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Unexpected formation and crystal structure of tetrakis(1*H*-pyrazole- κ N²)palladium(II) dichloride

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The title salt, [Pd(C₃H₄N₂)₄]Cl₂, was obtained unexpectedly by the reaction of palladium(II) dichloride with equimolar amounts of 1-chloro-1-nitro-2,2,2-tris(pyrazolyl)ethane in methanol solution. The Pd²⁺ cation is located on an inversion centre and has a square-planar coordination sphere defined by four N atoms of four neutral pyrazole ligands. The average Pd–N distance is 2.000 (2) Å. The two chloride anions are not coordinating to Pd²⁺. They are connected to the complex cations through N–H···Cl hydrogen bonds. In addition, C–H···Cl hydrogen bonds are observed, leading to a three-dimensional linkage of cations and anions.

1. Chemical context

Transition metal complexes containing pyrazole or substituted pyrazoles as ligands are of current interest due to their supramolecular arrangements (Lumme *et al.*, 1988; Takahashi *et al.*, 2006; Casarin *et al.*, 2007; Alsalme *et al.*, 2013). In the course of an investigation on the coordination chemistry of various azolyl-nitrochloroalkanes (Zapol'skii & Kaufmann, 2008), we have previously studied the reaction of copper(II) perchlorate hexahydrate with equimolar amounts of 1-chloro-1-nitro-2,2,2-tris(pyrazolyl)ethane, Cl(NO₂)CH–C(C₃H₃N₂)₃ (Fig. 1) in methanol solution (Edlmann *et al.*, 2008). Quite unexpectedly, a complete degradation of the starting material took place during the course of this reaction. As a result, the dark-blue compound *trans*-bis(perchlorato)-tetrakis(pyrazole)copper(II), [Cu(C₃H₄N₂)₄(ClO₄)₂], was isolated. The formation of free pyrazole could only be explained by a solvolytic degradation of the starting material. This degradation must have taken place to a large extent as the isolated yield was 64% (Edlmann *et al.*, 2008).

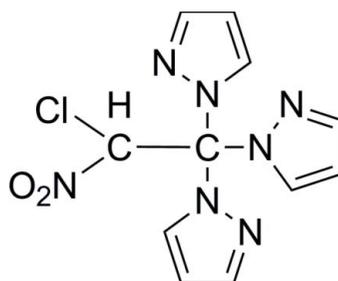
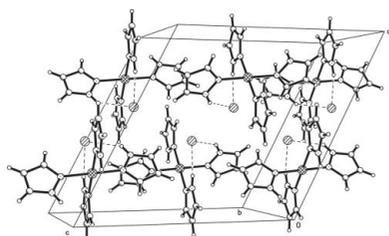
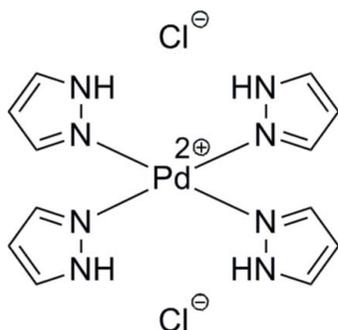


Figure 1
Structure diagram of the starting material 1-chloro-1-nitro-2,2,2-tris(pyrazolyl)ethane.

We have now carried out a closely related reaction of 1-chloro-1-nitro-2,2,2-tris(pyrazolyl)ethane with palladium(II) dichloride in methanol solution. Structure determination of the yellow reaction product using X-ray analysis surprisingly again revealed the presence of a homoleptic pyrazole complex. The structure of the resultant title compound, $[\text{Pd}(\text{C}_3\text{H}_4\text{N}_2)_4]\text{Cl}_2$ is presented here. An elemental analysis of the title compound was also in very good agreement with the composition $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{PdN}_8$. In this case, too, the yield was fairly high (56%), indicating a far-reaching decomposition of the starting material. Apparently, the ligand degradation of azolyl-nitrochloroalkanes in the presence of transition metal salts is a more common phenomenon than originally anticipated.



