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Structure of Bis(benzaldehyde azine)dichloropalladium(II)

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Abstract. $[Pd(C_{14}H_{12}N_2)_2]Cl_2$, $M_r = 593{\cdot}86$, monoclinic, $P2_1/n$, $a = 11{\cdot}922\,(3)$, $b = 7{\cdot}908\,(2)$, $c = 13{\cdot}982\,(3)$ Å, $\beta = 103{\cdot}89\,(2)°$, $V = 1279{\cdot}6\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}54$, $D_m = 1{\cdot}564$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 9{\cdot}08$ cm^{-1}, $F(000) = 600$, $T = 298$ K, $R = 0{\cdot}0319$ for 1170 significant reflections. The Pd$^{\text{II}}$ ion is in a *trans* square-planar arrangement surrounded by two Cl and two N atoms. This planar geometry is rigorously imposed by the presence of a crystallographic inversion center at the Pd$^{\text{II}}$ ion. Only one of the two N atoms in each benzalazine ligand is bonded to the Pd ion. The long chains in these ligands are in a zigzag shape approximately perpendicular to the $PdCl_2N_2$ plane.

Introduction. The coordination chemistry of benzalazine and its derivatives is rarely explored, although there are several interesting possible bonding modes for the coordination of this ligand to metal ions. To date, no example of a metal complex containing a coordinated azine is known. The reaction of benzalazine with $Fe_3(CO)_{12}$ led to the formation of $(\mu\text{-}C_6H_5CHN)_2Fe_2(CO)_6$ and an *ortho*-metallated complex $(o\text{-}C_6H_4CH_2N{-}N{=}CHC_6H_5)\text{-}Fe_2(CO)_6$ (Nametkin, Tyurin, Trusov, Batsanov & Struchkov, 1981, and references cited therein). The reaction of ketone azines with Cp_2Zr resulted in the formation of $Cp_2Zr(N{=}CR_2)_2$ (Erker, Frömberg, Krüger & Raabe, 1988). In an attempt to synthesize Pd–benzalazine complexes from the reactions of $PdCl_2$ and $PdCl_2(CH_3CN)_2$ with the ligand in chloroform solutions, we obtained white and pale-yellow precipitates, respectively. Both precipitates have the same empircial formula, $(PhCHNNCHPh)_2Cl_2Pd$. In order to distinguish between the structures of these two isomers, an X-ray structural determination of the pale-yellow crystal was undertaken. In this paper, we report the results of the investigation.

Experimental. The palladium complex was prepared by the addition of 2 equivalents of benzalazine to $PdCl_2(CH_3CN)_2$ in chloroform. The undissolved material was filtered. A crystalline product was obtained by evaporation of the filtrate. The product was redissolved in chloroform and pale-yellow crystals were grown by slow evaporation of the solvent in a refrigerator. A crystal of size $0{\cdot}16 \times 0{\cdot}15 \times 0{\cdot}08$ mm was selected for X-ray intensity measurement. D_m was determined by flotation in a mixture of carbon tetrachloride and *n*-hexane. A MicroVAX II computer-controlled Nicolet *R*3*m*/*V* diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å) was used for intensity-data collection. The unit-cell parameters were determined by a least-squares fit of 22 reflection peaks with $6{\cdot}0 \le 2\theta \le 24{\cdot}0°$. $\theta/2\theta$ scan data were collected at room temperature (298 K) out to a 2θ limit of $50{\cdot}0°$ (h $-13\rightarrow 13$, k $0\rightarrow 9$, l $0\rightarrow 15$) with a variable scan speed of $2{\cdot}93$–$14{\cdot}65°$ min^{-1}. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deteriora-

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement coefficients* (Å^2 × 10^3)

	x	y	z	U_{eq}*
Pd	0	0	5000	25 (1)
Cl	26 (3)	2884 (2)	4975 (3)	42 (1)
N(1)	1709 (3)	−143 (13)	5654 (3)	31 (2)
N(2)	2516 (4)	−380 (7)	5069 (4)	35 (2)
C(1)	2189 (5)	−361 (8)	6571 (4)	30 (3)
C(2)	1716 (4)	−77 (17)	7431 (3)	35 (2)
C(3)	686 (5)	713 (9)	7428 (5)	44 (2)
C(4)	359 (6)	994 (10)	8301 (5)	51 (3)
C(5)	1065 (6)	431 (9)	9179 (5)	47 (3)
C(6)	2079 (6)	−400 (10)	9194 (5)	48 (3)
C(7)	2403 (6)	−632 (9)	8319 (5)	40 (2)
C(8)	2259 (5)	308 (11)	4231 (5)	33 (3)
C(9)	3026 (4)	128 (18)	3556 (4)	36 (2)
C(10)	4043 (5)	−779 (9)	3825 (5)	43 (2)
C(11)	4726 (6)	−990 (10)	3150 (6)	50 (3)
C(12)	4398 (6)	−283 (13)	2231 (6)	50 (3)
C(13)	3403 (7)	677 (10)	1971 (5)	54 (3)
C(14)	2712 (6)	863 (10)	2626 (5)	48 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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

