 (4)	0.015 (4)	0.009 (4)	0.013 (4)
C9	0.062 (6)	0.050 (5)	0.045 (5)	0.028 (4)	0.028 (4)	0.017 (4)
N10	0.035 (3)	0.033 (3)	0.048 (4)	0.011 (3)	0.013 (3)	0.012 (3)
N11	0.031 (3)	0.039 (4)	0.040 (4)	0.015 (3)	0.009 (3)	0.015 (3)
N12	0.035 (4)	0.044 (4)	0.051 (4)	0.018 (3)	0.009 (3)	0.017 (3)
C13	0.047 (5)	0.043 (5)	0.042 (5)	0.019 (4)	0.012 (4)	0.013 (4)
C14	0.048 (5)	0.049 (5)	0.053 (5)	0.007 (4)	0.009 (4)	0.025 (4)
C15	0.040 (4)	0.042 (5)	0.038 (4)	0.006 (4)	0.008 (3)	0.017 (4)
C16	0.065 (6)	0.059 (6)	0.071 (6)	0.038 (5)	0.013 (5)	0.030 (5)
C17	0.032 (4)	0.071 (6)	0.061 (6)	0.006 (4)	0.010 (4)	0.027 (5)
C18	0.029 (4)	0.042 (5)	0.065 (6)	0.011 (4)	0.003 (4)	0.018 (4)
C19	0.038 (4)	0.037 (5)	0.066 (6)	0.011 (4)	0.020 (4)	0.015 (4)
Pd2	0.0361 (3)	0.0380 (3)	0.0417 (3)	0.0144 (3)	0.0132 (3)	0.0122 (3)
I2	0.0549 (4)	0.0480 (3)	0.0688 (4)	0.0130 (3)	0.0295 (3)	0.0026 (3)
N21	0.042 (4)	0.040 (4)	0.038 (4)	0.014 (3)	0.009 (3)	0.009 (3)
N22	0.039 (4)	0.046 (4)	0.039 (4)	0.014 (3)	0.010 (3)	0.015 (3)
C23	0.034 (4)	0.054 (5)	0.051 (5)	0.018 (4)	0.013 (4)	0.023 (4)
C24	0.043 (5)	0.060 (6)	0.055 (6)	0.011 (4)	0.007 (4)	0.027 (5)
C25	0.030 (4)	0.060 (6)	0.036 (4)	0.006 (4)	0.009 (3)	0.022 (4)
C26	0.062 (6)	0.042 (5)	0.084 (7)	0.016 (4)	0.018 (5)	0.029 (5)
C27	0.063 (6)	0.063 (6)	0.043 (5)	0.006 (5)	0.013 (4)	0.019 (5)
C28	0.048 (5)	0.045 (5)	0.040 (5)	0.018 (4)	0.006 (4)	0.008 (4)
C29	0.052 (5)	0.050 (5)	0.038 (4)	0.028 (4)	0.012 (4)	0.017 (4)
N30	0.040 (4)	0.041 (4)	0.037 (3)	0.020 (3)	0.009 (3)	0.014 (3)
N31	0.036 (4)	0.038 (4)	0.062 (4)	0.015 (3)	0.018 (3)	0.019 (3)
N32	0.034 (4)	0.045 (4)	0.056 (4)	0.014 (3)	0.012 (3)	0.020 (3)
C33	0.052 (5)	0.047 (5)	0.067 (6)	0.020 (4)	0.019 (4)	0.032 (5)
C34	0.063 (6)	0.058 (6)	0.088 (7)	0.036 (5)	0.023 (5)	0.044 (5)
C35	0.041 (5)	0.042 (5)	0.085 (7)	0.018 (4)	0.010 (5)	0.026 (5)
C36	0.062 (6)	0.080 (7)	0.091 (7)	0.028 (5)	0.034 (6)	0.053 (6)
C37	0.048 (6)	0.082 (8)	0.124 (9)	0.031 (5)	0.019 (6)	0.052 (7)
C38	0.027 (4)	0.060 (6)	0.046 (5)	0.013 (4)	0.009 (3)	0.020 (4)
C39	0.034 (4)	0.054 (5)	0.052 (5)	0.023 (4)	0.013 (4)	0.025 (4)
I3	0.0659 (4)	0.0564 (4)	0.0662 (4)	0.0252 (3)	0.0144 (3)	0.0195 (3)
I4	0.1379 (7)	0.0760 (5)	0.0587 (4)	0.0551 (5)	0.0243 (4)	0.0319 (4)
O1	0.123 (7)	0.129 (7)	0.089 (6)	0.055 (6)	−0.014 (5)	0.047 (5)

Geometric parameters (Å, º)

Pd1—N11	1.999 (6)	Pd2—N31	2.026 (6)
Pd1—N1	2.018 (6)	Pd2—N30	2.071 (6)
Pd1—N10	2.061 (6)	Pd2—I2	2.5987 (11)

Pd1—I1	2.5910 (11)	N21—C25	1.307 (9)
N1—C5	1.330 (10)	N21—N22	1.374 (8)
N1—N2	1.376 (8)	N22—C23	1.349 (10)
N2—C3	1.343 (10)	N22—C28	1.467 (9)
N2—C8	1.440 (10)	C23—C24	1.355 (11)
C3—C4	1.356 (11)	C23—C26	1.480 (12)
C3—C6	1.487 (11)	C24—C25	1.395 (12)
C4—C5	1.389 (11)	C24—H24A	0.9300
C4—H4A	0.9300	C25—C27	1.472 (11)
C5—C7	1.483 (11)	C26—H26A	0.9600
C6—H6A	0.9600	C26—H26B	0.9600
C6—H6B	0.9600	C26—H26C	0.9600
C6—H6C	0.9600	C27—H27A	0.9600
C7—H7A	0.9600	C27—H27B	0.9600
C7—H7B	0.9600	C27—H27C	0.9600
C7—H7C	0.9600	C28—C29	1.504 (11)
C8—C9	1.505 (11)	C28—H28A	0.9700
C8—H8A	0.9700	C28—H28B	0.9700
C8—H8B	0.9700	C29—N30	1.446 (9)
C9—N10	1.477 (10)	C29—H29A	0.9700
C9—H9A	0.9700	C29—H29B	0.9700
C9—H9B	0.9700	N30—C39	1.481 (9)
N10—C19	1.471 (10)	N30—H30A	0.9000
N10—H10A	0.9000	N31—C35	1.331 (10)
N11—C15	1.329 (9)	N31—N32	1.370 (8)
N11—N12	1.371 (8)	N32—C33	1.326 (10)
N12—C13	1.337 (10)	N32—C38	1.442 (9)
N12—C18	1.448 (10)	C33—C34	1.371 (12)
C13—C14	1.371 (11)	C33—C36	1.496 (12)
C13—C16	1.481 (11)	C34—C35	1.370 (12)
C14—C15	1.381 (11)	C34—H34A	0.9300
C14—H14A	0.9300	C35—C37	1.503 (12)
C15—C17	1.488 (11)	C36—H36A	0.9600
C16—H16A	0.9600	C36—H36B	0.9600
C16—H16B	0.9600	C36—H36C	0.9600
C16—H16C	0.9600	C37—H37A	0.9600
C17—H17A	0.9600	C37—H37B	0.9600
C17—H17B	0.9600	C37—H37C	0.9600
C17—H17C	0.9600	C38—C39	1.497 (11)
C18—C19	1.519 (11)	C38—H38A	0.9700
C18—H18A	0.9700	C38—H38B	0.9700
C18—H18B	0.9700	C39—H39A	0.9700
C19—H19A	0.9700	C39—H39B	0.9700
C19—H19B	0.9700	O1—H1	0.8507
Pd2—N21	2.023 (6)	O1—H2	0.8502
N11—Pd1—N1	172.4 (2)	N21—Pd2—N30	89.6 (2)
N11—Pd1—N10	82.6 (2)	N31—Pd2—N30	83.6 (2)