2. Structural commentary

In the crystal structure of the title compound, the Pd^{2+} ion is located on an inversion centre and is bonded to four neutral pyrazole ligands within a square-planar coordination environment (Fig. 2). The average $\text{Pd}-\text{N}$ distance in the $[\text{Pd}(\text{pyrazole})_4]^{2+}$ cation is 2.000 (2) Å. This is exactly the same value as found for the $\text{Cu}-\text{N}$ distance in *trans*-bis(perchlorato)-tetrakis(pyrazole)copper(II) [2.000 (1) Å; Edlmann *et al.*, 2008]. The two chloride anions are not coordinating to the Pd^{2+} cation. This is in marked contrast to the analogous copper(II) complex $[\text{Cu}(\text{pyrazole})_4\text{Cl}_2]$ (Xing *et al.*, 2006), in which the Cu^{2+} ion is six-coordinated by four N atoms from four pyrazole ligands and two Cl^- ions. The same octahedral coordination has also been reported for the manganese(II) analog $[\text{Mn}(\text{pyrazole})_4\text{Cl}_2]$ (Lumme, 1985).

3. Supramolecular features

In the title compound, the crystal packing is stabilized by two $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds (Table 1) between the complex

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}2\text{N}\cdots\text{Cl}$	0.87 (2)	2.50 (3)	3.254 (3)	145 (3)
$\text{N}4-\text{H}4\text{N}\cdots\text{Cl}$	0.88 (2)	2.33 (2)	3.147 (3)	156 (4)
$\text{C}1-\text{H}1\cdots\text{Cl}^{\text{i}}$	0.95	2.75	3.625 (4)	153
$\text{C}4-\text{H}4\cdots\text{Cl}^{\text{ii}}$	0.95	2.73	3.656 (4)	164

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

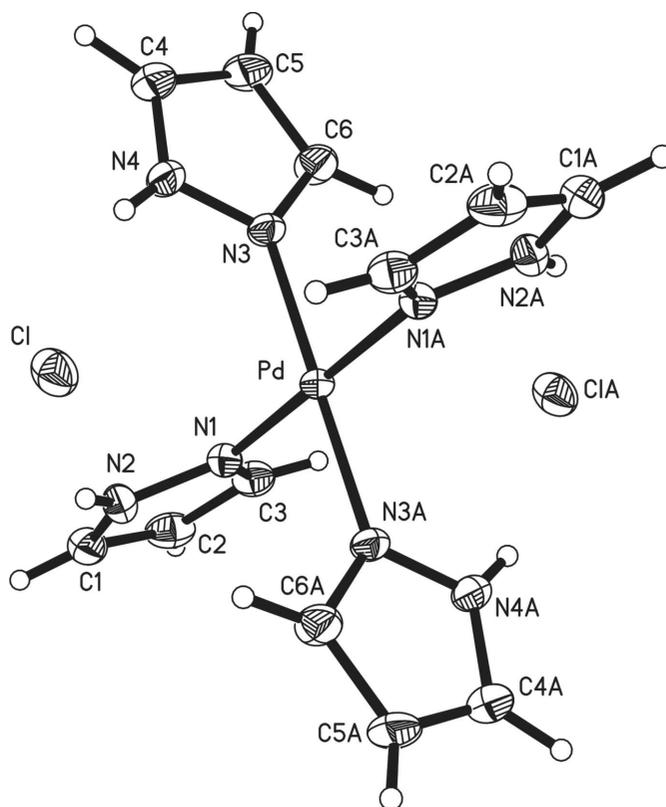


Figure 2

The coordination sphere of Pd^{2+} and the Cl^- counter-ions in the title compound. Displacement ellipsoids represent the 50% probability level. [Symmetry code (A): $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]

cations and the Cl^- counter-anions (Fig. 3). Weaker $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds are also observed, stabilizing a three-dimensional network. The crystal structures of the formally analogous complexes $[\text{M}(\text{pyrazole})_4\text{Cl}_2]$ show related features. In the structures with $M = \text{Mn}$ and Cu and an octahedral coordination of the metal cation, the crystal structures likewise exhibit $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds which, in combination, yield three-dimensional networks.

