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Structure of Dichlorobis(3,5-dimethylpyrazole)palladium

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Abstract. $[PdCl_2(C_5H_8N_2)_2]$, $M_r = 369{\cdot}6$, monoclinic, $P2_1/c$, $a = 16{\cdot}239\ (4)$, $b = 11{\cdot}258\ (3)$, $c = 17{\cdot}663\ (7)$ Å, $\beta = 111{\cdot}59\ (2)°$, $V = 3002\ (2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}635$, $D_m = 1{\cdot}635$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71073$ Å, $\mu = 15{\cdot}65$ cm^{-1}, $F(000) = 1472$, $T = 295$ K, $R = 0{\cdot}0272$, $wR = 0{\cdot}0286$ for 3432 observed reflections. The palladium(II) center is in a planar arrangement with the two chloro ligands *trans* to each other. Only one of the two N atoms in each pyrazole ligand is coordinated to the metal ion. The other nitrogen is connected to a chloride ligand *via* an intermolecular hydrogen bond. The complex appears as a dimer in the solid state due to the formation of four such hydrogen bonds.

Introduction. The coordination chemistry of pyrazole and its derivatives has been intensively studied (Uson, Oro, Ciriano, Pinillos, Tiripicchio & Camellini, 1981) due to the rich bonding modes of these ligands. One interesting type of bonding which, however, receives little attention is that in which one of the two N atoms in the pyrazole ligand is coordinated to the metal center, while the acidic hydrogen on the second nitrogen interacts with an electron lone pair to form a hydrogen bond. Examples of such interactions are known including cobalt complexes $[(\pi\text{-}C_5H_5)CoR_F(C_3H_3N_2)_2H]$, where R_F = perfluoroalkyl (King & Bond, 1974), and nickel species $[Ni(C_3H_4N_2)_4X_2]$, X = Cl, Br (Reimann, 1969, 1970). In all these complexes, the hydrogen bonding is intramolecular. In this paper, we present the X-ray structure of $[Pd\{3,5\text{-}(CH_3)_2C_3H_2N_2\}_2Cl_2]$, which exhibits unique intermolecular hydrogen bonding between the pyrazole group and chloride ligand.

Experimental. 1·14 mmol of $PdCl_2$ was added to 2·3 mmol of 3,5-dimethylpyrazole in 10 ml of chloroform. The mixture was stirred for 12 h and was filtered. Addition of hexane to the filtrate afforded the product. Orange crystals were obtained from a chloroform solution after slow evaporation. A single crystal of dimensions 0·68 × 0·42 × 0·40 mm was selected for X-ray intensity measurement. Density measured by flotation.

A MicroVAXII computer-controlled Nicolet *R3m*/V diffractometer equipped with a graphite monochromator was used for intensity data collection. Lattice constants were obtained from 16 reflections with $6{\cdot}50 \leq 2\theta \leq 29{\cdot}48°$. The space group is $P2_1/c$. $\theta/2\theta$ scan data were collected at room temperature (295 K) for two octants of the sphere ($0 \leq h \leq 18$, $-12 \leq k \leq 0$, $-20 \leq l \leq 18$) out to the 2θ limit of 48·0° with variable scan speed of 2·93–14·65° min^{-1}. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The data were corrected for absorption, Lorentz and polarization effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. Max./min. transmission factors: 0·897/0·806. 5533 reflections were collected, 4714 unique, of which 3432 observed reflections with $I \geq 3\sigma(I)$ were used for refinement of the structure. The structure was solved by a direct method using *SHELXTL-Plus* (Sheldrick, 1986) and full-matrix least-squares refinement on F with anomalous-dispersion corrections for Pd and Cl was used. Neutral-atom scattering form factors were from *International Tables for X-ray Crystallography* (1974). The weights had the form $w = [\sigma^2(F) + gF^2]^{-1}$ with $g = 0{\cdot}0003$. The H atoms in the pyrazole rings were placed in idealized positions (C—H = 0·96, N—H = 0·90 Å) with fixed U (0·08 Å^2) after the non-H atoms had been refined anisotropically. $R = 0{\cdot}0272$, $wR = 0{\cdot}0286$, $S = 1{\cdot}29$, $(\Delta/\sigma)_{\max} = 0{\cdot}005$, $\Delta\rho_{\max} = 0{\cdot}30$, $\Delta\rho_{\min} = -0{\cdot}32$ e Å^{-3} for 308 variables and 3432 reflections. All calculations were performed on a MicroVAXII computer system using *SHELXTL-Plus* (Sheldrick, 1986).

