Crystal and Molecular Stucture of (*NN*-Dimethylbenzylamine-2*C*,*N*)-(*N*-phenylsalicylaldiminato)palladium(II)

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The title compound crystallizes in the monoclinic space group $P2_1$, with a = 8·629(5), b = 10·755(8), c = 11·116(9) Å, β = 107·2(1)°, and Z = 2. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined to R 0·048 for 1967 independent non-zero reflections. The crystals are built up of discrete molecules, the palladium atom having approximate square planar geometry, with the two nitrogen atoms mutually *trans*. Bond distances are: Pd–O 2·094, Pd–N(1)(imine) 2·037, Pd–N(2)(amine) 2·090, and Pd–C(16) 1·981 Å.

REACTION of the chloro-bridged dimer di-μ-chloro-bis-[(*NN*-dimethylbenzylamine-2*C*,*N*)metal], [(dmba)MCl]$_2$, where metal = Pd or Pt, with the thallium(I) salt of the Schiff-base *N*-phenylsalicylaldimine, (Hsal:NPh), in dichloromethane yields complexes of the type (dmba)M(sal:NPh).[1] N.m.r. data indicate that the two nitrogen donor-atoms occupy *trans*-positions around the central metal atom. The platinum derivative crystallizes in two crystal modifications.

In order to confirm the *trans*-nature of the nitrogen donor-atoms and to assist in the investigation of the two crystal modifications of the platinum derivative the crystal structure of [(dmba)Pd(sal:NPh)] has been determined.

EXPERIMENTAL

Crystal Data.—$C_{22}H_{22}N_2OPd$, M = 436·8, Monoclinic, a = 8·629(5), b = 10·755(8), c = 11·116(9) Å, β = 107·2(1)°, U = 985·5 Å^3. D_m = *ca.* 1·50 g cm^{-3} (by flotation), Z = 2, D_c = 1·46 g cm^{-3}, $F(000)$ = 444. Cu-K_α radiation, λ = 1·5418 Å, μ(Cu-K_α) = 78·8 cm^{-1}. Space group $P2_1/m$ (C^2_{2h}, No. 11) or $P2_1$ (C^2_2, No. 4) from systematic absences $0k0$ for $k = 2n + 1$, shown to be the latter by the subsequent successful structure determination. No physical tests for the absence of centrosymmetry were carried out.

Unit-cell parameters were determined by use of a standard Philips PW 1100 *X*-ray diffractometer computer programme, which investigates rows in the reciprocal lattice through the origin and scans the four highest weighted reflections and their anti-reflections (weighted by intensity and sin θ). The centres of gravity of these eight profiles are then used in a least-squares refinement of the spacing for that row.

Intensity Measurements.—The intensity data were measured on a Philips PW 1100 automatic *X*-ray diffractometer, with graphite-monochromated Cu-K_α radiation, from a crystal of dimensions 0·18 × 0·21 × 0·14 mm. 2022 reflections of the unique data set with θ(Cu-K_α) <70° were collected, of which 1967 having $F_o^2 > 3\sigma(F_o^2)$ were used in the subsequent refinement. Three nearly orthogonal standard reflections, monitored every 2 h throughout data collection, showed no significant variation in intensity. Data were collected with a θ—2θ scan and a symmetric scan range of ±1·20° in 2θ from the calculated scattering angle at a scan rate of 0·0168° s^{-1}.

Intensity data were processed by use of a programme[2] written specifically for the PW 1100 diffractometer. Background-corrected intensities were assigned standard deviations according to: $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where CT is the total integrated peak count obtained in a scan time, t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$; p was 0·04. The inclusion of this last term is to allow for 'machine errors.' The values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects. A spherical absorption correction (r = 0·008 cm) was also applied.

Structure Determination and Refinement.—In the least-squares calculations, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$.

If the space group were $P2_1/m$ the molecule would be required to possess internal symmetry (no. of equivalent positions for $P2_1/m$ is 4 and Z = 2). It was obvious that the molecule could not possess a centre of symmetry and it was considered unlikely that the molecule would be perfectly flat, a requirement for the presence of a mirror plane. Thus the structure determination and refinement were carried out in space group $P2_1$, which implies no molecular symmetry constraints except that all the molecules in a single crystal should be of one enantiomeric form.

