

Structure of *cis*-Dichlorobis(cyclohexyl isocyanide)palladium(II)

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(Received 22 December 1980; accepted 7 April 1981)

Abstract. [Pd(C₇H₁₁N)₂Cl₂], C₁₄H₂₂Cl₂N₂Pd, $M_r = 395.7$, monoclinic, $P2_1/c$, $a = 12.299$ (4), $b = 9.604$ (3), $c = 17.383$ (5) Å, $\beta = 127.59$ (2)°, $V = 1627.0$ Å³, $D_m = 1.605$, $D_x = 1.615$ Mg m⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 1.42$ mm⁻¹. The structure was refined to $R = 0.038$ for 2308 reflections. The Pd atom has a square-planar coordination with the two Cl atoms and the two isocyanide groups respectively *cis*. One isocyanide group occupies the axial position with respect to the cyclohexane ring of the chair form while the other occupies the equatorial position.

Introduction. In the course of a study of palladium complexes, new bis(cyclohexyl isocyanide)palladium halides, PdX₂(C₆H₁₁NC)₂ and PdX₂(C₆H₁₁NC)₂(C₆H₆) (X=Cl, Br) were isolated and characterized by spectroscopic methods but no detailed configuration could be assigned from the spectra (Kajimoto, Kitano, Takahashi & Tsuji, 1981). Therefore one of the complexes, PdCl₂(C₆H₁₁NC)₂, was subjected to a crystal-structure investigation to determine a precise configuration.

Single crystals of the complex were grown as yellow plates by recrystallization from a hot toluene solution. Preliminary diffraction analysis showed that the crystal belongs to the monoclinic system with one molecule in the asymmetric unit. The cell dimensions were refined by a least-squares technique for 20 reflections measured on a Rigaku AFC-6A automated four-circle diffractometer. The density was measured by flotation in a toluene–methyl iodide mixture.

A well shaped crystal of 0.2 × 0.3 × 0.1 mm was selected for the data collection. The intensities of 3280 reflections with $2\theta \leq 55^\circ$ were measured with the 2θ - ω scan technique, with a speed of $8^\circ(\omega)$ min⁻¹ and range of $(1.849 + 0.5 \tan \theta)^\circ(\omega)$ with graphite-monochromated Mo $K\alpha$ radiation. No significant changes were observed in the intensities of standard reflections measured periodically throughout the data collection. The measured intensities were corrected for usual Lorentz–polarization factors, but no absorption correction was applied. 2308 reflections with $I \geq 2\sigma(I)$ were used in the refinement of the structure.

Table 1. Positional ($\times 10^4$; for Pd $\times 10^5$) and thermal parameters for the non-H atoms

The equivalent isotropic temperature factor is as defined by Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Pd	33489 (4)	58279 (4)	43326 (3)	2.9 (0.1)
Cl(1)	3316 (2)	5461 (2)	3011 (1)	4.3 (0.6)
Cl(2)	4234 (2)	8039 (2)	4589 (1)	4.1 (0.5)
N(1)	3257 (5)	6195 (5)	6049 (3)	3.3 (2)
N(2)	2307 (5)	2859 (5)	4141 (3)	3.3 (2)
C(1)	3296 (6)	6089 (6)	5412 (4)	3.5 (2)
C(2)	3267 (7)	6294 (6)	6884 (4)	3.6 (2)
C(3)	1848 (6)	6021 (6)	6580 (5)	3.8 (2)
C(4)	1431 (6)	4537 (8)	6308 (5)	4.4 (3)
C(5)	2459 (8)	3567 (7)	7108 (5)	5.1 (3)
C(6)	3869 (6)	3777 (7)	7370 (4)	4.3 (3)
C(7)	4336 (6)	5269 (7)	7654 (4)	4.2 (2)
C(8)	2667 (6)	3956 (6)	4182 (4)	3.5 (2)
C(9)	2067 (5)	1397 (5)	4204 (4)	2.9 (2)
C(10)	667 (5)	938 (7)	3294 (4)	3.4 (2)
C(11)	496 (6)	-611 (6)	3403 (4)	4.3 (2)
C(12)	653 (7)	-907 (6)	4327 (5)	4.2 (2)
C(13)	1973 (6)	-351 (7)	5212 (4)	3.9 (2)
C(14)	2173 (6)	1182 (6)	5111 (4)	3.2 (2)