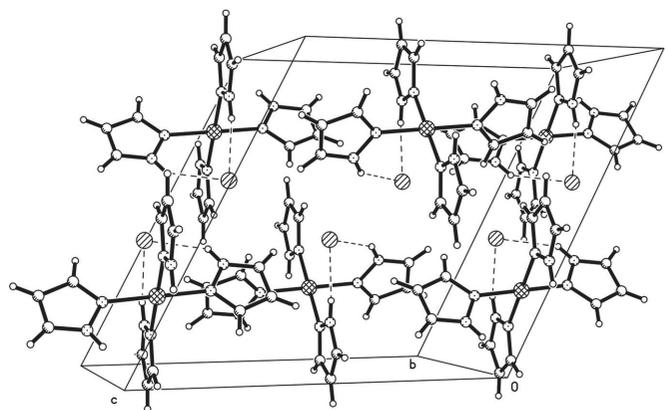


Figure 3

A packing diagram of the title compound. Dashed lines indicate $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen-bonding interactions.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Pd(C ₁₂ H ₁₆ N ₈)]Cl ₂
<i>M_r</i>	449.63
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.797 (3), 9.6560 (19), 14.174 (3)
β (°)	117.80 (3)
<i>V</i> (Å ³)	1670.4 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.44
Crystal size (mm)	0.40 × 0.40 × 0.20
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Multi-scan (Blessing, 1995)
<i>T</i> _{min} , <i>T</i> _{max}	0.562, 0.750
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7700, 2253, 2030
<i>R</i> _{int}	0.054
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.686
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.094, 1.12
No. of reflections	2253
No. of parameters	112
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.79, -1.73

Computer programs: *X-AREA* and *X-RED32* (Stoe, 2008), *SHELXS97*, *SHELXL97* and *XP* (Sheldrick, 2008).

4. Relation with other compounds

Various closely related homoleptic metal–pyrazole complexes are known from the literature (Misra *et al.*, 1998; Reedijk, 1969; Sastry *et al.*, 1986). Analogous complexes of composition [*M*(pyrazole)₄Cl₂] have previously been reported for *M* = Mn, Fe, Co, Ni, and Cu (Daugherty & Swisher, 1968; Bagley *et al.*, 1970; Nicholls & Warburton, 1970, 1971; Lumme, 1985; Sun *et al.*, 2001; Xing *et al.*, 2006). Generally, these compounds are prepared in a more straightforward manner by treatment of the transition metal dichlorides with four equivalents of pyrazole in suitable solvents such as methanol. While the analogous nickel(II) complex has been studied frequently (Daugherty & Swisher, 1968; Nicholls & Warburton, 1970), to the best of our knowledge neither the title compound nor the platinum homologue [Pt(pyrazole)₄]Cl₂ have ever been reported.

5. Synthesis and crystallization

Solid palladium(II) dichloride (0.28 g, 1.6 mmol) was added to a solution of 1-chloro-1-nitro-2,2,2-tris(pyrazolyl)ethane (0.50 g, 1.6 mmol) in methanol (100 ml). After stirring for 48 h at room temperature, a small amount of unreacted PdCl₂ was removed by filtration. Crystallization from the clear filtrate at

276–279 K for 14 d afforded bright-yellow crystals of the title compound. Yield: 0.4 g (56%). Analysis calculated for C₁₂H₁₆Cl₂PdN₈: C 32.06%; H 3.59%; N 24.92%; Cl 15.77%; found: C 31.55%; H 3.38%; N 25.13%; Cl 15.25%. IR (KBr): 3090*vs*, 2977*vs*, 2371*m*, 1798*w*, 1772*w*, 1632*w*, 1518*m*, 1487*m*, 1472*s*, 1401*m*, 1367*s*, 1312*m*, 1264*m*, 1251*m*, 1209*w*, 1181*vs*, 1169*m*, 1139*s*, 1123*s*, 1078*vs*, 1052*vs*, 983*m*, 956*m*, 913*m*, 908*m*, 899*m*, 886*m*, 878*m*, 779*vs*, 739*s*, 615*s*, 606*s* cm⁻¹.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms attached to carbon were included using a riding model, with C–H = 0.95 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C). The hydrogen atoms attached to nitrogen were refined with a restrained distance N–H = 0.88 (2) Å and with *U*_{iso}(H) = 1.2*U*_{eq}(N).