N1—Pd1—N10	90.1 (2)	N21—Pd2—I2	93.85 (17)
N11—Pd1—I1	91.33 (17)	N31—Pd2—I2	93.00 (18)
N1—Pd1—I1	95.91 (17)	N30—Pd2—I2	175.52 (17)
N10—Pd1—I1	173.96 (17)	C25—N21—N22	106.8 (6)
C5—N1—N2	105.8 (6)	C25—N21—Pd2	135.2 (6)
C5—N1—Pd1	136.5 (5)	N22—N21—Pd2	118.0 (5)
N2—N1—Pd1	117.6 (5)	C23—N22—N21	110.3 (6)
C3—N2—N1	109.8 (6)	C23—N22—C28	126.8 (7)
C3—N2—C8	129.0 (7)	N21—N22—C28	119.3 (6)
N1—N2—C8	119.1 (6)	N22—C23—C24	106.1 (7)
N2—C3—C4	108.0 (7)	N22—C23—C26	123.0 (7)
N2—C3—C6	123.6 (8)	C24—C23—C26	131.0 (8)
C4—C3—C6	128.3 (8)	C23—C24—C25	107.6 (8)
C3—C4—C5	106.1 (7)	C23—C24—H24A	126.2
C3—C4—H4A	126.9	C25—C24—H24A	126.2
C5—C4—H4A	126.9	N21—C25—C24	109.1 (7)
N1—C5—C4	110.1 (7)	N21—C25—C27	122.5 (8)
N1—C5—C7	121.7 (7)	C24—C25—C27	128.3 (8)
C4—C5—C7	128.2 (8)	C23—C26—H26A	109.5
C3—C6—H6A	109.5	C23—C26—H26B	109.5
C3—C6—H6B	109.5	H26A—C26—H26B	109.5
H6A—C6—H6B	109.5	C23—C26—H26C	109.5
C3—C6—H6C	109.5	H26A—C26—H26C	109.5
H6A—C6—H6C	109.5	H26B—C26—H26C	109.5
H6B—C6—H6C	109.5	C25—C27—H27A	109.5
C5—C7—H7A	109.5	C25—C27—H27B	109.5
C5—C7—H7B	109.5	H27A—C27—H27B	109.5
H7A—C7—H7B	109.5	C25—C27—H27C	109.5
C5—C7—H7C	109.5	H27A—C27—H27C	109.5
H7A—C7—H7C	109.5	H27B—C27—H27C	109.5
H7B—C7—H7C	109.5	N22—C28—C29	109.8 (6)
N2—C8—C9	111.2 (6)	N22—C28—H28A	109.7
N2—C8—H8A	109.4	C29—C28—H28A	109.7
C9—C8—H8A	109.4	N22—C28—H28B	109.7
N2—C8—H8B	109.4	C29—C28—H28B	109.7
C9—C8—H8B	109.4	H28A—C28—H28B	108.2
H8A—C8—H8B	108.0	N30—C29—C28	111.9 (6)
N10—C9—C8	111.5 (6)	N30—C29—H29A	109.2
N10—C9—H9A	109.3	C28—C29—H29A	109.2
C8—C9—H9A	109.3	N30—C29—H29B	109.2
N10—C9—H9B	109.3	C28—C29—H29B	109.2
C8—C9—H9B	109.3	H29A—C29—H29B	107.9
H9A—C9—H9B	108.0	C29—N30—C39	112.6 (6)
C19—N10—C9	114.8 (6)	C29—N30—Pd2	117.1 (5)
C19—N10—Pd1	109.8 (5)	C39—N30—Pd2	113.2 (5)
C9—N10—Pd1	116.8 (4)	C29—N30—H30A	104.0
C19—N10—H10A	104.6	C39—N30—H30A	104.0
C9—N10—H10A	104.6	Pd2—N30—H30A	104.0

Pd1—N10—H10A	104.6	C35—N31—N32	104.9 (6)
C15—N11—N12	106.5 (6)	C35—N31—Pd2	136.2 (6)
C15—N11—Pd1	137.8 (5)	N32—N31—Pd2	114.9 (5)
N12—N11—Pd1	115.4 (4)	C33—N32—N31	111.6 (6)
C13—N12—N11	110.1 (6)	C33—N32—C38	129.8 (7)
C13—N12—C18	131.7 (6)	N31—N32—C38	117.9 (6)
N11—N12—C18	118.1 (6)	N32—C33—C34	106.4 (7)
N12—C13—C14	107.1 (7)	N32—C33—C36	122.2 (8)
N12—C13—C16	123.2 (7)	C34—C33—C36	131.4 (8)
C14—C13—C16	129.7 (8)	C35—C34—C33	106.8 (8)
C13—C14—C15	106.8 (7)	C35—C34—H34A	126.6
C13—C14—H14A	126.6	C33—C34—H34A	126.6
C15—C14—H14A	126.6	N31—C35—C34	110.4 (7)
N11—C15—C14	109.4 (7)	N31—C35—C37	122.7 (8)
N11—C15—C17	121.0 (7)	C34—C35—C37	126.9 (8)
C14—C15—C17	129.5 (7)	C33—C36—H36A	109.5
C13—C16—H16A	109.5	C33—C36—H36B	109.5
C13—C16—H16B	109.5	H36A—C36—H36B	109.5
H16A—C16—H16B	109.5	C33—C36—H36C	109.5
C13—C16—H16C	109.5	H36A—C36—H36C	109.5
H16A—C16—H16C	109.5	H36B—C36—H36C	109.5
H16B—C16—H16C	109.5	C35—C37—H37A	109.5
C15—C17—H17A	109.5	C35—C37—H37B	109.5
C15—C17—H17B	109.5	H37A—C37—H37B	109.5
H17A—C17—H17B	109.5	C35—C37—H37C	109.5
C15—C17—H17C	109.5	H37A—C37—H37C	109.5
H17A—C17—H17C	109.5	H37B—C37—H37C	109.5
H17B—C17—H17C	109.5	N32—C38—C39	111.9 (6)
N12—C18—C19	112.9 (6)	N32—C38—H38A	109.2
N12—C18—H18A	109.0	C39—C38—H38A	109.2
C19—C18—H18A	109.0	N32—C38—H38B	109.2
N12—C18—H18B	109.0	C39—C38—H38B	109.2
C19—C18—H18B	109.0	H38A—C38—H38B	107.9
H18A—C18—H18B	107.8	N30—C39—C38	110.8 (6)
N10—C19—C18	113.5 (6)	N30—C39—H39A	109.5
N10—C19—H19A	108.9	C38—C39—H39A	109.5
C18—C19—H19A	108.9	N30—C39—H39B	109.5
N10—C19—H19B	108.9	C38—C39—H39B	109.5
C18—C19—H19B	108.9	H39A—C39—H39B	108.1
H19A—C19—H19B	107.7	H1—O1—H2	103.6
N21—Pd2—N31	173.1 (2)		