The structure was solved by the usual Patterson and Fourier methods and refined by the block-diagonal least-squares procedure with anisotropic temperature factors for all the non-H atoms. H atoms were refined with individual isotropic temperature factors in the final stage of the refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the final R index ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.038 for the observed reflections. All scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Most of the calculations were carried out on a PANAFACOM 1300 computer with the programs of the Rigaku crystallographic package RASA II. Tables 1 and 2 show the final atomic parameters and Table 3 gives the bond lengths and bond angles.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36072 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional ($\times 10^3$) and isotropic thermal ($\times 10$) parameters for the H atoms

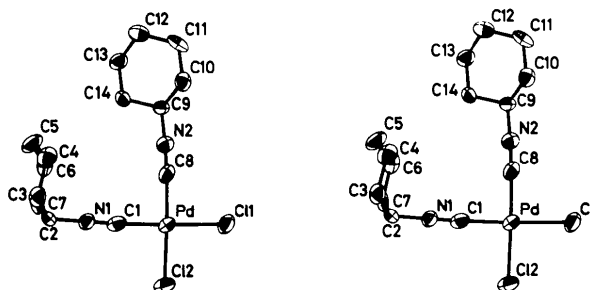
	x	y	z	B (\AA^2)
H(C2)	352 (6)	700 (7)	712 (4)	25 (15)
H1(C3)	120 (6)	678 (7)	606 (4)	25 (15)
H2(C3)	185 (6)	626 (6)	713 (4)	19 (13)
H1(C4)	138 (6)	416 (7)	575 (4)	31 (15)
H2(C4)	69 (6)	437 (7)	620 (4)	34 (16)
H1(C5)	271 (6)	370 (6)	770 (4)	21 (14)
H2(C5)	227 (6)	272 (6)	699 (4)	26 (14)
H1(C6)	368 (5)	361 (6)	679 (4)	9 (11)
H2(C6)	449 (6)	326 (6)	788 (4)	23 (14)
H1(C7)	442 (6)	532 (7)	816 (4)	20 (14)
H2(C7)	515 (6)	556 (6)	780 (4)	21 (14)
H(C9)	287 (6)	88 (7)	422 (4)	26 (14)
H1(C10)	63 (5)	108 (6)	275 (4)	17 (13)
H2(C10)	1 (6)	125 (6)	317 (4)	22 (13)
H1(C11)	-26 (6)	-93 (6)	294 (4)	21 (14)
H2(C11)	126 (6)	-110 (7)	339 (4)	25 (14)
H1(C12)	81 (6)	-158 (6)	446 (4)	24 (14)
H2(C12)	0 (6)	-41 (7)	429 (4)	21 (14)
H1(C13)	271 (6)	-96 (6)	534 (4)	21 (13)
H2(C13)	206 (6)	-38 (6)	579 (4)	22 (14)
H1(C14)	283 (6)	146 (6)	568 (4)	19 (13)
H2(C14)	153 (6)	161 (7)	508 (4)	26 (15)

Table 3. Bond lengths (\AA) and angles ($^\circ$)

Pd—Cl(1)	2.300 (2)	C(4)—C(5)	1.502 (13)
Pd—Cl(2)	2.302 (2)	C(5)—C(6)	1.513 (12)
Pd—C(1)	1.932 (7)	C(6)—C(7)	1.510 (11)
Pd—C(8)	1.933 (7)	C(2)—C(7)	1.530 (11)
N(1)—C(1)	1.142 (9)	C(9)—C(10)	1.529 (9)
N(2)—C(8)	1.127 (9)	C(10)—C(11)	1.532 (10)
N(1)—C(2)	1.448 (10)	C(11)—C(12)	1.522 (11)
N(2)—C(9)	1.453 (9)	C(12)—C(13)	1.497 (11)
C(2)—C(3)	1.506 (11)	C(13)—C(14)	1.521 (11)
C(3)—C(4)	1.491 (11)	C(9)—C(14)	1.515 (10)
Cl(1)—Pd—C(1)	177.3 (2)	N(2)—C(9)—C(14)	108.5 (5)
Cl(2)—Pd—C(8)	177.3 (2)	C(3)—C(2)—C(7)	112.8 (7)
Cl(1)—Pd—Cl(2)	93.1 (1)	C(2)—C(3)—C(4)	112.3 (7)
C(1)—Pd—C(8)	89.0 (3)	C(3)—C(4)—C(5)	111.5 (7)
Cl(1)—Pd—C(8)	88.9 (2)	C(4)—C(5)—C(6)	111.0 (7)
Cl(2)—Pd—C(1)	89.1 (2)	C(5)—C(6)—C(7)	111.2 (7)
Pd—C(1)—N(1)	177.6 (7)	C(2)—C(7)—C(6)	111.8 (6)
C(1)—N(1)—C(2)	177.3 (7)	C(10)—C(9)—C(14)	111.4 (6)
N(1)—C(2)—C(3)	109.7 (6)	C(9)—C(10)—C(11)	107.8 (6)
N(1)—C(2)—C(7)	108.2 (6)	C(10)—C(11)—C(12)	111.9 (6)
Pd—C(8)—N(2)	176.7 (6)	C(11)—C(12)—C(13)	112.2 (7)
C(8)—N(2)—C(9)	171.1 (7)	C(12)—C(13)—C(14)	112.2 (6)
N(2)—C(9)—C(10)	110.7 (6)	C(9)—C(14)—C(13)	109.5 (6)