Acknowledgements

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Unexpected formation and crystal structure of tetrakis(1*H*-pyrazole- κ N²)palladium(II) dichloride

Thomas Wagner, Nena Christiansen, Cristian G. Hrib, Dieter E. Kaufmann and Frank T. Edelmann

Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-RED32* (Stoe, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Tetrakis(1*H*-pyrazole- κ N²)palladium(II) dichloride

Crystal data

[Pd(C₁₂H₁₆N₈)]Cl₂

M_r = 449.63

Monoclinic, *C2/c*

Hall symbol: -C 2yc

a = 13.797 (3) Å

b = 9.6560 (19) Å

c = 14.174 (3) Å

β = 117.80 (3)°

V = 1670.4 (6) Å³

Z = 4

F(000) = 896

449.6

D_x = 1.788 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 15423 reflections

θ = 2.7–29.6°

μ = 1.44 mm⁻¹

T = 150 K

Prism, yellow

0.40 × 0.40 × 0.20 mm

Data collection

Stoe IPDS-2T

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

ω -scans

Absorption correction: multi-scan

(Blessing, 1995)

T_{min} = 0.562, *T_{max}* = 0.750

7700 measured reflections

2253 independent reflections

2030 reflections with *I* > 2 σ (*I*)

R_{int} = 0.054

θ_{\max} = 29.2°, θ_{\min} = 2.7°

h = -18→18

k = -13→13

l = -17→19

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.039

wR(*F*²) = 0.094

S = 1.12

2253 reflections

112 parameters

2 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 4.2172P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.79 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.73 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd	0.2500	0.2500	0.0000	0.01539 (11)
Cl	0.09118 (6)	-0.02409 (9)	-0.06859 (6)	0.02881 (17)
N1	0.2363 (2)	0.2373 (2)	0.1343 (2)	0.0190 (5)
N2	0.1606 (2)	0.1607 (3)	0.1453 (2)	0.0225 (5)
H2N	0.116 (3)	0.109 (4)	0.093 (2)	0.027*
N3	0.36913 (18)	0.1080 (3)	0.05645 (18)	0.0189 (4)
N4	0.3490 (2)	-0.0279 (3)	0.0486 (2)	0.0234 (5)
H4N	0.2803 (18)	-0.054 (5)	0.015 (2)	0.028*
C1	0.1706 (3)	0.1749 (3)	0.2435 (2)	0.0269 (6)
H1	0.1268	0.1311	0.2702	0.032*
C2	0.2560 (3)	0.2644 (3)	0.2984 (3)	0.0284 (7)
H2	0.2832	0.2944	0.3702	0.034*
C3	0.2943 (2)	0.3019 (3)	0.2264 (2)	0.0234 (5)
H3	0.3529	0.3642	0.2412	0.028*
C4	0.4419 (3)	-0.0999 (4)	0.0945 (3)	0.0302 (6)
H4	0.4484	-0.1979	0.0986	0.036*
C5	0.5262 (3)	-0.0071 (4)	0.1346 (3)	0.0316 (7)
H5	0.6023	-0.0271	0.1721	0.038*
C6	0.4771 (2)	0.1239 (3)	0.1089 (2)	0.0267 (6)
H6	0.5148	0.2099	0.1263	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd	0.01373 (15)	0.01505 (16)	0.01795 (15)	0.00207 (9)	0.00784 (11)	0.00096 (9)
Cl	0.0255 (3)	0.0302 (4)	0.0336 (3)	-0.0083 (3)	0.0162 (3)	-0.0104 (3)
N1	0.0183 (10)	0.0186 (12)	0.0216 (10)	0.0018 (8)	0.0105 (9)	0.0021 (8)
N2	0.0227 (11)	0.0210 (12)	0.0275 (11)	-0.0027 (9)	0.0149 (9)	-0.0005 (9)
N3	0.0160 (10)	0.0175 (11)	0.0222 (10)	0.0035 (8)	0.0080 (8)	0.0017 (8)
N4	0.0199 (10)	0.0173 (11)	0.0329 (12)	0.0025 (9)	0.0122 (9)	0.0016 (10)
C1	0.0286 (14)	0.0259 (16)	0.0322 (14)	0.0049 (12)	0.0192 (12)	0.0057 (12)

C2	0.0299 (15)	0.0337 (18)	0.0213 (13)	0.0118 (12)	0.0117 (12)	0.0023 (11)
C3	0.0202 (12)	0.0248 (14)	0.0218 (12)	0.0037 (11)	0.0069 (10)	-0.0016 (11)
C4	0.0303 (14)	0.0252 (16)	0.0391 (16)	0.0093 (12)	0.0195 (13)	0.0067 (13)
C5	0.0216 (13)	0.0325 (18)	0.0392 (16)	0.0134 (12)	0.0128 (12)	0.0094 (13)
C6	0.0158 (11)	0.0238 (15)	0.0342 (15)	0.0005 (10)	0.0063 (11)	-0.0009 (12)