C5—N1—N2—C3	0.4 (8)	C25—N21—N22—C23	−0.5 (8)
Pd1—N1—N2—C3	−178.9 (5)	Pd2—N21—N22—C23	179.8 (5)
C5—N1—N2—C8	−164.4 (6)	C25—N21—N22—C28	−160.6 (6)
Pd1—N1—N2—C8	16.2 (8)	Pd2—N21—N22—C28	19.8 (8)
N1—N2—C3—C4	1.1 (8)	N21—N22—C23—C24	1.9 (8)
C8—N2—C3—C4	164.1 (7)	C28—N22—C23—C24	160.1 (7)

N1—N2—C3—C6	179.5 (7)	N21—N22—C23—C26	−177.3 (7)
C8—N2—C3—C6	−17.5 (12)	C28—N22—C23—C26	−19.1 (12)
N2—C3—C4—C5	−2.2 (9)	N22—C23—C24—C25	−2.5 (9)
C6—C3—C4—C5	179.5 (8)	C26—C23—C24—C25	176.6 (8)
N2—N1—C5—C4	−1.8 (8)	N22—N21—C25—C24	−1.1 (8)
Pd1—N1—C5—C4	177.4 (6)	Pd2—N21—C25—C24	178.5 (6)
N2—N1—C5—C7	176.5 (7)	N22—N21—C25—C27	175.3 (7)
Pd1—N1—C5—C7	−4.2 (12)	Pd2—N21—C25—C27	−5.1 (12)
C3—C4—C5—N1	2.6 (9)	C23—C24—C25—N21	2.3 (9)
C3—C4—C5—C7	−175.7 (8)	C23—C24—C25—C27	−173.8 (8)
C3—N2—C8—C9	−109.2 (8)	C23—N22—C28—C29	−108.1 (8)
N1—N2—C8—C9	52.5 (9)	N21—N22—C28—C29	48.3 (9)
N2—C8—C9—N10	−76.7 (8)	N22—C28—C29—N30	−78.6 (8)
C8—C9—N10—C19	158.1 (7)	C28—C29—N30—C39	167.7 (6)
C8—C9—N10—Pd1	27.4 (8)	C28—C29—N30—Pd2	33.9 (8)
C15—N11—N12—C13	1.1 (8)	C35—N31—N32—C33	−1.7 (9)
Pd1—N11—N12—C13	175.7 (5)	Pd2—N31—N32—C33	159.5 (6)
C15—N11—N12—C18	−177.0 (6)	C35—N31—N32—C38	−173.3 (7)
Pd1—N11—N12—C18	−2.3 (8)	Pd2—N31—N32—C38	−12.0 (8)
N11—N12—C13—C14	0.7 (9)	N31—N32—C33—C34	2.0 (10)
C18—N12—C13—C14	178.4 (8)	C38—N32—C33—C34	172.3 (8)
N11—N12—C13—C16	−179.4 (7)	N31—N32—C33—C36	−176.9 (8)
C18—N12—C13—C16	−1.7 (13)	C38—N32—C33—C36	−6.6 (14)
N12—C13—C14—C15	−2.1 (9)	N32—C33—C34—C35	−1.5 (11)
C16—C13—C14—C15	177.9 (8)	C36—C33—C34—C35	177.3 (10)
N12—N11—C15—C14	−2.4 (8)	N32—N31—C35—C34	0.7 (10)
Pd1—N11—C15—C14	−175.2 (6)	Pd2—N31—C35—C34	−154.4 (7)
N12—N11—C15—C17	175.1 (7)	N32—N31—C35—C37	177.6 (9)
Pd1—N11—C15—C17	2.3 (12)	Pd2—N31—C35—C37	22.5 (14)
C13—C14—C15—N11	2.9 (9)	C33—C34—C35—N31	0.5 (11)
C13—C14—C15—C17	−174.4 (8)	C33—C34—C35—C37	−176.3 (10)
C13—N12—C18—C19	−113.8 (9)	C33—N32—C38—C39	−95.7 (10)
N11—N12—C18—C19	63.7 (9)	N31—N32—C38—C39	74.1 (8)
C9—N10—C19—C18	−164.8 (6)	C29—N30—C39—C38	−162.3 (6)
Pd1—N10—C19—C18	−30.8 (7)	Pd2—N30—C39—C38	−26.7 (7)
N12—C18—C19—N10	−41.1 (9)	N32—C38—C39—N30	−46.9 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···I3	0.85	2.68	3.497 (7)	161
O1—H2···I4	0.85	2.66	3.443 (10)	155
N10—H10*A*···I3^{i}	0.90	2.94	3.653 (6)	137
N30—H30*A*···O1^{ii}	0.90	2.22	3.011 (9)	146
N30—H30*A*···I4^{ii}	0.90	3.30	3.853 (6)	122

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

(4) Azido{bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}palladium azide monohydrate

Crystal data

$[Pd(N_3)(C_{14}H_{23}N_5)]N_3 \cdot H_2O$
$M_r = 469.85$
Monoclinic, $P2_1/c$
$a = 8.132$ (3) Å
$b = 22.851$ (5) Å
$c = 11.372$ (3) Å
$\beta = 109.03$ (2)°
$V = 1997.8$ (10) Å^3
$Z = 4$
$F(000) = 960$
$D_x = 1.562$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 65 reflections
$\theta = 4.7$–$12.6°$
$\mu = 0.96$ mm^{-1}
$T = 296$ K
Prism, yellow
0.5 × 0.4 × 0.4 mm

Data collection

Siemens P4 diffractometer
Radiation source: fine-focus sealed tube, FN4
Graphite monochromator
$2\theta/\omega$ scans
Absorption correction: ψ scan (XSCANS; Siemens, 1996)
$T_{min} = 0.266$, $T_{max} = 0.366$
8431 measured reflections
4032 independent reflections
3528 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 26.3°$, $\theta_{min} = 1.8°$
$h = -10 \rightarrow 10$
$k = -28 \rightarrow 1$
$l = -13 \rightarrow 14$
3 standard reflections every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.08$
4032 reflections
248 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 1.7119P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -1.04$ e Å^{-3}

Special details

Refinement. Geometry of the water molecule first regularized with soft restraints: *DFIX* 0.85 0.02 O1 H1 O1 H2 DANG 1.34 0.04 H1 H2 then fixed in last l.s. cycles.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.35885 (3)	0.66267 (2)	0.24025 (2)	0.04508 (11)
N1	0.1428 (3)	0.62778 (11)	0.1211 (2)	0.0464 (6)
N2	−0.0024 (3)	0.62721 (12)	0.1552 (3)	0.0517 (6)
C3	−0.1283 (4)	0.59569 (14)	0.0740 (3)	0.0537 (8)
C4	−0.0629 (4)	0.57587 (15)	−0.0140 (3)	0.0565 (8)
H4A	−0.1212	0.5534	−0.0832	0.068*
C5	0.1059 (4)	0.59528 (13)	0.0184 (3)	0.0464 (7)
C6	−0.3035 (5)	0.5885 (2)	0.0869 (5)	0.0792 (12)
H6A	−0.2931	0.5670	0.1616	0.119*