The palladium atom was found by Patterson methods and several structure-factor calculations, each followed by a difference-Fourier synthesis, enabled location of the other 25 non-hydrogen atoms; R was then 0·229. Three full-matrix least-squares refinement cycles of all atomic positional co-ordinates (except the y co-ordinate of Pd which was set at zero to define the origin of the cell) and isotropic temperature factors gave R 0·109 and R' 0·110 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. The Fourier synthesis indicated that anisotropic thermal parameters should be introduced for the metal atom at this stage and after several block-diagonal least-squares refinement cycles the positional and thermal parameters converged to give R 0·051 and R' 0·072.

Idealized co-ordinates for the hydrogen atoms (Table 1) were calculated assuming C–H 1·07 Å, and the position agreed well with peaks in the difference Fourier.

A final structure-factor calculation including all hydrogen atoms, which were assigned isotropic thermal parameters of 1 Å^2 greater than B for the carbon to which they were bonded, gave R 0·048 and R' 0·071. The hydrogen atom parameters were not refined.

The final difference-Fourier synthesis had no major characteristics >0·2 eÅ^{-3}. Final observed and calculated structure factors are given in Supplementary Publication No. SUP 21007 (4 pp., 1 microfiche).*

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

[1] B. E. Reichert and B. O. West, *J. Organometallic Chem.*, 1973, **54**, 391.

[2] J. Hornstra and B. Stubbe, PW 1100 Data Processing Program, Philips Research Laboratories, Eindhoven, Holland.

Final parameters for all non-hydrogen atoms are listed in Table 2, together with their estimated standard deviations, which were derived from the inverse least-squares matrix. Atomic scattering factors used were taken from ref. 3.

Table 1

Idealized hydrogen atom positions

	x/a	y/b	z/c
HC(2)	0·456	−0·035	0·765
HC(3)	0·696	0·095	0·843
HC(4)	0·760	0·257	0·710
HC(5)	0·603	0·274	0·489
HC(7)	0·430	0·183	0·311
HC(9)	0·117	−0·074	0·123
HC(10)	0·045	−0·054	−0·105
HC(11)	0·059	0·151	−0·194
HC(12)	0·161	0·334	−0·057
HC(13)	0·244	0·303	0·177
HC(17)	−0·089	0·205	0·170
HC(18)	−0·367	0·233	0·029
HC(19)	−0·572	0·070	0·017
HC(20)	−0·514	−0·095	0·162
HC(22)A	−0·172	−0·233	0·299
HC(22)B	−0·313	−0·183	0·373
HC(14)A	−0·209	−0·044	0·485
HC(14)B	−0·225	−0·091	0·568
HC(14)C	−0·046	−0·003	0·613
HC(15)A	0·061	−0·276	0·469
HC(15)B	0·106	−0·184	0·604
HC(15)C	−0·073	−0·272	0·560

Table 2

Fractional co-ordinates and isotropic thermal parameters,* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Pd	0·07288(5)	0·0	0·37567(4)	*
N(1)	0·2246(8)	0·0919(7)	0·2964(6)	3·41(11)
N(2)	−0·0791(10)	−0·1090(9)	0·4481(7)	4·84(15)
O	0·2653(8)	−0·0338(7)	0·5383(6)	5·14(14)
C(1)	0·3902(11)	0·0372(8)	0·5738(8)	4·28(16)
C(2)	0·4877(14)	0·0297(12)	0·7031(11)	6·19(24)
C(3)	0·6211(15)	0·1052(15)	0·7482(12)	6·55(26)
C(4)	0·6604(15)	0·1953(13)	0·6718(11)	5·89(23)
C(5)	0·5718(13)	0·2058(11)	0·5475(9)	4·88(18)
C(6)	0·4397(10)	0·1260(9)	0·4974(8)	4·01(15)
C(7)	0·3624(10)	0·1343(9)	0·3626(8)	3·92(14)
C(8)	0·1821(10)	0·1098(9)	0·1617(8)	4·05(15)
C(9)	0·1280(10)	0·0155(11)	0·0832(7)	4·43(14)
C(10)	0·0852(14)	0·0254(13)	−0·0452(10)	6·12(24)
C(11)	0·0954(18)	0·1395(19)	−0·0939(15)	7·67(32)
C(12)	0·1527(19)	0·2445(16)	−0·0168(13)	7·04(29)
C(13)	0·1979(14)	0·2265(12)	0·1146(9)	5·21(20)
C(14)	−0·1444(13)	−0·0344(10)	0·5347(9)	5·23(20)
C(15)	0·0103(20)	−0·2187(16)	0·5264(12)	7·26(31)
C(16)	−0·1385(10)	0·0307(8)	0·2477(7)	3·87(15)
C(17)	−0·1792(13)	0·1368(11)	0·1681(10)	5·13(19)
C(18)	−0·3371(16)	0·1522(14)	0·0875(12)	6·30(24)
C(19)	−0·4539(18)	0·0624(15)	0·0841(13)	6·85(27)
C(20)	−0·4197(15)	−0·0305(13)	0·1620(11)	6·71(28)
C(21)	−0·2613(13)	−0·0494(11)	0·2480(9)	4·95(18)
C(22)	−0·2125(15)	−0·1554(14)	0·3414(11)	6·10(24)