Pd—Cl	2·281 (1)	Pd—N(1)	2·026 (4)
N(1)—N(2)	1·417 (7)	N(1)—C(1)	1·285 (7)
N(2)—C(8)	1·261 (8)	C(1)—C(2)	1·462 (9)
C(2)—C(3)	1·376 (10)	C(2)—C(7)	1·384 (8)
C(3)—C(4)	1·387 (10)	C(4)—C(5)	1·384 (9)
C(5)—C(6)	1·372 (11)	C(6)—C(7)	1·380 (10)
C(8)—C(9)	1·469 (9)	C(9)—C(10)	1·382 (11)
C(9)—C(14)	1·392 (10)	C(10)—C(11)	1·396 (12)
C(11)—C(12)	1·369 (11)	C(12)—C(13)	1·382 (11)
C(13)—C(14)	1·379 (11)		
Cl—Pd—N(1)	92·7 (3)	Cl—Pd—Cl*A*	180·0
N(1)—Pd—Cl*A*	87·3 (3)	N(1)—Pd—N(1*A*)	180·0
Pd—N(1)—N(2)	119·7 (3)	Pd—N(1)—C(1)	128·1 (4)
N(2)—N(1)—C(1)	110·9 (4)	N(1)—N(2)—C(8)	115·6 (5)
N(1)—C(1)—C(2)	129·2 (5)	C(1)—C(2)—C(3)	125·9 (6)
C(1)—C(2)—C(7)	115·2 (6)	C(3)—C(2)—C(7)	118·8 (6)
C(2)—C(3)—C(4)	120·6 (5)	C(3)—C(4)—C(5)	119·3 (7)
C(4)—C(5)—C(6)	120·9 (7)	C(5)—C(6)—C(7)	118·9 (6)
C(2)—C(7)—C(6)	121·4 (6)	N(2)—C(8)—C(9)	120·3 (6)
C(8)—C(9)—C(10)	121·1 (7)	C(8)—C(9)—C(14)	119·4 (7)
C(10)—C(9)—C(14)	119·6 (6)	C(9)—C(10)—C(11)	119·6 (6)
C(10)—C(11)—C(12)	120·3 (7)	C(11)—C(12)—C(13)	120·4 (8)
C(12)—C(13)—C(14)	119·7 (7)	C(9)—C(14)—C(13)	120·4 (6)

tion. The data were corrected for absorption, Lorentz and polarization effects. Corrections for absorption were based on ψ scans of three reflections: $\bar{2}\bar{1}3$, $\bar{4}\bar{1}5$, $\bar{4}\bar{2}6$ (North, Phillips & Mathews, 1968). Max./min. transmission factors: 0·772/0·735. 2335 reflections were collected, 2064 unique, of which 1170 observed reflections with $I \geq 2{\cdot}5\sigma(I)$ were used for refinement of the structure. The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1986) and refined by full-matrix least squares based on F values. Neutral-atom scattering form factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). The H atoms were calculated and fixed after anisotropic refinement of all the non-H atoms. The refinement of 161 parameters with the weighting scheme $1/w = \sigma^2(F_o) + 0{\cdot}000092F_o^2$ converged at $R = 0{\cdot}0319$, $wR = 0{\cdot}0271$, $S = 1{\cdot}35$, $(\Delta/\sigma)_{\max} = 0{\cdot}018$. In the final difference Fourier map the deepest hole was $-0{\cdot}37$ e Å^{-3}, and the highest peak $0{\cdot}47$ e Å^{-3}. All calculations were performed on a MicroVAX II computer system using *SHELXTL-Plus* (Sheldrick, 1986).

Discussion. The atomic parameters are listed in Table 1, and bond lengths and bond angles in Table 2.* Fig. 1 shows the numbering scheme of the molecule and a stereoview of the packing of the molecules in a unit cell is depicted in Fig. 2. The Pd^{II} ion occupies a crystallographic inversion center, and is surrounded by two Cl and two N atoms in a *trans* square-planar arrangement. Only one of the two N atoms in each benzalazine is coordinated to the metal center. The

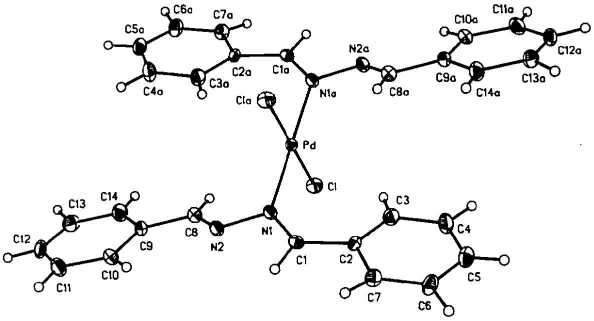

Fig. 1. Numbering scheme of the molecule.