Discussion. Fig. 1 shows a stereoscopic drawing of the complex with the numbering scheme. The molecular geometry is shown in Table 4.

The centered Pd atom has a *cis* square-planar coordination with two Cl atoms and two cyclohexyl isocyanide groups. However, there is a slight distortion since the Cl(1)—Pd—Cl(2) angle has opened some 3° from the theoretical value of 90° . One cyclohexyl isocyanide ligand forms an almost linear Pd—C(1)—N(1)—C(2) chain and the C(1), N(1) and C(2) atoms lie on the coordination plane, whereas the other

Fig. 1. Stereoscopic drawing of $\text{PdCl}_2(\text{C}_6\text{H}_{11}\text{NC})_2$. The ellipsoid encloses the region in which the center of the atom is found with 50% probability.Table 4. Least-squares plane defined by atomic positions and deviations of the atoms (\AA) from this plane

X , Y and Z are coordinates referred to the orthogonal axes expressed by $X = ax + cz \cos \beta$, $Y = by$ and $Z = cz \cos \beta$.

Plane: Cl(1), Cl(2), C(1) and C(8)

$$0.7088X - 0.3686Y + 0.6014Z = 1.1931$$

Cl(1)	-0.004 (8)	Cl(2)	0.004 (8)	C(1)	-0.059 (11)
C(8)	0.053 (11)	Pd*	-0.004 (8)	N(1)*	-0.082 (10)
N(2)*	0.124 (10)	C(2)*	-0.044 (11)	C(9)*	0.437 (10)

* Atoms not included in the calculation of the plane.

isocyanide ligand shows slight distortion from linearity. The C(8)—N(2)—C(9) angle is 171.1° and the N(2) and C(9) atoms deviate 0.124 and 0.437 \AA from the coordination plane. The average Pd—Cl bond length of 2.301 (2) \AA is significantly shorter than the values of 2.387 \AA found in $\text{PdCl}_2[(\text{CH}_3)_2\text{C}_2\text{N}_4\text{H}_4]$ (Butler & Enemark, 1971) and 2.362 \AA in $\text{PdCl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$ (Martin & Jacobson, 1971) but in good agreement with those found in $\text{PdCl}_2\text{Se}_2\text{C}_8\text{H}_{18}$ (2.32 \AA) (Whitfield, 1970), $\text{PdCl}_2\text{C}_{10}\text{H}_{26}\text{N}_2\text{O}_{13}$ (2.30 \AA) (Robinson & Kennard, 1970) and $\text{PdCl}_2\text{C}_7\text{H}_8$ (2.31 \AA) (Baenziger, Doyle & Carpenter, 1961). The average Pd—C bond length of 1.933 (7) \AA is a little shorter than the values of 1.963 and 2.049 \AA in $[\text{Pd}_2(\text{CNCH}_3)_6](\text{PF}_6)_2 \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$ (Goldberg & Eisenberg, 1976) but agrees well with the value of 1.948 \AA in $\text{PdCl}_2[(\text{CH}_3)_2\text{C}_2\text{N}_2\text{H}_4]$ (Butler & Enemark, 1971). The mean bond lengths within the isocyanide ligands of 1.135 (9) \AA for $\text{C}\equiv\text{N}$ and 1.451 (10) \AA for N—C are similar to the values of 1.139 and 1.449 \AA in $[\text{Pd}_2(\text{CNCH}_3)_6](\text{PF}_6)_2 \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$ (Goldberg & Eisenberg, 1976) and 1.17 and 1.42 \AA in $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ (Day, Day, Kristoff, Hirsekorn & Muetterties, 1975).