* Pd anisotropic temperature factors of the form: $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$, with parameters ($\times 10^2$):

B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
379(2)	280(2)	417(2)	−2(2)	181(2)	26(2)

Calculations.—The major calculations during the refinement were carried out by use of modified versions of the full-matrix least-squares refinement programme of Busing, Martin, and Levy,[4] the block-diagonal least-squares programme of Shiono,[5] and the Fourier programme of White.[6] All diagrams were drawn by use of the programme ORTEP.[7]

DESCRIPTION AND DISCUSSION OF STRUCTURE

The crystals are built up of discrete molecules of (dmba)Pd(sal:NPh), a stereoscopic view and numbering scheme of which is given in Figure 1. Figure 2 shows the packing arrangement (including hydrogen atoms) and Table 3 gives all relevant bond lengths and angles together with their estimated standard deviations.

Table 3

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths

Pd–N(1)	2·037(8)	C(5)–C(6)	1·403(14)
Pd–N(2)	2·090(10)	C(6)–C(7)	1·452(12)
Pd–O	2·094(6)	C(8)–C(9)	1·330(13)
Pd–C(16)	1·981(7)	C(8)–C(13)	1·382(16)
N(1)–C(7)	1·284(10)	C(9)–C(10)	1·369(13)
N(1)–C(8)	1·445(11)	C(10)–C(11)	1·354(24)
N(2)–C(14)	1·486(15)	C(11)–C(12)	1·416(24)
N(2)–C(15)	1·532(18)	C(12)–C(13)	1·410(17)
N(2)–C(22)	1·474(13)	C(16)–C(17)	1·423(14)
O–C(1)	1·284(11)	C(16)–C(21)	1·366(14)
C(1)–C(2)	1·437(14)	C(17)–C(18)	1·402(15)
C(1)–C(6)	1·425(14)	C(18)–C(19)	1·388(21)
C(2)–C(3)	1·376(18)	C(19)–C(20)	1·298(20)
C(3)–C(4)	1·395(21)	C(20)–C(21)	1·431(14)
C(4)–C(5)	1·372(14)	C(21)–C(22)	1·516(17)

(*b*) Angles

N(1)–Pd–O	90·6(3)	C(2)–C(1)–C(6)	116·3(9)
N(1)–Pd–C(16)	100·5(3)	C(1)–C(2)–C(3)	120·7(11)
N(2)–Pd–O	89·8(3)	C(2)–C(3)–C(4)	121·1(12)
N(2)–Pd–C(16)	79·7(3)	C(3)–C(4)–C(5)	120·4(12)
Pd–N(1)–C(7)	122·0(6)	C(4)–C(5)–C(6)	119·7(10)
Pd–N(1)–C(8)	121·0(6)	C(1)–C(6)–C(5)	121·7(9)
C(7)–N(1)–C(8)	117·0(7)	C(9)–C(8)–C(13)	120·0(9)
Pd–N(2)–C(14)	110·4(6)	C(8)–C(9)–C(10)	124·0(9)
Pd–N(2)–C(15)	112·5(8)	C(9)–C(10)–C(11)	117·3(12)
Pd–N(2)–C(22)	108·0(7)	C(10)–C(11)–C(12)	112·2(15)
C(14)–N(2)–C(15)	105·8(9)	C(11)–C(12)–C(13)	117·2(14)
Pd–O–C(1)	122·8(6)	C(8)–C(13)–C(12)	119·3(11)
Pd–C(16)–C(21)	116·3(7)	C(17)–C(16)–C(21)	117·2(9)
O–C(1)–C(6)	126·0(9)	C(16)–C(17)–C(18)	120·5(10)
C(1)–C(6)–C(7)	122·0(8)	C(17)–C(18)–C(19)	119·7(12)
N(1)–C(7)–C(6)	129·4(8)	C(18)–C(19)–C(20)	119·9(14)
C(16)–C(21)–C(22)	114·6(9)	C(19)–C(20)–C(21)	122·5(13)
N(2)–C(22)–C(21)	106·8(10)	C(16)–C(21)–C(20)	119·9(10)