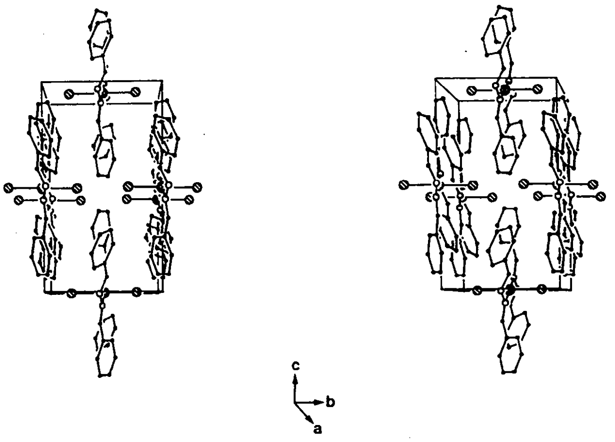

Fig. 2. A stereoview of the packing of molecules in the unit cell projected along the a axis.

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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 52019 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordination of N(1) to Pd enlarges the Pd—N(1)—C(1), N(1)—C(1)—C(2) and C(1)—C(2)—C(3) angles from approximately 120° to 128°, 129° and 126°, respectively, while reducing the C(1)—N(1)—N(2) angle to 111°. Presumably, these angle distortions arise from steric repulsion between the adjacent phenyl ring and the Pd coordination sphere. The chain from C(2) to C(9) in the coordinated benzalazine has a zigzag shape, nearly perpendicular to the $PdCl_2N_2$ plane. The C(1)N(1)N(2) and $PdCl_2N_2$ planes intersect at an angle of 89·5°. These steric arrangements further reduce the nonbonding interactions in the complex. The Pd—N and Pd—Cl bond distances of 2·026 (4) and 2·281 (1) Å, respectively, are comparable with the values of 2·030 (3) Å for Pd—N and 2·297 (1) Å for Pd—Cl in $Pd[(CH_3)_2C(C_3H_3N_2)_2]Cl_2$ (Minghetti, Cinnellu, Bandini, Banditelli, Demartin & Manassero, 1986).

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Simple, Direct Synthesis and Structure of Hexa-μ-chloro-tetrakis-(1-methylimidazole)-μ_4-oxo-tetracopper(II)

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Abstract. $[Cu_4Cl_6O(C_4H_6N_2)_4]$, $M_r = 811{\cdot}32$, orthorhombic, $Pbca$, $a = 18{\cdot}985\,(7)$, $b = 33{\cdot}197\,(7)$, $c = 18{\cdot}917\,(5)$ Å, $V = 11922\,(6)$ Å^3, $Z = 16$, $D_m = 1{\cdot}80$, $D_x = 1{\cdot}81$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 84{\cdot}2$ cm^{-1}, $F(000) = 6432$, $T = 293$ K, $R = 0{\cdot}051$ for 6860 reflections with $F_o \geq 4\sigma(F_o)$. $[Cu_4Cl_6O(1\text{-MeIm})_4]$ is readily synthesized by simply mixing concentrated methanolic solutions of copper(II) chloride hydrate and 1-methylimidazole under ambient conditions. Each of the two molecules in the asymmetric unit consists of a μ_4-O atom surrounded by a tetrahedron of Cu atoms with μ_2-Cl atoms bridging between the Cu atoms, and with 1-methylimidazole completing the distorted trigonal bipyramidal coordination around the Cu atoms. The average Cu—O bond distance is 1·902 (7) Å while the average Cu—Cl bond length is 2·417 (30) Å. Deviations of the coordination polyhedron from ideal trigonal bipyramidal symmetry in this and related compounds are also examined.

Introduction. The first example of the general class of compounds of the form $[Cu_4OX_6L_4]$ was described by Bertrand & Kelley (1966) (X = Cl and L = triphenylphosphine), see Fig. 1. It is now clear that the thermodynamic factors governing the formation of these compounds make their preparation relatively favored as evidenced by the facts that they have been encountered during the recrystallization of other products (Ainscough, Bingham, Brodie & Brown, 1984; Bertrand, 1967; Bertrand & Kelley, 1966, 1970; Davies & El-Sayed, 1983; El-Toukhy, Guang-Zuan, Davies, Gilbert, Onan & Veidis, 1984; Watt & Durney, 1974); as unexpected major products during the attempted synthesis of some other species (Harlow & Simonsen, 1977; Yampol'skaya & Ablov, 1976); as minor by-products (Kilbourn & Dunitz, 1967; Churchill, de Boer & Mendak, 1975; Carr & Harrod, 1972) and in other ways (Belford, Fenton & Truter, 1972; Davies, El-Shazly, Rupich, Churchill & Rotella, 1978; Churchill & Rotella, 1979; de Boer,

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