Geometric parameters (Å, °)

Pd—N3	1.999 (2)	N4—H4N	0.875 (19)
Pd—N3 ⁱ	1.999 (2)	C1—C2	1.372 (5)
Pd—N1 ⁱ	2.002 (3)	C1—H1	0.9500
Pd—N1	2.002 (3)	C2—C3	1.399 (4)
N1—C3	1.327 (4)	C2—H2	0.9500
N1—N2	1.347 (3)	C3—H3	0.9500
N2—C1	1.340 (4)	C4—C5	1.365 (5)
N2—H2N	0.869 (18)	C4—H4	0.9500
N3—C6	1.327 (4)	C5—C6	1.400 (4)
N3—N4	1.336 (3)	C5—H5	0.9500
N4—C4	1.332 (4)	C6—H6	0.9500
N3—Pd—N3 ⁱ	180.00 (11)	N2—C1—C2	107.4 (3)
N3—Pd—N1 ⁱ	89.89 (10)	N2—C1—H1	126.3
N3 ⁱ —Pd—N1 ⁱ	90.11 (10)	C2—C1—H1	126.3
N3—Pd—N1	90.11 (10)	C1—C2—C3	105.4 (3)
N3 ⁱ —Pd—N1	89.89 (10)	C1—C2—H2	127.3
N1 ⁱ —Pd—N1	180.0 (2)	C3—C2—H2	127.3
C3—N1—N2	106.7 (2)	N1—C3—C2	109.7 (3)
C3—N1—Pd	128.7 (2)	N1—C3—H3	125.2
N2—N1—Pd	124.51 (19)	C2—C3—H3	125.2
C1—N2—N1	110.8 (3)	N4—C4—C5	107.4 (3)
C1—N2—H2N	130 (3)	N4—C4—H4	126.3
N1—N2—H2N	119 (3)	C5—C4—H4	126.3
C6—N3—N4	107.2 (2)	C4—C5—C6	105.7 (3)
C6—N3—Pd	130.1 (2)	C4—C5—H5	127.2
N4—N3—Pd	122.71 (18)	C6—C5—H5	127.2
C4—N4—N3	110.9 (3)	N3—C6—C5	108.8 (3)
C4—N4—H4N	132 (3)	N3—C6—H6	125.6
N3—N4—H4N	117 (3)	C5—C6—H6	125.6
N3—Pd—N1—C3	84.2 (3)	N1—Pd—N3—N4	83.8 (2)
N3 ⁱ —Pd—N1—C3	-95.8 (3)	C6—N3—N4—C4	-0.4 (3)
N1 ⁱ —Pd—N1—C3	-138 (100)	Pd—N3—N4—C4	-178.5 (2)
N3—Pd—N1—N2	-97.9 (2)	N1—N2—C1—C2	0.1 (3)
N3 ⁱ —Pd—N1—N2	82.1 (2)	N2—C1—C2—C3	0.4 (3)
N1 ⁱ —Pd—N1—N2	40 (100)	N2—N1—C3—C2	0.9 (3)
C3—N1—N2—C1	-0.6 (3)	Pd—N1—C3—C2	179.0 (2)
Pd—N1—N2—C1	-178.9 (2)	C1—C2—C3—N1	-0.8 (3)
N3 ⁱ —Pd—N3—C6	127 (100)	N3—N4—C4—C5	0.4 (4)

N1 ⁱ —Pd—N3—C6	86.1 (3)	N4—C4—C5—C6	-0.3 (4)
N1—Pd—N3—C6	-93.9 (3)	N4—N3—C6—C5	0.2 (4)
N3 ⁱ —Pd—N3—N4	-55 (100)	Pd—N3—C6—C5	178.1 (2)
N1 ⁱ —Pd—N3—N4	-96.2 (2)	C4—C5—C6—N3	0.1 (4)

Symmetry code: (i) $-x+1/2, -y+1/2, -z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2N...Cl	0.87 (2)	2.50 (3)	3.254 (3)	145 (3)
N4—H4N...Cl	0.88 (2)	2.33 (2)	3.147 (3)	156 (4)
C1—H1...Cl ⁱⁱ	0.95	2.75	3.625 (4)	153
C4—H4...Cl ⁱⁱⁱ	0.95	2.73	3.656 (4)	164

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