H6B	−0.3777	0.5675	0.0164	0.119*
H6C	−0.3526	0.6263	0.0913	0.119*
C7	0.2369 (5)	0.58174 (18)	−0.0428 (4)	0.0643 (9)
H7A	0.1815	0.5620	−0.1201	0.096*
H7B	0.3256	0.5570	0.0105	0.096*
H7C	0.2885	0.6174	−0.0584	0.096*
C8	0.0001 (6)	0.65831 (19)	0.2670 (4)	0.0703 (11)
H8A	−0.1165	0.6594	0.2723	0.084*
H8B	0.0375	0.6983	0.2626	0.084*
C9	0.1213 (7)	0.6293 (3)	0.3823 (4)	0.0890 (15)
H9A	0.1389	0.6553	0.4528	0.107*
H9B	0.0675	0.5938	0.3988	0.107*
N10	0.2933 (5)	0.61468 (16)	0.3697 (3)	0.0689 (9)
H10	0.2793	0.5781	0.3385	0.083*
N11	0.5755 (4)	0.69476 (13)	0.3678 (2)	0.0563 (7)
N12	0.6733 (4)	0.65951 (14)	0.4606 (3)	0.0622 (8)
C13	0.8151 (5)	0.6887 (2)	0.5324 (3)	0.0683 (10)
C14	0.8074 (5)	0.7426 (2)	0.4839 (4)	0.0738 (12)
H14A	0.8889	0.7722	0.5131	0.089*
C15	0.6568 (5)	0.74619 (17)	0.3827 (3)	0.0597 (9)
C16	0.9454 (7)	0.6607 (3)	0.6430 (4)	0.0970 (17)
H16A	1.0466	0.6852	0.6721	0.146*
H16B	0.9778	0.6231	0.6199	0.146*
H16C	0.8952	0.6560	0.7080	0.146*
C17	0.5864 (7)	0.79739 (18)	0.3015 (5)	0.0816 (13)
H17A	0.6404	0.8325	0.3426	0.122*
H17B	0.4630	0.7997	0.2847	0.122*
H17C	0.6103	0.7931	0.2247	0.122*
C18	0.6068 (7)	0.6028 (2)	0.4785 (4)	0.0870 (15)
H18A	0.6858	0.5846	0.5524	0.104*
H18B	0.5994	0.5779	0.4078	0.104*
C19	0.4296 (7)	0.6086 (3)	0.4921 (4)	0.0988 (18)
H19A	0.4058	0.5744	0.5343	0.119*
H19B	0.4278	0.6427	0.5427	0.119*
N20	0.4246 (4)	0.70475 (14)	0.1065 (3)	0.0600 (7)
N21	0.3172 (4)	0.71867 (13)	0.0122 (3)	0.0589 (7)
N22	0.2246 (6)	0.7317 (2)	−0.0830 (4)	0.1040 (15)
N30	0.542 (2)	0.4721 (5)	0.2466 (9)	0.203 (6)
N31	0.416 (2)	0.4860 (4)	0.2612 (6)	0.157 (6)
N32	0.2861 (19)	0.4965 (4)	0.2913 (8)	0.183 (6)
O1	0.9351 (15)	0.4889 (3)	0.3750 (6)	0.244 (5)
H11	0.9691	0.4949	0.3136	0.366*
H12	0.8315	0.5015	0.3571	0.366*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.04258 (15)	0.05370 (16)	0.03330 (14)	−0.01038 (9)	0.00459 (10)	0.00120 (9)

N1	0.0367 (12)	0.0553 (15)	0.0446 (13)	−0.0056 (11)	0.0099 (11)	−0.0003 (11)
N2	0.0407 (14)	0.0581 (16)	0.0564 (16)	−0.0047 (11)	0.0159 (12)	−0.0024 (12)
C3	0.0363 (15)	0.0486 (17)	0.071 (2)	−0.0015 (13)	0.0100 (15)	0.0008 (15)
C4	0.0394 (16)	0.0531 (18)	0.065 (2)	−0.0003 (13)	0.0004 (15)	−0.0092 (15)
C5	0.0367 (14)	0.0488 (16)	0.0464 (16)	0.0012 (12)	0.0033 (12)	−0.0028 (13)
C6	0.0398 (19)	0.083 (3)	0.116 (4)	−0.0074 (18)	0.027 (2)	−0.006 (3)
C7	0.0514 (19)	0.073 (2)	0.065 (2)	−0.0005 (17)	0.0144 (17)	−0.0200 (18)
C8	0.063 (2)	0.088 (3)	0.071 (3)	−0.0140 (19)	0.036 (2)	−0.013 (2)
C9	0.084 (3)	0.127 (4)	0.062 (2)	−0.029 (3)	0.031 (2)	0.009 (3)
N10	0.072 (2)	0.082 (2)	0.0445 (15)	−0.0231 (17)	0.0080 (15)	0.0131 (15)
N11	0.0532 (16)	0.0667 (17)	0.0399 (14)	−0.0133 (13)	0.0028 (12)	−0.0016 (12)
N12	0.0562 (18)	0.078 (2)	0.0396 (15)	−0.0063 (14)	−0.0024 (13)	−0.0018 (13)
C13	0.050 (2)	0.100 (3)	0.0449 (18)	−0.001 (2)	0.0018 (15)	−0.022 (2)
C14	0.056 (2)	0.091 (3)	0.064 (2)	−0.021 (2)	0.0061 (18)	−0.028 (2)
C15	0.0526 (19)	0.068 (2)	0.0548 (19)	−0.0141 (16)	0.0129 (16)	−0.0172 (16)
C16	0.068 (3)	0.147 (5)	0.053 (2)	0.012 (3)	−0.012 (2)	−0.014 (3)
C17	0.090 (3)	0.060 (2)	0.084 (3)	−0.021 (2)	0.014 (3)	−0.003 (2)
C18	0.091 (3)	0.085 (3)	0.057 (2)	−0.012 (2)	−0.014 (2)	0.023 (2)
C19	0.098 (4)	0.135 (4)	0.047 (2)	−0.042 (3)	0.001 (2)	0.033 (2)
N20	0.0526 (16)	0.078 (2)	0.0443 (15)	−0.0160 (14)	0.0094 (14)	0.0058 (14)
N21	0.0582 (17)	0.0623 (17)	0.0562 (18)	0.0005 (14)	0.0188 (15)	0.0111 (14)
N22	0.093 (3)	0.124 (4)	0.077 (3)	0.006 (3)	0.004 (2)	0.048 (3)
N30	0.361 (17)	0.170 (8)	0.121 (6)	−0.016 (10)	0.140 (9)	0.001 (5)
N31	0.296 (17)	0.101 (5)	0.044 (3)	−0.072 (9)	0.014 (6)	−0.004 (3)
N32	0.293 (15)	0.094 (5)	0.087 (6)	−0.068 (7)	−0.041 (6)	0.019 (4)
O1	0.406 (14)	0.215 (7)	0.160 (6)	−0.041 (8)	0.159 (8)	−0.020 (5)

Geometric parameters (Å, º)

