Acta Cryst. (1976). B**32**, 2472

The Crystal Structure of Bis(histamino)palladium Dichloride, $(N_3C_5H_9)_2PdCl_2$

By Françoise Dahan

Laboratoire de Cristallochimie, CNRS (E.R. n° 63), *Tour* 44, 11 *Quai Saint-Bernard*, 75005 *Paris, France*

(*Received* 26 *January* 1976; *accepted* 28 *February* 1976)

The structure of bis(histamino)palladium dichloride, $(N_3C_5H_9)_2PdCl_2$, has been determined by the heavy-atom method and refined by full-matrix least squares to a final R of 0·032 for 1135 independent non-zero reflexions. The crystals are monoclinic, space group $P2_1/c$, with $a=9{\cdot}124$ (3), $b=9{\cdot}687$ (3), $c=9{\cdot}191$ (3) Å, $\beta=109{\cdot}26°$, $Z=2$. The Pd atom is in a square-planar arrangement. The structure is characterized by hydrogen bonds between the Cl ion and N atoms, one from the side chain and one from the imidazole ring.

Introduction

Many complexes of histamine with metals of the first transition series have been reported. Bis(histamino)palladium dichloride is one of the first complexes of histamine with a metal of the second transition series to have been crystallized (Valladas-Dubois & Cain, 1973; Cain & Valladas-Dubois, 1975).

Experimental

A single crystal, 0·08 × 0·10 × 0·20 mm, was selected for the X-ray investigation.

The lattice constants were obtained from a least-squares analysis of the setting of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å).

The intensities were collected on a Philips PW1100 computer-controlled four-circle diffractometer in the ω-scan (scan width = 1·50°, scan speed = 0·02 s^{-1}) in Dr Pascard's Laboratory (ICSN, Gif ^{s}/Yvette, France).

1678 reflexions up to $\theta=27°$ were measured. Throughout the data collection, three reference reflexions were recorded after each sequence of 22 measured reflexions. The intensities of the standard reflexions remained constant to within ± 1·5%.

With $I \leq 2\sigma(I)$, 543 reflexions were omitted as unobserved. Standard deviations were calculated from counting statistics. The remaining 1135 reflexions were all used in the structural determination. The crystal data are given in Table 1. The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu=15{\cdot}3$ cm^{-1}).

Table 1. *Crystal data*

Formula $(N_3C_5H_9)_2PdCl_2$
M.W. 399·3
Space group $P2_1/c$
$a=9{\cdot}124$ (3), $b=9{\cdot}687$ (3), $c=9{\cdot}191$ (3) Å
$\beta=109{\cdot}26$ (5)°, $U=766{\cdot}9$ Å^3, $Z=2$
$D_m=1{\cdot}72$ (by flotation in a mixture of bromoform and carbon tetrachloride); $D_c=1{\cdot}730$ g cm^{-3}

Structure determination

The Pd atom is in a special position at the origin. A structure-factor calculation based on the coordinates of this atom gave an R of 0·33 ($R=\sum w\|F_o|-|F_c\|/\sum w|F_o|$). A Fourier map phased on Pd resulted in the location of all non-hydrogen atoms.

The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for Pd, Cl^-, N and C, and from Stewart, Davidson & Simpson (1965) for H. Corrections for anomalous dispersion were carried out for Pd ($\Delta f'=-1{\cdot}0$) and Cl ($\Delta f'=0{\cdot}1$).

Table 2. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^4)

$$T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

Estimated standard deviations are in parentheses.

B (in Å^2) is: $\frac{4}{3}(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2+2\beta_{12}ab\cos\gamma+2\beta_{13}ac\cos\beta+2\beta_{23}bc\cos\alpha)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Pd	0	0	0	64 (0)	46 (0)	50 (0)	−4 (1)	8 (0)	0 (1)	1·94
Cl	2405 (1)	−1100 (1)	5100 (1)	98 (2)	116 (2)	72 (2)	23 (2)	7 (1)	−6 (1)	2·96
N(1)	2294 (4)	457 (4)	612 (4)	64 (7)	63 (6)	61 (7)	−5 (5)	9 (5)	1 (5)	2·22
C(1)	3414 (5)	210 (6)	1940 (5)	70 (8)	83 (11)	71 (8)	−3 (7)	0 (6)	0 (7)	2·64
N(2)	4723 (5)	810 (5)	1943 (5)	73 (8)	97 (8)	90 (8)	−6 (6)	11 (6)	−3 (7)	3·08
C(2)	4453 (6)	1480 (6)	560 (7)	86 (10)	91 (10)	108 (11)	−15 (8)	25 (8)	−2 (8)	3·42
C(3)	2944 (6)	1247 (5)	−264 (5)	87 (9)	64 (7)	71 (8)	−6 (7)	25 (7)	4 (7)	2·61
C(4)	1983 (7)	1761 (7)	−1824 (6)	111 (11)	108 (10)	78 (10)	3 (9)	36 (8)	32 (8)	3·44
C(5)	623 (6)	2593 (6)	−1706 (7)	110 (11)	58 (8)	99 (10)	−5 (7)	16 (9)	35 (7)	3·10
N(3)	−582 (5)	1668 (4)	−1465 (5)	80 (7)	45 (5)	69 (7)	−6 (5)	10 (6)	11 (5)	2·27