Discussion. Final atomic parameters are presented in Table 1 and geometric data in Table 2.* Fig. 1 displays a stereoview of the packing for the molecules in the unit cell, while the atomic numbering is shown in Fig. 2. In the solid state, the complex surprisingly appears as a dimer. The long Pd—Pd

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52235 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	1718 (1)	5552 (1)	6765 (1)	47 (1)
Pd(2)	3271 (1)	4316 (1)	8818 (1)	47 (1)
Cl(1)	539 (1)	4925 (1)	7080 (1)	62 (1)
Cl(2)	2949 (1)	6122 (1)	6503 (1)	64 (1)
Cl(3)	4183 (1)	5921 (1)	8922 (1)	62 (1)
Cl(4)	2333 (1)	2723 (1)	8660 (1)	61 (1)
N(1)	1741 (2)	7126 (3)	7308 (2)	56 (2)
N(2)	2454 (2)	7429 (3)	7957 (2)	58 (2)
N(3)	1721 (2)	3959 (3)	6262 (2)	52 (2)
N(4)	1889 (2)	2972 (3)	6724 (2)	54 (2)
N(5)	3943 (2)	3429 (3)	8236 (2)	53 (2)
N(6)	3929 (3)	3821 (3)	7510 (2)	60 (2)
N(7)	2574 (2)	5224 (3)	9358 (2)	50 (2)
N(8)	1714 (2)	5495 (3)	8945 (2)	54 (2)
C(1)	2321 (3)	8426 (4)	8320 (3)	61 (2)
C(2)	1479 (3)	8764 (5)	7872 (3)	67 (2)
C(3)	1125 (3)	7958 (4)	7242 (3)	61 (2)
C(4)	3025 (4)	8913 (5)	9055 (4)	91 (3)
C(5)	244 (3)	7931 (5)	6576 (3)	87 (3)
C(6)	1940 (3)	2008 (4)	6300 (3)	61 (2)
C(7)	1777 (3)	2394 (5)	5526 (3)	73 (3)
C(8)	1640 (3)	3608 (5)	5517 (3)	58 (2)
C(9)	2139 (5)	827 (4)	6696 (4)	95 (3)
C(10)	1421 (4)	4476 (5)	4837 (3)	89 (3)
C(11)	4337 (3)	3066 (5)	7181 (3)	69 (2)
C(12)	4642 (3)	2162 (5)	7729 (3)	72 (2)
C(13)	4388 (3)	2410 (4)	8379 (3)	60 (2)
C(14)	4383 (5)	3315 (6)	6367 (4)	108 (4)
C(15)	4577 (4)	1757 (5)	9152 (3)	86 (3)
C(16)	1392 (3)	6210 (4)	9369 (3)	57 (2)
C(17)	2060 (3)	6403 (4)	10098 (3)	63 (2)
C(18)	2798 (3)	5784 (4)	10074 (3)	54 (2)
C(19)	454 (3)	6644 (5)	9038 (4)	89 (3)
C(20)	3690 (3)	5662 (5)	10715 (3)	85 (3)