Pd1—N1	2.002 (3)	N11—C15	1.332 (5)
Pd1—N20	2.014 (3)	N11—N12	1.360 (4)
Pd1—N11	2.020 (3)	N12—C13	1.351 (5)
Pd1—N10	2.041 (3)	N12—C18	1.443 (5)
N1—C5	1.334 (4)	C13—C14	1.342 (6)
N1—N2	1.358 (4)	C13—C16	1.498 (6)
N2—C3	1.343 (4)	C14—C15	1.383 (5)
N2—C8	1.451 (5)	C14—H14A	0.9300
C3—C4	1.355 (5)	C15—C17	1.485 (6)
C3—C6	1.488 (5)	C16—H16A	0.9600
C4—C5	1.373 (5)	C16—H16B	0.9600
C4—H4A	0.9300	C16—H16C	0.9600
C5—C7	1.483 (5)	C17—H17A	0.9600
C6—H6A	0.9600	C17—H17B	0.9600
C6—H6B	0.9600	C17—H17C	0.9600
C6—H6C	0.9600	C18—C19	1.504 (8)
C7—H7A	0.9600	C18—H18A	0.9700
C7—H7B	0.9600	C18—H18B	0.9700
C7—H7C	0.9600	C19—H19A	0.9700

C8—C9	1.512 (7)	C19—H19B	0.9700
C8—H8A	0.9700	N20—N21	1.184 (4)
C8—H8B	0.9700	N21—N22	1.139 (5)
C9—N10	1.490 (6)	N30—N31	1.129 (16)
C9—H9A	0.9700	N31—N32	1.239 (17)
C9—H9B	0.9700	O1—H11	0.8421
N10—C19	1.477 (5)	O1—H12	0.8503
N10—H10	0.9000		

N1—Pd1—N20	93.98 (11)	C9—N10—Pd1	115.0 (3)
N1—Pd1—N11	176.78 (11)	C19—N10—H10	104.1
N20—Pd1—N11	89.15 (12)	C9—N10—H10	104.1
N1—Pd1—N10	84.03 (12)	Pd1—N10—H10	104.1
N20—Pd1—N10	175.99 (14)	C15—N11—N12	106.5 (3)
N11—Pd1—N10	92.80 (12)	C15—N11—Pd1	133.8 (3)
C5—N1—N2	106.1 (2)	N12—N11—Pd1	119.7 (2)
C5—N1—Pd1	135.4 (2)	C13—N12—N11	110.2 (3)
N2—N1—Pd1	117.6 (2)	C13—N12—C18	130.0 (4)
C3—N2—N1	110.3 (3)	N11—N12—C18	119.3 (3)
C3—N2—C8	131.0 (3)	C14—C13—N12	106.7 (4)
N1—N2—C8	118.7 (3)	C14—C13—C16	131.4 (4)
N2—C3—C4	107.0 (3)	N12—C13—C16	121.8 (5)
N2—C3—C6	122.1 (4)	C13—C14—C15	107.9 (4)
C4—C3—C6	130.9 (3)	C13—C14—H14A	126.1
C3—C4—C5	107.1 (3)	C15—C14—H14A	126.1
C3—C4—H4A	126.5	N11—C15—C14	108.7 (4)
C5—C4—H4A	126.5	N11—C15—C17	122.8 (3)
N1—C5—C4	109.5 (3)	C14—C15—C17	128.5 (4)
N1—C5—C7	122.4 (3)	C13—C16—H16A	109.5
C4—C5—C7	128.0 (3)	C13—C16—H16B	109.5
C3—C6—H6A	109.5	H16A—C16—H16B	109.5
C3—C6—H6B	109.5	C13—C16—H16C	109.5
H6A—C6—H6B	109.5	H16A—C16—H16C	109.5
C3—C6—H6C	109.5	H16B—C16—H16C	109.5
H6A—C6—H6C	109.5	C15—C17—H17A	109.5
H6B—C6—H6C	109.5	C15—C17—H17B	109.5
C5—C7—H7A	109.5	H17A—C17—H17B	109.5
C5—C7—H7B	109.5	C15—C17—H17C	109.5
H7A—C7—H7B	109.5	H17A—C17—H17C	109.5
C5—C7—H7C	109.5	H17B—C17—H17C	109.5
H7A—C7—H7C	109.5	N12—C18—C19	110.5 (4)
H7B—C7—H7C	109.5	N12—C18—H18A	109.5
N2—C8—C9	111.4 (4)	C19—C18—H18A	109.5
N2—C8—H8A	109.4	N12—C18—H18B	109.5
C9—C8—H8A	109.4	C19—C18—H18B	109.5
N2—C8—H8B	109.4	H18A—C18—H18B	108.1
C9—C8—H8B	109.4	N10—C19—C18	111.1 (4)
H8A—C8—H8B	108.0	N10—C19—H19A	109.4

N10—C9—C8	112.5 (3)	C18—C19—H19A	109.4
N10—C9—H9A	109.1	N10—C19—H19B	109.4
C8—C9—H9A	109.1	C18—C19—H19B	109.4
N10—C9—H9B	109.1	H19A—C19—H19B	108.0
C8—C9—H9B	109.1	N21—N20—Pd1	120.9 (2)
H9A—C9—H9B	107.8	N22—N21—N20	174.2 (4)
C19—N10—C9	111.7 (4)	N30—N31—N32	171.4 (11)
C19—N10—Pd1	116.0 (3)	H11—O1—H12	108.2
C5—N1—N2—C3	−1.0 (4)	C15—N11—N12—C13	−0.4 (4)
Pd1—N1—N2—C3	−171.8 (2)	Pd1—N11—N12—C13	177.6 (3)
C5—N1—N2—C8	178.7 (3)	C15—N11—N12—C18	172.2 (4)
Pd1—N1—N2—C8	7.9 (4)	Pd1—N11—N12—C18	−9.9 (5)
N1—N2—C3—C4	−0.2 (4)	N11—N12—C13—C14	−0.5 (5)
C8—N2—C3—C4	−179.8 (4)	C18—N12—C13—C14	−172.0 (5)
N1—N2—C3—C6	−178.9 (3)	N11—N12—C13—C16	179.2 (4)
C8—N2—C3—C6	1.5 (6)	C18—N12—C13—C16	7.7 (7)
N2—C3—C4—C5	1.3 (4)	N12—C13—C14—C15	1.2 (5)
C6—C3—C4—C5	179.8 (4)	C16—C13—C14—C15	−178.5 (5)
N2—N1—C5—C4	1.8 (4)	N12—N11—C15—C14	1.1 (4)
Pd1—N1—C5—C4	170.1 (2)	Pd1—N11—C15—C14	−176.5 (3)
N2—N1—C5—C7	−175.5 (3)	N12—N11—C15—C17	−177.7 (4)
Pd1—N1—C5—C7	−7.2 (5)	Pd1—N11—C15—C17	4.7 (6)
C3—C4—C5—N1	−1.9 (4)	C13—C14—C15—N11	−1.4 (5)
C3—C4—C5—C7	175.2 (3)	C13—C14—C15—C17	177.3 (4)
C3—N2—C8—C9	111.5 (5)	C13—N12—C18—C19	117.0 (5)
N1—N2—C8—C9	−68.1 (4)	N11—N12—C18—C19	−53.8 (5)
N2—C8—C9—N10	46.9 (5)	C9—N10—C19—C18	−171.5 (4)
C8—C9—N10—C19	157.6 (4)	Pd1—N10—C19—C18	−37.1 (6)
C8—C9—N10—Pd1	22.7 (5)	N12—C18—C19—N10	80.6 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10···N32	0.90	1.95	2.838 (11)	171
N10—H10···N31	0.90	2.66	3.460 (13)	148
O1—H11···N32^{i}	0.84	2.67	3.295 (19)	132
O1—H12···N30	0.85	2.38	3.08 (2)	140