The square-planar co-ordination of the palladium atom is slightly distorted towards tetrahedral geometry,

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[3] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[4] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, A Fortran Crystallographic Least-Squares Programme, Oak Ridge National Laboratory, Tennessee, Report ORNL TM 305, 1962.

[5] R. Shiono, Department of Crystallography, University of Pittsburgh, Pa. 15213, U.S.A.

[6] J. C. B. White, Melbourne University Fourier Programme MUFR3. See J. S. Rollett in 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' eds. R. Pepkinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford, 1961, p. 87.

[7] C. K. Johnson, ORTEP, Fortran Ellipsoid Plot Programme for Crystal Structure Illustrations, Oak Ridge National Laboratory, Tennessee, Report ORNL 3794.

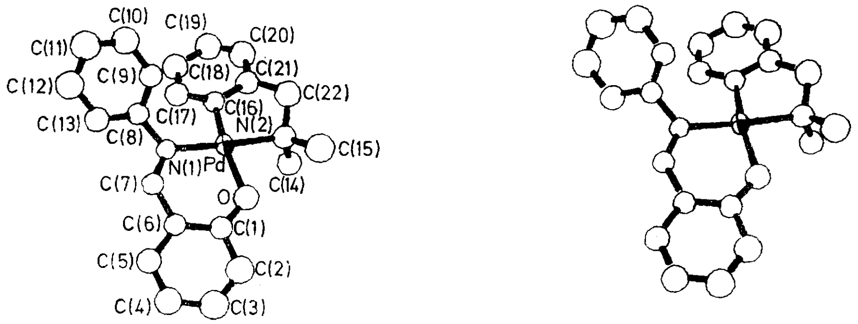

FIGURE 1 A stereoscopic view of the molecule with hydrogen atoms omitted for clarity. Thermal ellipsoid for Pd drawn at the 50% level

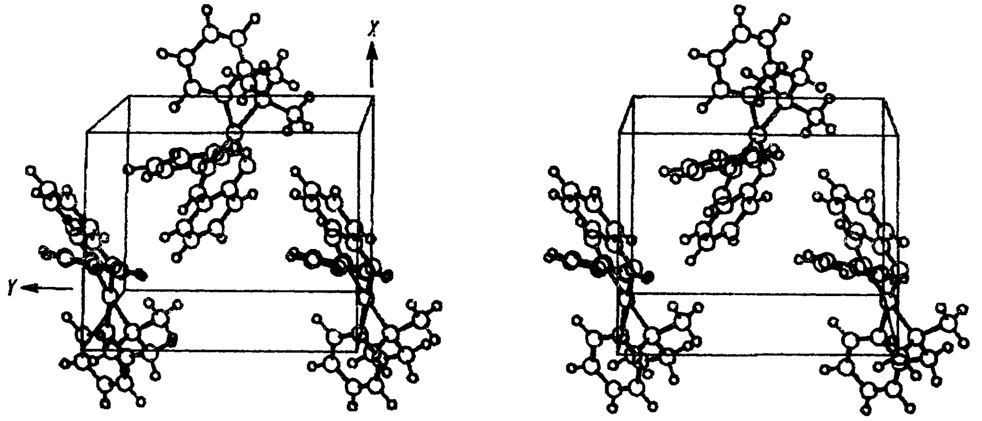

FIGURE 2 The packing arrangement of the molecule viewed down c^*. Thermal ellipsoids for all non-hydrogen atoms have been assigned the same value, and those for hydrogen have been reduced, for clarity

TABLE 4

Equations of mean planes in the form $lX + mY + nZ - p = 0$ where X, Y, and Z are orthogonal axes. Deviations (Å) of atoms in the plane and other relevant atoms are given in square brackets