All calculations were performed on an IBM 370/168 computer. A full-matrix least-squares calculation, with the local version *SIRIUS* of *ORFLS* (Busing, Martin & Levy, 1962), was used to refine the atomic coordinates of all non-hydrogen atoms. *R* fell to 0·070 and was reduced to 0·039 with anisotropic thermal parameters.

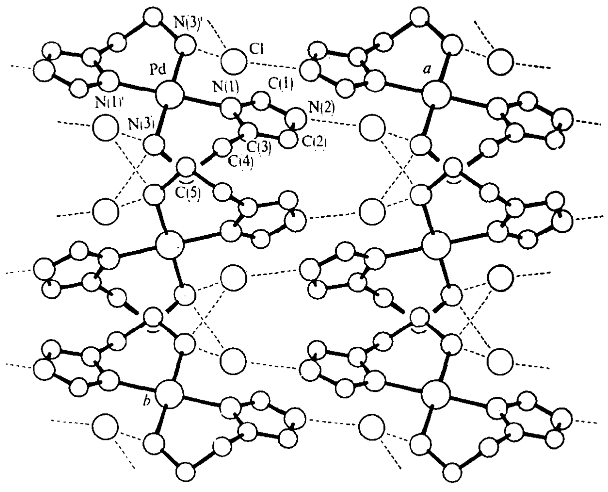

Fig. 1. Projection of the structure along **c** with hydrogen bonds represented by dotted lines.

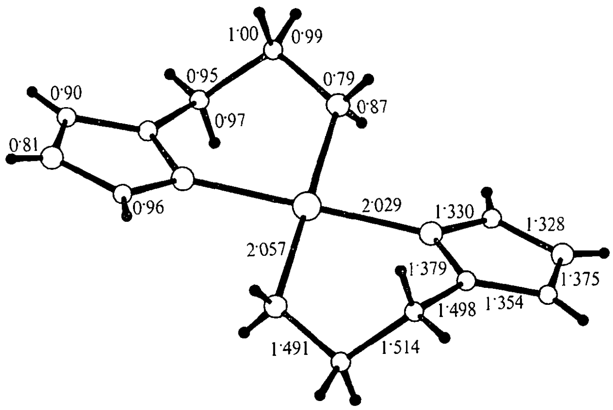

Fig. 2. Bond lengths (Å).

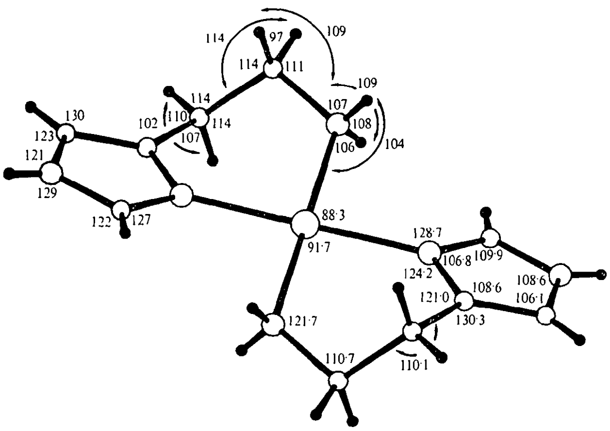

Fig. 3. Bond angles (°).

All H atoms were located on a difference synthesis. The refinement of their coordinates (the isotropic thermal parameters were those of the atoms to which they are bonded) resulted in an *R* of 0·033.

The initial weights were $w=1\cdot0$ ($w=1/\sigma^2$). During the last cycles of refinement, the weighting scheme was $w=(0\cdot0015|F_o|^2-0\cdot20|F_c|+9\cdot60)^{-1}$. The final *R* was 0·032, with $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}=0\cdot037$.