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

(5) Bis[{bis[2-(3,5-dimethylpyrazol-1-yl-κN^2)ethyl]amine-κN}(thiocyanato-κN)palladium] tetrakis(thiocyanato-κS)palladate

Crystal data

$[Pd(NCS)(C_{14}H_{23}N_5)]_2[Pd(NCS)_4]$
M_r = 1190.43
Triclinic, $P\overline{1}$
a = 9.0286 (17) Å
b = 10.532 (2) Å
c = 13.066 (3) Å
α = 94.838 (14)°
β = 100.947 (12)°

γ = 103.989 (13)°
V = 1172.5 (4) Å^3
Z = 1
F(000) = 596
D_x = 1.686 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 75 reflections
θ = 4.7–12.4°
μ = 1.45 mm^{-1}
T = 298 K
Irregular_Plate, pink
0.40 × 0.40 × 0.12 mm

Data collection

Siemens P4
diffractometer
Radiation source: fine-focus sealed tube, FN4
Graphite monochromator
2θ/ω scans
Absorption correction: ψ scan
(XSCANS; Siemens, 1996)
T_{min} = 0.256, T_{max} = 0.378
8889 measured reflections

5367 independent reflections
4874 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −11→6
k = −13→13
l = −16→16
3 standard reflections every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.107
S = 1.06
5367 reflections
282 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 1.1014P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −1.06 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Pd1	0.36057 (3)	0.61306 (2)	0.33358 (2)	0.03862 (9)	
S1	0.88007 (13)	0.60961 (16)	0.47191 (8)	0.0735 (4)	
N1	0.3690 (3)	0.4656 (3)	0.2291 (2)	0.0420 (6)	
N2	0.2424 (3)	0.3584 (3)	0.2003 (2)	0.0453 (6)	
C3	0.2603 (4)	0.2765 (4)	0.1225 (3)	0.0526 (8)	
C4	0.4009 (5)	0.3330 (4)	0.0994 (3)	0.0545 (9)	
H4A	0.4443	0.2987	0.0479	0.065*	
C5	0.4667 (4)	0.4500 (4)	0.1663 (2)	0.0448 (7)	
C6	0.1425 (6)	0.1487 (5)	0.0757 (4)	0.0814 (15)	
H6A	0.0469	0.1661	0.0415	0.122*	
H6B	0.1228	0.0957	0.1304	0.122*	
H6C	0.1822	0.1024	0.0253	0.122*	
C7	0.6181 (5)	0.5472 (5)	0.1716 (3)	0.0610 (9)	
H7A	0.6078	0.6349	0.1879	0.091*	
H7B	0.6475	0.5390	0.1050	0.091*	
H7C	0.6969	0.5308	0.2254	0.091*	
C8	0.1152 (4)	0.3501 (4)	0.2545 (3)	0.0531 (8)	
H8A	0.1555	0.3552	0.3295	0.064*	

H8B	0.0391	0.2653	0.2308	0.064*	
C9	0.0363 (4)	0.4580 (4)	0.2354 (3)	0.0564 (9)	
H9A	−0.0338	0.4356	0.1666	0.068*	0.770 (18)
H9B	−0.0264	0.4637	0.2874	0.068*	0.770 (18)
H9C	0.0179	0.4648	0.1608	0.068*	0.230 (18)
H9D	−0.0650	0.4328	0.2538	0.068*	0.230 (18)
N10A	0.1465 (5)	0.5881 (4)	0.2405 (5)	0.0423 (14)	0.770 (18)
H10A	0.1658	0.5870	0.1754	0.051*	0.770 (18)
N10B	0.1157 (15)	0.5806 (14)	0.2894 (18)	0.041 (4)	0.230 (18)
H10B	0.0858	0.5793	0.3513	0.049*	0.230 (18)
N11	0.3365 (3)	0.7611 (3)	0.4311 (2)	0.0450 (6)	
N12	0.2638 (3)	0.8493 (3)	0.3896 (2)	0.0490 (6)	
C13	0.2571 (5)	0.9392 (4)	0.4656 (4)	0.0641 (11)	
C14	0.3268 (6)	0.9078 (5)	0.5585 (4)	0.0698 (12)	
H14A	0.3399	0.9534	0.6251	0.084*	
C15	0.3743 (5)	0.7964 (4)	0.5356 (3)	0.0571 (9)	
C16	0.1801 (7)	1.0477 (6)	0.4450 (6)	0.0965 (19)	
H16A	0.2306	1.1016	0.3993	0.145*	
H16B	0.1883	1.1009	0.5102	0.145*	
H16C	0.0717	1.0105	0.4120	0.145*	
C17	0.4503 (7)	0.7208 (6)	0.6096 (3)	0.0769 (13)	
H17A	0.5170	0.6803	0.5766	0.115*	
H17B	0.3717	0.6535	0.6288	0.115*	
H17C	0.5115	0.7793	0.6716	0.115*	
C18	0.1923 (5)	0.8273 (4)	0.2784 (3)	0.0552 (9)	
H18A	0.2722	0.8288	0.2380	0.066*	
H18B	0.1442	0.8981	0.2613	0.066*	
C19	0.0713 (4)	0.6981 (4)	0.2488 (3)	0.0517 (8)	
H19A	0.0083	0.6857	0.3014	0.062*	0.770 (18)
H19B	0.0028	0.6979	0.1818	0.062*	0.770 (18)
H19C	0.0421	0.6799	0.1726	0.062*	0.230 (18)
H19D	−0.0209	0.7072	0.2734	0.062*	0.230 (18)
N20	0.5799 (4)	0.6337 (3)	0.4077 (3)	0.0558 (8)	
C21	0.7053 (4)	0.6233 (4)	0.4336 (3)	0.0517 (8)	
Pd2	0.5000	1.0000	1.0000	0.03984 (10)	
S22	0.27722 (13)	0.83780 (12)	0.91759 (10)	0.0736 (3)	
C23	0.2457 (4)	0.7188 (5)	0.9922 (3)	0.0567 (9)	
N24	0.2159 (6)	0.6323 (5)	1.0375 (3)	0.0849 (13)	
S25	0.45759 (12)	1.11365 (12)	0.85705 (8)	0.0604 (3)	
C26	0.2664 (5)	1.0806 (5)	0.8121 (3)	0.0617 (10)	
N27	0.1366 (6)	1.0626 (6)	0.7789 (4)	0.1036 (18)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.03258 (13)	0.04589 (15)	0.03637 (13)	0.01607 (10)	0.00092 (9)	−0.00186 (9)
S1	0.0489 (5)	0.1354 (11)	0.0481 (5)	0.0505 (6)	0.0069 (4)	0.0103 (6)
N1	0.0391 (13)	0.0488 (15)	0.0379 (12)	0.0161 (11)	0.0053 (10)	−0.0014 (11)