Plane (1)	l	m	n	p
Pd, N(1), O	0·3284	−0·8582	−0·3946	−1·7733
[N(2) 0·194(9), C(16) −0·208(8)]				
Plane (2)				
Pd, N(1), O, C(1), C(6), C(7)	0·5333	−0·7921	−0·2969	−1·3212
[Pd −0·187(0), N(1) 0·118(7), O 0·189(7), C(1) −0·016(9), C(6) −0·169(10), C(7) 0·066(9)]				
Plane (3)				
Pd, N(2), C(16), C(21). C(22)	0·5216	−0·6757	−0·5210	−2·5528
[Pd 0·158(0), N(2) −0·259(9), C(16) −0·089(8), C(21) −0·062(11), C(22) 0·251(14)]				
Plane (4)				
Pd, N(2), C(16), C(21)	0·4234	−0·7660	−0·4837	−2·2614
[Pd 0·075(0), N(2) −0·055(9), C(16) −0·115(8), C(21) 0·095(11), C(22) 0·536(14)]				
Plane (5)				
N(1), O, C(1)—(7)	0·6836	−0·6911	−0·2347	−0·7014
[N(1) −0·062(7), O −0·035(7), C(1) 0·006(10), C(2) 0·024(13), C(3) 0·036(15), C(4) −0·040(14), C(5) −0·051(12), C(6) 0·000(10), C(7) 0·122(9)]				

the deviations of N(2) and C(16) from the plane containing Pd, N(1), and O being 0·194(9) and −0·208(8) Å. Table 4 lists this plane and several others of interest.

The Pd–N(1) bond length [2·037(8) Å] is similar to those lengths in other palladium–Schiff-base complexes.[8-10] The Pd–O bond length [2·094(6) Å] is significantly longer (10σ) than that in any other similar complex,[8-10] which may be due to the *trans*-effect of the σ-carbon bond.[1,11,12] Bond lengths and angles of the Schiff base are similar to those in bis-(*N*-phenylsalicylaldiminato)copper(II) complexes,[13,14] and the Schiff-base moiety is planar, making an angle of 24° 27′ with the Pd, N(1), O plane.

The Pd–N(2) bond distance is similar to those in other amine complexes.[15,16] The Pd–C(16) σ-bond length

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[8] E. Frasson, C. Panattoni, and L. Sacconi, *Acta Cryst.*, 1964, **17**, 85.

[9] R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, 1967, **22**, 787.

[10] P. C. Jain and E. C. Lingafelter, *Acta Cryst.*, 1967, **23**, 127.

[11] G. Bombieri, L. Caglioti, L. Cattalini, E. Forsellini, F. Gasparrini, R. Graziani, and P. A. Vigato, *Chem. Comm.*, 1971, 1415.

[12] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91.

[13] L. Wei, R. M. Stogsdill, and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1058.

[14] D. Hall, S. V. Sheat-Rumball, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 2721.

[15] A. J. Carty and P. C. Chieh, *J.C.S. Chem. Comm.*, 1972, 158.

[16] G. J. Palenik and G. R. Clark, *Inorg. Chem.*, 1970, **9**, 2754, and references therein.

[1·981(7) Å] is similar to the Pd–C(σ) bond distance [1·998(13) Å] in *trans*-Pd(PEt$_3$)(C$_{12}$H$_9$N$_2$)Cl [17] and in the palladium complex of biacetyl-bis-(*N*-methyl-*N*-phenyl)-osazone [1·94(2) Å],[11] but is significantly shorter (10σ) than the 2·05 Å predicted from the sum of the Pd–C(sp^2) σ-bonded covalent radii [Pd^{II} 1·31 and C(sp^2) 0·74].

The five-membered ring formed by the dmba ligand and the metal atom is significantly puckered [Table 4, Plane (4)], C(22) being 0·54(1) Å out of the plane of Pd, N(2), C(16), C(21). The single proton n.m.r. resonance for the hydrogens on C(22) indicates rapid flipping of the ring in solution.[1]

Structural parameters for the dmba ligand are in good agreement with those recently reported.[18] There are no unusual intermolecular contacts, the shortest, excluding hydrogen atom contacts, being 3·36 Å between Pd and C(15).

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[17] R. W. Siekman and D. L. Weaver, *Chem. Comm.*, 1968, 1021; D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2250.

[18] R. G. Little and R. J. Doedens, *Inorg. Chem.*, 1973, **12**, 844.