The final atomic and thermal parameters are listed in Tables 2 and 3.*

Table 3. *Hydrogen-atom parameters* ($\times 10^3$) *with estimated standard deviations in parentheses*

The isotropic thermal parameters are those of the atoms to which they are bonded.

	x	*y*	*z*
H(C1)	332 (6)	−25 (7)	283 (7)
H(N2)	559 (7)	78 (7)	258 (8)
H(C2)	518 (8)	196 (7)	32 (7)
H'(C4)	261 (7)	225 (7)	−229 (8)
H''(C4)	168 (7)	95 (7)	−249 (8)
H'(C5)	91 (7)	330 (7)	−88 (8)
H''(C5)	17 (7)	323 (7)	−258 (8)
H'(N3)	−122 (7)	215 (7)	−116 (7)
H''(N3)	−104 (7)	135 (6)	−227 (7)

Description and discussion of the structure

All geometrical calculations were made with NRC crystallographic programs (Ahmed, Hall, Pippy & Huber, 1966).

Fig. 1 shows the structure in projection along **c**. Figs. 2 and 3 give the bond lengths and angles. The figures were drawn with *ORTEP* (Johnson, 1965).

The average standard deviations are 0·004 on Pd–N; 0·007 on N–C and C–C; and 0·07 Å on C–H and N–H; 0·1 on N–Pd–N; 0·4 on Pd–N–C, C–N–C, C–C–N and C–C–C; 4 on H–C–C, H–C–N and H–N–C; and 6° on H–N–H and H–C–H.

The Pd atom is in a square-planar arrangement. It is situated at the centre of the plane defined by N(3) and N(3^{v}) of the side chains and N(1) and N(1^{i}) of the imidazole rings.

The Pd–N lengths are 2·057 (4) and 2·029 (4) Å for Pd–N(3) and Pd–N(1) respectively. They may be compared with 2·077, 2·101, 1·985 and 2·089 Å in $[PdN_3(N_3C_{12}H_{29})]NO_3.\frac{1}{2}H_2O$ (Bresciani Pahor & Delise, 1975), 1·978 Å in $PdCl_2C_2N_2H_8$ (Iball, MacDougall & Scrimgeour, 1975) and 1·95 and 2·00 Å in $Pd(C_6H_5N_2O_2)_2$ (von Leichert & Weiss, 1975).

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31713 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The imidazole ring is planar (Table 4). The angle between this plane and plane 1 is 26·0°. The side chain C(3), C(4), C(5), N(3) is not planar as found in complexes of Cu and Ni (Bonnet & Jeannin, 1970*a*,*b*) and of Co (Bonnet & Jeannin, 1972).

Table 4. *Equations of the mean planes and deviations* (Å) *of atoms from these planes*

Each plane is represented by an equation of the type $lX+mY+nZ-P=0$, referred to an orthogonal system of axes, which has X along a, Y in the ab plane and Z along c^*.

Plane 1: Pd, N(1), N(3)

$$0{\cdot}3404X-0{\cdot}5700Y-0{\cdot}7478Z=0$$

Plane 2: N(1), C(1), N(2), C(2), C(3)

$$0{\cdot}4040X-0{\cdot}8292Y-0{\cdot}3862Z-0{\cdot}2003=0$$

Plane 1		Plane 2	
Pd	0·000	N(1)	−0·002 (4)
N(1)	0·000	C(1)	0·002 (5)
N(3)	0·000	N(2)	0·001 (5)
C(1)*	−0·515 (5)	C(2)	−0·004 (6)
N(2)*	−0·442 (5)	C(3)	0·004 (6)
C(2)*	0·144 (6)	C(4)*	−0·049 (6)
C(3)*	0·424 (5)	C(5)*	−1·273 (6)
C(4)*	1·016 (6)	N(3)*	−1·084 (4)
C(5)*	0·045 (6)		

* Atoms not included in the calculation of the least-squares planes.

The bond lengths and angles found in the imidazole ring are compared with those in other compounds in Table 5.

Hydrogen bonding

Hydrogen-bond distances and angles are listed in Table 6. The three hydrogen-bond distances are in the usual range. The hydrogen-bond scheme is shown in Fig. 1. The acceptor Cl^- ion is approximately tetrahedrally surrounded and we can reasonably think that N(3) is in the form $>NH_2^+$ as in DL-proline hydrochloride (Mitsui, Tsuboi & Iitaka, 1969).

We have seen in this crystal-structure study that histamine atoms cannot be distributed in two planes, the side chain being non-planar, and that N(3) of the side chain is involved in hydrogen bonds in contrast to other complexes of first-row transition metals (Bonnet & Jeannin, 1970*a*,*b*, 1972). This may be due to the different environments of the metal atoms, square planar for Pd and octahedral for Ni, Cu and Co, the steric hindrance being different.