N2	0.0382 (13)	0.0543 (16)	0.0404 (13)	0.0122 (12)	0.0071 (11)	−0.0062 (11)
C3	0.0485 (18)	0.060 (2)	0.0478 (17)	0.0214 (16)	0.0059 (14)	−0.0103 (15)
C4	0.051 (2)	0.069 (2)	0.0476 (18)	0.0254 (18)	0.0139 (15)	−0.0029 (16)
C5	0.0432 (16)	0.0583 (19)	0.0394 (15)	0.0249 (15)	0.0095 (12)	0.0067 (13)
C6	0.069 (3)	0.077 (3)	0.085 (3)	0.005 (2)	0.021 (2)	−0.031 (3)
C7	0.053 (2)	0.071 (3)	0.066 (2)	0.0196 (19)	0.0231 (18)	0.0106 (19)
C8	0.0507 (19)	0.058 (2)	0.0485 (18)	0.0084 (16)	0.0190 (15)	−0.0036 (15)
C9	0.0334 (16)	0.070 (2)	0.062 (2)	0.0129 (15)	0.0098 (15)	−0.0085 (18)
N10A	0.0321 (19)	0.059 (2)	0.038 (3)	0.0197 (16)	0.0053 (18)	0.0015 (17)
N10B	0.025 (5)	0.064 (8)	0.037 (9)	0.017 (5)	0.010 (5)	0.000 (6)
N11	0.0449 (14)	0.0451 (15)	0.0455 (14)	0.0178 (12)	0.0061 (11)	−0.0001 (11)
N12	0.0422 (14)	0.0464 (15)	0.0599 (17)	0.0171 (12)	0.0089 (12)	0.0043 (13)
C13	0.051 (2)	0.046 (2)	0.091 (3)	0.0135 (16)	0.012 (2)	−0.0113 (19)
C14	0.071 (3)	0.066 (3)	0.065 (2)	0.017 (2)	0.012 (2)	−0.021 (2)
C15	0.062 (2)	0.055 (2)	0.0474 (18)	0.0104 (17)	0.0080 (16)	−0.0063 (15)
C16	0.085 (4)	0.062 (3)	0.142 (5)	0.037 (3)	0.014 (4)	−0.015 (3)
C17	0.093 (4)	0.085 (3)	0.045 (2)	0.022 (3)	0.001 (2)	0.005 (2)
C18	0.0502 (19)	0.065 (2)	0.062 (2)	0.0296 (17)	0.0175 (16)	0.0199 (18)
C19	0.0364 (16)	0.075 (2)	0.0500 (18)	0.0282 (16)	0.0056 (13)	0.0091 (16)
N20	0.0388 (15)	0.0595 (19)	0.0648 (19)	0.0215 (13)	−0.0024 (13)	−0.0102 (15)
C21	0.0473 (19)	0.065 (2)	0.0425 (16)	0.0237 (16)	0.0014 (14)	−0.0029 (15)
Pd2	0.02961 (16)	0.0489 (2)	0.04031 (18)	0.01548 (13)	0.00172 (12)	0.00076 (14)
S22	0.0517 (6)	0.0667 (7)	0.0806 (7)	0.0003 (5)	−0.0215 (5)	0.0161 (5)
C23	0.0440 (18)	0.070 (2)	0.0495 (19)	0.0088 (17)	0.0082 (15)	−0.0040 (17)
N24	0.085 (3)	0.096 (3)	0.057 (2)	−0.007 (2)	0.015 (2)	0.016 (2)
S25	0.0460 (5)	0.0790 (7)	0.0549 (5)	0.0166 (4)	0.0031 (4)	0.0192 (5)
C26	0.056 (2)	0.081 (3)	0.051 (2)	0.032 (2)	0.0013 (17)	0.0122 (19)
N27	0.062 (3)	0.153 (5)	0.103 (4)	0.046 (3)	−0.001 (2)	0.044 (4)

Geometric parameters (Å, º)

Pd1—N20	1.984 (3)	N10B—H10B	0.9000
Pd1—N1	2.005 (3)	N11—C15	1.340 (5)
Pd1—N11	2.009 (3)	N11—N12	1.353 (4)
Pd1—N10A	2.022 (4)	N12—C13	1.335 (5)
Pd1—N10B	2.111 (12)	N12—C18	1.447 (5)
S1—C21	1.607 (4)	C13—C14	1.362 (7)
N1—C5	1.342 (4)	C13—C16	1.493 (7)
N1—N2	1.365 (4)	C14—C15	1.372 (6)
N2—C3	1.336 (4)	C14—H14A	0.9300
N2—C8	1.449 (4)	C15—C17	1.478 (6)
C3—C4	1.366 (6)	C16—H16A	0.9600
C3—C6	1.496 (6)	C16—H16B	0.9600
C4—C5	1.379 (5)	C16—H16C	0.9600
C4—H4A	0.9300	C17—H17A	0.9600
C5—C7	1.482 (5)	C17—H17B	0.9600
C6—H6A	0.9600	C17—H17C	0.9600
C6—H6B	0.9600	C18—C19	1.493 (6)

C6—H6C	0.9600	C18—H18A	0.9700
C7—H7A	0.9600	C18—H18B	0.9700
C7—H7B	0.9600	C19—H19A	0.9700
C7—H7C	0.9600	C19—H19B	0.9700
C8—C9	1.494 (6)	C19—H19C	0.9700
C8—H8A	0.9700	C19—H19D	0.9700
C8—H8B	0.9700	N20—C21	1.153 (5)
C9—N10B	1.373 (14)	Pd2—S22	2.3085 (12)
C9—N10A	1.474 (6)	Pd2—S22^{i}	2.3085 (12)
C9—H9A	0.9700	Pd2—S25	2.3227 (11)
C9—H9B	0.9700	Pd2—S25^{i}	2.3227 (11)
C9—H9C	0.9700	S22—C23	1.656 (5)
C9—H9D	0.9700	C23—N24	1.133 (6)
N10A—C19	1.483 (5)	S25—C26	1.654 (4)
N10A—H10A	0.9000	C26—N27	1.133 (6)
N10B—C19	1.498 (15)		