The main feature of the complex is the conformation of the two cyclohexyl isocyanides. One isocyanide group C(1)—N(1) occupies the axial position with respect to the cyclohexane ring and the dihedral angle between the plane through C(3), C(4), C(6) and C(7) and the metal coordination plane is $92.8(2)^\circ$. The

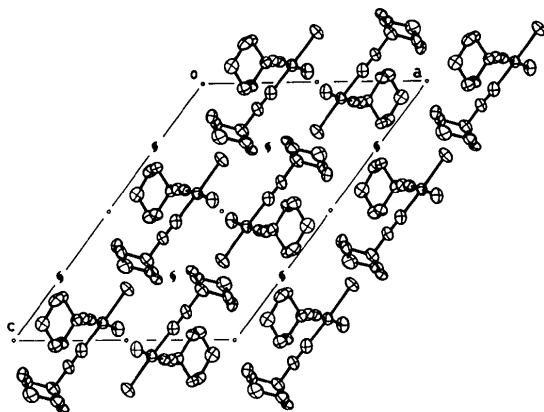


Fig. 2. Projection of the crystal structure of $\text{PdCl}_2(\text{C}_6\text{H}_{11}\text{NC})_2$ along b .

other isocyanide group C(8)—N(2), on the other hand, adopts the equatorial position and the dihedral angle between the plane through C(10), C(11), C(13) and C(14) and the coordination plane is $36.5(2)^\circ$. Each cyclohexane ring is in the chair conformation. The ring bond lengths and angles are normal.

The molecular arrangement in the crystal viewed along b is illustrated in Fig. 2. The crystal is built up of discrete molecules of $\text{PdCl}_2(\text{C}_6\text{H}_{11}\text{NC})_2$, with the adjacent molecules held together by van der Waals forces. There are no abnormally short distances.

Acta Cryst. (1981). **B37**, 1921–1923

5-Iodo-2'-deoxycytidine

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(Received 28 January 1981; accepted 30 March 1981)

Abstract. $\text{C}_9\text{H}_{12}\text{IN}_3\text{O}_4$, monoclinic, $P2_1$, $a = 12.743(10)$, $b = 4.750(5)$, $c = 9.963(8)$ Å, $\beta = 97.70(10)^\circ$, $U = 597.6$ Å³, $Z = 2$, $D_x = 1.962$ Mg m⁻³. Diffractometer data, Mo $K\alpha$ radiation. Final $R = 0.061$ for 1313 unique reflexions. The molecule is in the *anti* conformation and the C(5')—O(5') bond is in the *gauche-trans* conformation. The sugar pucker is C(3')-*exo*—C(4')-*endo* relative to the mean plane of the ring.

Introduction. Crystals were obtained by slow evaporation of an aqueous solution of 5-iodo-2'-deoxycytidine (Fig. 1). The intensities of 1712 unique reflexions in the range up to $2\theta = 55^\circ$ were measured on a Stoe two-circle diffractometer with graphite-

The authors are indebted to Dr Tsunesuke Kajimoto of Basic Research Laboratories of Toray Industries Inc., for supplying the complex. The authors' thanks are also due to Professor Tamaichi Ashida of Nagoya University and Professor Yukio Kinoshita of Shiga Prefectural Junior College for their useful discussions.

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monochromated Mo $K\alpha$ radiation. Of these, 1313 with $F_o > 5\sigma(F_o)$ were used for the structure analysis. Data were collected from a crystal mounted about b . Lorentz, polarization and absorption corrections were applied.

The structure was determined by the heavy-atom method. Full-matrix least-squares refinement of positional and isotropic thermal parameters and inter-layer scale factors was made, and then the H-atom positions were calculated on the basis of the chemical structure and H-bonding scheme suggested by the interatomic distances and angles. With fixed H-atom coordinates and temperature factors, refinement of the positional parameters of the non-H atoms, the anisotropic thermal parameters of the I atom and the isotropic thermal