Table 6. *Hydrogen-bond distances* (Å) *and angles* (°)

Symmetry code

Superscript			
None	x	y	z
i	$-x$	$-y$	$-z$
ii	$1-x$	$-y$	$1-z$
iii	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

N(3)–H′(N3) $\cdots Cl^{iii}$	3·224 (4)	H′(N3) $\cdots Cl^{iii}$	2·38 (6)
N(3)–H″(N3) $\cdots Cl^{i}$	3·250 (4)	H″(N3) $\cdots Cl^{i}$	2·50 (6)
N(2)–H(N2) $\cdots Cl^{ii}$	3·104 (5)	H(N2) $\cdots Cl^{ii}$	2·33 (6)

N(3)–H′(N3) $\cdots Cl^{iii}$	165 (6)
N(3)–H″(N3) $\cdots Cl^{i}$	162 (6)
N(2)–H(N2) $\cdots Cl^{ii}$	160 (6)
Pd—N(3) $\cdots Cl^{iii}$	109·1 (1)
C(5)–N(3) $\cdots Cl^{iii}$	98·9 (3)
Pd—N(3) $\cdots Cl^{i}$	118·3 (2)
C(5)–N(3) $\cdots Cl^{i}$	95·8 (3)
C(1)–N(2) $\cdots Cl^{ii}$	122·7 (3)
C(2)–N(2) $\cdots Cl^{ii}$	127·5 (3)

I thank Dr C. Stora for her kind interest throughout this work, Dr J. Guilhem for the registration of the data and Dr S. Valladas for crystallizing the samples.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, p. 52. Utrecht: Oosthoek.

BONNET, J. J. & IBERS, J. A. (1973). *J. Amer. Chem. Soc.* **95**, 4829–4833.

BONNET, J. J. & JEANNIN, Y. (1970*a*). *Acta Cryst.* **B26**, 318–326.

BONNET, J. J. & JEANNIN, Y. (1970*b*). *Bull. Soc. Fr. Minér. Crist.* **93**, 287–299.

BONNET, J. J. & JEANNIN, Y. (1972). *Acta Cryst.* **B28**, 1079–1085.

BRESCIANI PAHOR, N. & DELISE, P. (1975). *Cryst. Struct. Commun.* **4**, 483–486.

Table 5. *Bond lengths* (Å) *and angles* (°) *in imidazole rings*

N=CH	CH–NH	NH–CH	CH=C	–C–N	N=CH–NH	CH–NH–CH	NH–CH=C	CH=C–N	–C–N=CH	
1·330	1·328	1·375	1·354	1·379	109·9	108·6	106·1	108·6	106·8	(*a*)
1·334	1·372	1·365	1·351	1·390	107·9	109·4	106·0	109·3	107·4	(*b*)
1·315	1·341	1·392	1·362	1·397	112·0	106·6	106·9	108·2	106·3	
1·36	1·35	1·37	1·39	1·36	110·1	108·7	105·5	110·0	105·6	(*c*)
1·31	1·34	1·37	1·39	1·39	116·6	107·4	106·7	107·0	106·7	
1·353	1·340	1·386	1·347	1·415	110·2	108·2	107·4	108·1	105·8	(*d*)
1·314	1·311	1·408	1·368	1·359	109·8	108·5	105·1	107·8	109·1	(*e*)
1·327	1·328	1·382	1·338	1·369	112·0	106·6	106·3	110·3	104·9	(*f*)
1·314	1·359	1·374	1·374	1·385	111·6	107·4	105·6	109·7	105·7	(*g*)
1·349	1·303	1·380	1·356	1·365	112·3	104·5	110·8	105·1	107·3	(*h*)

(*a*) This work. (*b*) $Co(Im)_2(Ac)_2$ (Gadet, 1974). (*c*) Aquo-*cis*-bis(histamine)perchloratonickel(II) perchlorate (Bonnet & Jeannin, 1970*b*). (*d*) Bis(histamine)bis(perchlorato)copper(II) (Bonnet & Jeannin, 1970*a*). (*e*) Histaminium tetrachlorocobaltate(II) (Bonnet & Jeannin, 1972). (*f*) Bis-(5-ethyl-5-isoamylbarbiturato)bis(imidazole)nickel(II) (Nassimbeni & Rodgers, 1974). (*g*) DL-Histidine (Edington & Harding, 1974). (*h*) Histamine (Bonnet & Ibers, 1973).