N20—Pd1—N1	91.68 (12)	C19—N10B—Pd1	111.8 (9)
N20—Pd1—N11	92.64 (12)	C9—N10B—H10B	103.3
N1—Pd1—N11	175.60 (11)	C19—N10B—H10B	103.3
N20—Pd1—N10A	172.5 (2)	Pd1—N10B—H10B	103.3
N1—Pd1—N10A	82.54 (18)	C15—N11—N12	106.7 (3)
N11—Pd1—N10A	93.08 (18)	C15—N11—Pd1	134.6 (3)
N20—Pd1—N10B	166.4 (7)	N12—N11—Pd1	118.6 (2)
N1—Pd1—N10B	94.8 (5)	C13—N12—N11	110.3 (3)
N11—Pd1—N10B	81.2 (5)	C13—N12—C18	129.9 (3)
C5—N1—N2	106.4 (3)	N11—N12—C18	119.4 (3)
C5—N1—Pd1	134.7 (3)	N12—C13—C14	107.0 (4)
N2—N1—Pd1	118.4 (2)	N12—C13—C16	123.0 (5)
C3—N2—N1	110.7 (3)	C14—C13—C16	129.9 (5)
C3—N2—C8	130.8 (3)	C13—C14—C15	107.3 (4)
N1—N2—C8	118.5 (3)	C13—C14—H14A	126.4
N2—C3—C4	106.7 (3)	C15—C14—H14A	126.4
N2—C3—C6	123.2 (4)	N11—C15—C14	108.7 (4)
C4—C3—C6	130.1 (3)	N11—C15—C17	123.2 (4)
C3—C4—C5	107.6 (3)	C14—C15—C17	128.1 (4)
C3—C4—H4A	126.2	C13—C16—H16A	109.5
C5—C4—H4A	126.2	C13—C16—H16B	109.5
N1—C5—C4	108.6 (3)	H16A—C16—H16B	109.5
N1—C5—C7	123.2 (3)	C13—C16—H16C	109.5
C4—C5—C7	128.2 (3)	H16A—C16—H16C	109.5
C3—C6—H6A	109.5	H16B—C16—H16C	109.5
C3—C6—H6B	109.5	C15—C17—H17A	109.5
H6A—C6—H6B	109.5	C15—C17—H17B	109.5
C3—C6—H6C	109.5	H17A—C17—H17B	109.5
H6A—C6—H6C	109.5	C15—C17—H17C	109.5
H6B—C6—H6C	109.5	H17A—C17—H17C	109.5
C5—C7—H7A	109.5	H17B—C17—H17C	109.5

C5—C7—H7B	109.5	N12—C18—C19	111.4 (3)
H7A—C7—H7B	109.5	N12—C18—H18A	109.4
C5—C7—H7C	109.5	C19—C18—H18A	109.4
H7A—C7—H7C	109.5	N12—C18—H18B	109.4
H7B—C7—H7C	109.5	C19—C18—H18B	109.4
N2—C8—C9	112.1 (3)	H18A—C18—H18B	108.0
N2—C8—H8A	109.2	N10A—C19—C18	110.4 (3)
C9—C8—H8A	109.2	C18—C19—N10B	116.8 (5)
N2—C8—H8B	109.2	N10A—C19—H19A	109.6
C9—C8—H8B	109.2	C18—C19—H19A	109.6
H8A—C8—H8B	107.9	N10A—C19—H19B	109.6
N10B—C9—C8	115.9 (6)	C18—C19—H19B	109.6
N10A—C9—C8	113.3 (3)	H19A—C19—H19B	108.1
N10A—C9—H9A	108.9	C18—C19—H19C	108.1
C8—C9—H9A	108.9	N10B—C19—H19C	108.1
N10A—C9—H9B	108.9	C18—C19—H19D	108.1
C8—C9—H9B	108.9	N10B—C19—H19D	108.1
H9A—C9—H9B	107.7	H19C—C19—H19D	107.3
N10B—C9—H9C	108.3	C21—N20—Pd1	164.8 (3)
C8—C9—H9C	108.3	N20—C21—S1	179.0 (4)
N10B—C9—H9D	108.3	S22—Pd2—S22^{i}	180.0
C8—C9—H9D	108.3	S22—Pd2—S25	87.77 (4)
H9C—C9—H9D	107.4	S22^{i}—Pd2—S25	92.23 (4)
C9—N10A—C19	112.4 (4)	S22—Pd2—S25^{i}	92.23 (4)
C9—N10A—Pd1	115.1 (3)	S22^{i}—Pd2—S25^{i}	87.77 (4)
C19—N10A—Pd1	117.4 (3)	S25—Pd2—S25^{i}	180.0
C9—N10A—H10A	103.2	C23—S22—Pd2	109.52 (14)
C19—N10A—H10A	103.2	N24—C23—S22	175.1 (4)
Pd1—N10A—H10A	103.2	C26—S25—Pd2	107.53 (16)
C9—N10B—C19	117.7 (11)	N27—C26—S25	176.9 (5)
C9—N10B—Pd1	115.0 (8)		

C5—N1—N2—C3	0.8 (4)	C15—N11—N12—C13	0.6 (4)
Pd1—N1—N2—C3	173.4 (2)	Pd1—N11—N12—C13	179.3 (3)
C5—N1—N2—C8	−178.9 (3)	C15—N11—N12—C18	−172.6 (3)
Pd1—N1—N2—C8	−6.4 (4)	Pd1—N11—N12—C18	6.1 (4)
N1—N2—C3—C4	−0.9 (4)	N11—N12—C13—C14	−0.1 (5)
C8—N2—C3—C4	178.8 (4)	C18—N12—C13—C14	172.2 (4)
N1—N2—C3—C6	178.5 (4)	N11—N12—C13—C16	−178.4 (4)
C8—N2—C3—C6	−1.7 (7)	C18—N12—C13—C16	−6.1 (7)
N2—C3—C4—C5	0.6 (4)	N12—C13—C14—C15	−0.4 (5)
C6—C3—C4—C5	−178.8 (5)	C16—C13—C14—C15	177.7 (5)
N2—N1—C5—C4	−0.4 (4)	N12—N11—C15—C14	−0.8 (5)
Pd1—N1—C5—C4	−171.2 (3)	Pd1—N11—C15—C14	−179.3 (3)
N2—N1—C5—C7	179.1 (3)	N12—N11—C15—C17	177.5 (4)
Pd1—N1—C5—C7	8.3 (5)	Pd1—N11—C15—C17	−1.0 (7)
C3—C4—C5—N1	−0.1 (4)	C13—C14—C15—N11	0.8 (5)
C3—C4—C5—C7	−179.6 (4)	C13—C14—C15—C17	−177.4 (5)

C3—N2—C8—C9	−115.1 (4)	C13—N12—C18—C19	−113.4 (4)
N1—N2—C8—C9	64.6 (4)	N11—N12—C18—C19	58.3 (4)
N2—C8—C9—N10B	−75.9 (12)	C9—N10A—C19—C18	166.9 (4)
N2—C8—C9—N10A	−42.8 (5)	Pd1—N10A—C19—C18	30.0 (6)
N10B—C9—N10A—C19	−63.7 (12)	C9—N10A—C19—N10B	58.3 (11)
C8—C9—N10A—C19	−165.4 (4)	Pd1—N10A—C19—N10B	−78.6 (10)
N10B—C9—N10A—Pd1	74.3 (11)	N12—C18—C19—N10A	−77.7 (5)
C8—C9—N10A—Pd1	−27.4 (6)	N12—C18—C19—N10B	−46.7 (11)
N10A—C9—N10B—C19	68.0 (18)	C9—N10B—C19—N10A	−72.5 (18)
C8—C9—N10B—C19	160.4 (10)	Pd1—N10B—C19—N10A	64.0 (11)
N10A—C9—N10B—Pd1	−67.2 (12)	C9—N10B—C19—C18	−156.5 (11)
C8—C9—N10B—Pd1	25.2 (17)	Pd1—N10B—C19—C18	−20.0 (15)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10*A*—H10*A*···N24^{ii}	0.90	2.01	2.889 (9)	166
N10*B*—H10*B*···S1^{iii}	0.90	2.71	3.52 (2)	151

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