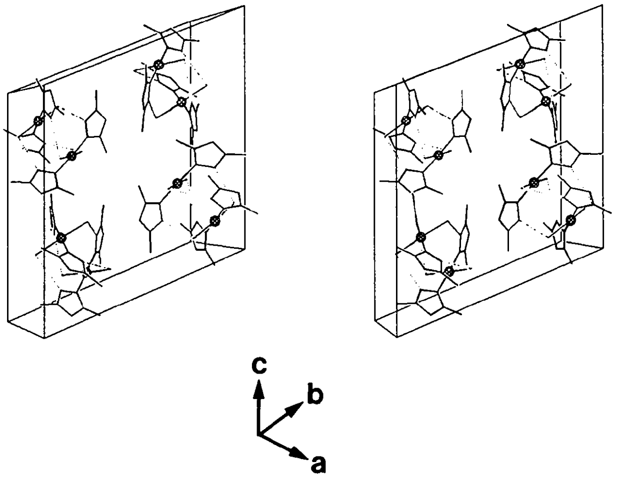

Fig. 1. A stereoview of the packing of molecules in the unit cell.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Pd(1)—Cl(1)	2·293 (2)	Pd(1)—Cl(2)	2·304 (2)
Pd(1)—N(1)	2·008 (4)	Pd(1)—N(3)	2·003 (4)
Pd(2)—Cl(3)	2·299 (2)	Pd(2)—Cl(4)	2·302 (2)
Pd(2)—N(5)	2·017 (4)	Pd(2)—N(7)	2·008 (4)
N(1)—N(2)	1·340 (5)	N(1)—C(3)	1·344 (6)
N(2)—C(1)	1·349 (7)	N(3)—N(4)	1·346 (5)
N(3)—C(8)	1·333 (6)	N(4)—C(6)	1·339 (7)
N(5)—N(6)	1·347 (6)	N(5)—C(13)	1·330 (6)
N(6)—C(11)	1·336 (8)	N(7)—N(8)	1·352 (5)
N(7)—C(18)	1·336 (6)	N(8)—C(16)	1·330 (7)
C(1)—C(2)	1·358 (6)	C(1)—C(4)	1·484 (7)
C(2)—C(3)	1·386 (7)	C(3)—C(5)	1·480 (6)
C(6)—C(7)	1·364 (8)	C(6)—C(9)	1·482 (7)
C(7)—C(8)	1·384 (8)	C(8)—C(10)	1·486 (7)
C(11)—C(12)	1·366 (7)	C(11)—C(14)	1·492 (10)
C(12)—C(13)	1·383 (9)	C(13)—C(15)	1·482 (8)
C(16)—C(17)	1·362 (6)	C(16)—C(19)	1·499 (7)
C(17)—C(18)	1·400 (8)	C(18)—C(20)	1·480 (6)
Cl(1)—Pd(1)—Cl(2)	177·0 (1)	Cl(1)—Pd(1)—N(1)	91·5 (1)
Cl(2)—Pd(1)—N(1)	89·2 (1)	Cl(1)—Pd(1)—N(3)	88·3 (1)
Cl(2)—Pd(1)—N(3)	90·9 (1)	N(1)—Pd(1)—N(3)	178·0 (1)
Cl(3)—Pd(2)—Cl(4)	177·7 (1)	Cl(3)—Pd(2)—N(5)	88·7 (1)
Cl(4)—Pd(2)—N(5)	90·6 (1)	Cl(3)—Pd(2)—N(7)	91·2 (1)
Cl(4)—Pd(2)—N(7)	89·5 (1)	N(5)—Pd(2)—N(7)	177·9 (1)
N(2)—N(1)—C(3)	106·1 (4)	N(1)—N(2)—C(1)	112·3 (4)
N(4)—N(3)—C(8)	106·2 (4)	N(3)—N(4)—C(6)	111·7 (4)
N(6)—N(5)—C(13)	106·3 (4)	N(5)—N(6)—C(11)	111·7 (7)
N(8)—N(7)—C(18)	105·8 (4)	N(7)—N(8)—C(16)	112·0 (3)
N(2)—C(1)—C(2)	105·0 (4)	N(2)—C(1)—C(4)	121·1 (4)
C(2)—C(1)—C(4)	133·9 (5)	C(1)—C(2)—C(3)	108·4 (5)
N(1)—C(3)—C(2)	108·1 (4)	N(1)—C(3)—C(5)	121·6 (5)
C(2)—C(3)—C(5)	130·2 (5)	N(4)—C(6)—C(7)	105·9 (4)
N(4)—C(6)—C(9)	120·7 (5)	C(7)—C(6)—C(9)	133·4 (5)
C(6)—C(7)—C(8)	107·3 (5)	N(3)—C(8)—C(7)	108·9 (4)
N(3)—C(8)—C(10)	120·6 (5)	C(7)—C(8)—C(10)	130·5 (5)
N(6)—C(11)—C(12)	105·9 (5)	N(6)—C(11)—C(14)	120·6 (5)
C(12)—C(11)—C(14)	133·5 (6)	C(11)—C(12)—C(13)	107·3 (5)
N(5)—C(13)—C(12)	108·9 (5)	N(5)—C(13)—C(15)	121·1 (5)
C(12)—C(13)—C(15)	129·9 (5)	N(8)—C(16)—C(17)	106·7 (4)
N(8)—C(16)—C(19)	122·1 (4)	C(17)—C(16)—C(19)	131·2 (5)
C(16)—C(17)—C(18)	106·6 (5)	N(7)—C(18)—C(17)	109·0 (4)
N(7)—C(18)—C(20)	121·9 (5)	C(17)—C(18)—C(20)	129·0 (5)

Hydrogen bonds

	Cl···N	∠Cl···H—N
Cl(1)···H(N8)—N(8)	3·207 (8) Å	168·6 (5)°
Cl(2)···H(N6)—N(6)	3·213 (8)	171·8 (4)
Cl(3)···H(N2)—N(2)	3·185 (8)	163·2 (5)
Cl(4)···H(N4)—N(4)	3·237 (8)	171·1 (5)