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

CAIN, M. & VALLADAS-DUBOIS, S. (1975). *C. R. Acad. Sci. Paris, Sér. C*, **280**, 9–12.

EDINGTON, P. & HARDING, M. M. (1974). *Acta Cryst.* B**30**, 204–206.

GADET, A. (1974). *Acta Cryst.* B**30**, 349–353.

IBALL, J., MACDOUGALL, M. & SCRIMGEOUR, S. (1975). *Acta Cryst.* B**31**, 1672–1674.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

LEICHERT, I. VON & WEISS, J. (1975). *Acta Cryst.* B**31**, 2709–2710.

MITSUI, Y., TSUBOI, M. & IITAKA, Y. (1969). *Acta Cryst.* B**25**, 2182–2192.

NASSIMBENI, L. & RODGERS, A. (1974). *Acta Cryst.* B**30**, 2593–2602.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VALLADAS-DUBOIS, S. & CAIN, M. (1973). *C. R. Acad. Sci. Paris, Sér. C*, **276**, 1003–1006.

Acta Cryst. (1976). B**32**, 2475

The Crystal and Molecular Structure of 3-Methoxypentafluorotropone at −50°C

BY M. J. HAMOR AND T. A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

(*Received* 21 *February* 1976; *accepted* 26 *March* 1976)

3-Methoxypentafluorotropone is monoclinic, space group $P2_1/c$, with $a=8{\cdot}61$ (1), $b=16{\cdot}32$ (1), $c=6{\cdot}07$ (1) Å, $\beta=100{\cdot}80$ (5)°, $Z=4$. The structure was determined by direct methods from X-ray counter data measured at −50 °C and refined by least-squares calculations to R 6·06% for 568 observed amplitudes. Estimated standard deviations average 0·01 Å for bond lengths and 0·8° for bond angles. The atoms of the ring deviate slightly from coplanarity such that the ring has a shallow boat-like conformation. The endocyclic bonds show marked alternation in length and it is concluded that the π-electron system is only partially delocalized.

Introduction

Hexafluorotropone (Dodsworth, Jenkins, Stephens & Tatlow, 1972) reacts readily with aqueous NaOH to give a mixture of hydroxypentafluorotropones. The major isomer on treatment with diazomethane formed the corresponding methoxypentafluorotropone. Mass spectrum, ^{19}F and ^{1}H NMR measurements indicated that this was most probably the 3-methoxy isomer (Allen, Jenkins, Stephens & Tatlow, 1974). The present analysis has been undertaken in order to confirm this structural assignment and, in addition, to provide further geometric data relevant to the understanding of the nature of the bonding in the cycloheptatrienone system. Recent structural work on tropones includes X-ray analyses of 2-chlorotropone (Watkin & Hamor, 1971), 3-azidotropone (Cruickshank, Filippini & Mills, 1972), tropone (Barrow, Mills & Filippini, 1973) and hexafluorotropone (Guy, Hamor & Jenkins, 1975).

Experimental

The crystals used in the analysis were grown by sublimation. Initial cell dimensions were obtained from oscillation and Weissenberg photographs. Inspection of the photographs indicated a rapid fall-off in reflexion intensities with increasing angle, and it was therefore decided to collect the intensities at low temperature. For this purpose a low-temperature device built by Dr A. J. Edwards of this Department was used in conjunction with a Stoe two-circle computer-controlled diffractometer, and unit-cell dimensions and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation at −50 °C, the lowest temperature accessible with the apparatus. Crystal data are given in Table 1. The crystal, 0·2 × 0·2 × 0·5 mm, was mounted inside a Pantak capillary tube and set about the direction of elongation (c). 1756 reflexions were scanned within the range $0{\cdot}1<\sin\theta/\lambda<0{\cdot}59$, of which 568 having $I>2{\cdot}5\sigma(I)$ were considered to be observed. The ω scan technique was used; for the zero layer 140 counts of 1s at intervals of 0·01° were taken for each reflexion, backgrounds being measured for 30s at each end of the scan; for layers 1 and 2 the range was increased to 150 counts at the same intervals. For reflexions on layers 3–6 a variable scan technique was used in order to increase the scan range at low values of the azimuth angle and high values of the equi-inclination angle. Intensity measurements were standardized by applying interlayer scale factors obtained by measuring three of the stronger reflexions from each layer at the end of data collection and comparing with the values found during the systematic data collection process. In the conversion of intensities to structure amplitudes, the polarization factor for monochromated radiation was used, but absorption corrections were not applied.