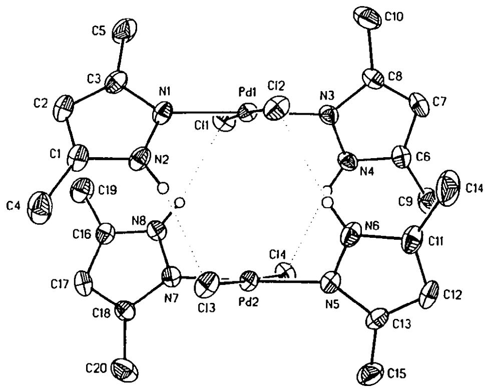

Fig. 2. Numbering scheme of the dimer, excluding the H atoms attached to C atoms.

distance of 3·837 (2) Å in the dimer excludes the possibility of the existence of a metal bond. The structure in Fig. 2 reveals that each N—H bond in the pyrazole ligands is pointing toward a chloride attached to another Pd^{II} ion. The N···Cl distances and directions of the N—H bonds suggest the formation of four N—H···Cl hydrogen bonds in the dimer, which are listed in Table 2. Apparently, the interactions are the driving force for the dimerization.

In the dimer, each palladium center is coplanar with two *trans* chlorides and two N atoms in the pyrazole rings. The two planes in the dimer are parallel to each other, but the second plane rotates about the Pd(1)—Pd(2) vector relative to the first by 39·3° leading to a staggered conformation. The rotation appears necessary for hydrogen bonding, in addition to the reduction of steric hindrance among the intermolecular ligands. As a consequence of the hydrogen bonds, all the N—H groups lie between the two planes, although such an arrangement would somewhat raise the repulsion between intermolecular pyrazole ligands. All four Pd—Cl bonds are equivalent within experimental error, as are the Pd—N bonds. These bond lengths are comparable with the reported values for Pd—Cl of 2·297 (1) Å and for Pd—N of 2·030 (3) Å in $[Pd\{(CH_3)_2C(C_3H_3N_2)_2\}Cl_2]$ (Minghetti, Cinellu, Bandini, Banditelli, Demartin & Manassero, 1986).

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Structure and Pseudosymmetry of Tetrabromobis(dimethyl sulfoxide)tin(IV)

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Abstract. $[SnBr_4(C_2H_6OS)_2]$, $M_r = 594·6$, monoclinic, $P2_1/n$, $a = 7·7728 (6)$, $b = 14·676 (2)$, $c = 13·632 (2)$ Å, $\beta = 91·11 (1)°$, $V = 1554·8 (5)$ Å^3, $Z = 4$, $D_x = 2·54$, $D_m = 2·55 (2)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 118·42$ cm^{-1}, $F(000) = 1096$, room temperature, $R = 0·076$ for 1260 unique reflections with $F > 6\sigma F$. The structure is isomorphous with $[SnCl_4(C_2H_6OS)_2]$ and consists of monomeric molecules with *cis*-octahedral coordination around Sn. The dimethyl sulfoxide ligands are bonded through O with Sn—O bond distances [2·153 (15) and 2·205 (15) Å] longer and S—O bond distances [1·507 (13) and 1·487 (14) Å] shorter than in $[SnCl_4(C_2H_6OS)_2]$, indicating that the Sn—dmso bond is weaker in the present compound. The Sn—Br bond lengths vary between 2·531 (3) and 2·549 (3) Å. The pseudosymmetry $C2/c$ is related to the existence of two concurrent packing models.

Introduction. The Sn—Cl distance in octahedral tin(IV) chloride complexes is related to the quadrupole splitting in the Mössbauer spectra (Tudela, Khan & Zuckerman, 1989). In the case of tin(IV) bromide complexes, few experimental data are available and more crystallographic and Mössbauer measurements are necessary before a similar relationship can be searched for. The IR spectrum of $[SnBr_4(Me_2SO)_2]$ suggests a *cis*-octahedral molecular structure with the Me_2SO ligands coordinated to tin through the O atom (Harrison, Lane & Zuckerman, 1972), and its Mössbauer quadrupole splitting agrees within experimental error with those of [*cis*-$SnBr_2Cl_2(Me_2SO)_2$] (Tudela, Fernández, Tornero & Vegas, 1986) and [*cis*-$SnCl_4(Me_2SO)_2$] (Tudela, Fernández & Tornero, 1985) whose crystal structures have been recently reported (Tudela *et al.*, 1986; Kisenyi, Willey & Drew, 1985). The crystal structure of the title compound has been determined for structural comparison with $[SnCl_4(Me_2SO)_2]$ and $[SnBr_2Cl_2(Me_2SO)_2]$. Particular attention is paid to problems arising from pseudosymmetry which affect the three structures to different degrees and had so far not been resolved.

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