

**The Crystal and Molecular Structures of *N,N'*-*o*-Phenylenebis(salicylaldiminato)-palladium(II) and  $\mu$ -*N,N'*-*o*-Phenylenebis(salicylaldiminato)-{bis[(2-*C,N*-acetophenone oxime)palladium(II)]}**

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Pd(salophen) crystals are orthorhombic, space group  $P2_12_12_1$ , with  $a=16.786$  (16),  $b=17.677$  (18),  $c=5.336$  (6) Å,  $Z=4$ . The structure was solved by Patterson and Fourier techniques, refined to  $R=0.078$  from 995 observed reflexions, and consists of discrete molecules, the Pd atom having approximate square-planar geometry. (ApoPd)<sub>2</sub>salophen crystals are monoclinic, space group  $P2_1/c$ , with  $a=7.109$  (4),  $b=25.321$  (13),  $c=17.979$  (8) Å,  $\beta=107.8$  (4)°,  $Z=4$ . The structure was solved by Patterson and Fourier techniques, refined to  $R=0.061$  from diffractometer data (3119 observed reflexions), and consists of discrete binuclear units, the salophen ligand bridging the two metal centres. The square-planar coordination about each Pd atom is completed by the acetophenone oxime ligand.

### Introduction

It has been proposed that salen and several of its derivatives can bridge two metal centres (Cozens, Murray & West, 1971; Reichert & West, 1972, 1973; Murray, Reichert & West, 1973), as has been shown for Co<sub>2</sub>(3MeOsalen)<sub>3</sub> by Calligaris, Nardin & Randaccio (1970), in which a 3-MeOsalen ligand acts as a bis-bidentate ligand occupying two *cis* coordination positions of each Co atom. This bridging arrangement, it had been suggested (Cozens, Murray & West, 1971), could not occur in the closely related ligand, *N,N'*-*o*-phenylenebis(salicylalimine) (salophen), due to conjugation in the ligand. A recent report by Murray, Reichert & West (1973) and Reichert (1974) on dimethylgold complexes, *viz* [Me<sub>2</sub>Au]<sub>2</sub>salophen and several Pd complexes, (dmbaPd)<sub>2</sub>salophen (dmba = *N,N*-dimethylbenzylamine), and (ApoPd)<sub>2</sub>salophen (Apo = acetophenone oxime), has thrown doubt on this conjecture.

The present paper describes the crystal and molecular structure of (ApoPd)<sub>2</sub>salophen and of Pd(salophen). A preliminary report of the (ApoPd)<sub>2</sub>salophen structure has been published (Fallon, Gatehouse, Reichert & West, 1974).

### Experimental

A sample of Pd(salophen), recrystallized from dichloromethane, gave fine needles which proved very difficult to shape because of their marked fibrous nature. A crystal, 0.1 × 0.1 × 0.2 mm, was finally obtained, from which intensities were collected.

#### Crystal data

(a) Pd(salophen). C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Pd,  $M=418.7$ , orthorhombic,  $a=16.786$  (16),  $b=17.677$  (18),  $c=5.336$  (6) Å,  $U=1583.3$  Å<sup>3</sup>.  $D_m=1.75$  (3) (by flotation in

carbon tetrachloride/1,1,2,2-tetrabromoethane),  $Z=4$ ,  $D_c=1.74$  g cm<sup>-3</sup>,  $F(000)=832$ ,  $\mu=11.7$  cm<sup>-1</sup> for Mo  $K\alpha$  radiation ( $\lambda=0.7107$  Å). Space group  $P2_12_12_1$  from systematic absences:  $h00$ ,  $h$  odd;  $0k0$ ,  $k$  odd;  $00l$ ,  $l$  odd. Unit-cell parameters were determined with a Philips PW 1100 diffractometer (Gatehouse & Miskin, 1974).

(b) (ApoPd)<sub>2</sub>salophen. C<sub>36</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>Pd<sub>2</sub>,  $M=797.5$ , monoclinic,  $a=7.109$  (4),  $b=25.321$  (13),  $c=17.979$  (8) Å,  $\beta=107.8$  (4)°,  $U=3081.4$  Å<sup>3</sup>.  $D_m=1.72$  (1) (by flotation),  $Z=4$ ,  $D_c=1.72$  g cm<sup>-3</sup>,  $F(000)=1592$ ,  $\mu=101.5$  cm<sup>-1</sup> for Cu  $K\alpha$  radiation ( $\lambda=1.5418$  Å). Space group  $P2_1/c$  from systematic absences:  $h0l$ ,  $l$  odd;  $0k0$ ,  $k$  odd. Unit-cell parameters were determined as described above.

#### Intensity measurements

(a) Pd(salophen). Data were collected to  $2\theta=56^\circ$  by the  $\omega$ -scan technique with graphite-monochromated Mo  $K\alpha$  radiation and a symmetric scan range of  $\pm 0.60^\circ$  in  $\omega$  from the calculated Bragg scattering angle, at a scan rate of  $0.03^\circ$  s<sup>-1</sup>. Of the 2210 unique reflexions measured, 995 were considered observed [ $F_o^2 > 3\sigma(F_o^2)$ ] and used in the subsequent refinement. Three reflexions measured at hourly intervals showed no systematic variation in intensity.

(b) (ApoPd)<sub>2</sub>salophen. A single crystal,  $0.07 \times 0.07 \times 0.09$  mm, was used to collect intensities by  $\omega$  scans for  $2\theta \leq 90^\circ$  and  $\theta-2\theta$  scans for  $90^\circ < 2\theta < 120^\circ$ , with a symmetric scan range of  $\pm 0.70^\circ$  in  $\omega$  from the calculated Bragg angle, at a scan rate of  $0.02^\circ$  s<sup>-1</sup>, with graphite-monochromated Cu  $K\alpha$  radiation. Of the 4562 unique reflexions measured, 3122 were found to be statistically above background,  $F_o^2 > 3\sigma(F_o^2)$ , and used in the subsequent refinement. No systematic variation was observed in three standard reflexions, measured at two-hourly intervals.

Both sets of data were processed with a program

written specifically for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). The background-corrected intensities were assigned standard deviations according to:  $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$  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  $I = CT - (t_c/t_b)(B_1 + B_2)$ ;  $\rho$  was 0.04. Values of  $I$  and  $\sigma(I)$  were then corrected for Lorentz and polarization effects. Neither extinction nor absorption corrections were applied.

### Structure determination and refinement

#### (a) Pd(salophen)

The position of the Pd atom was found by Patterson methods and two structure-factor calculations, each followed by a difference synthesis, gave the positions of all non-hydrogen atoms. After full-matrix least-squares refinement all positional and isotropic thermal parameters converged to give  $R_1$  0.090 and  $R_2$  0.087 ( $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ). A difference synthesis clearly showed that the Pd atom should be assigned an anisotropic temperature factor; this resulted in  $R_1$  0.082 and  $R_2$  0.080.

Table 1. Pd(salophen), idealized hydrogen-atom positions ( $\times 10^3$ )

	x	y	z
HC(2)	123	314	828
HC(3)	171	425	1008
HC(4)	303	463	935
HC(5)	360	425	546
HC(7)	382	330	253
HC(9)	-20	72	130
HC(10)	-68	-7	-167
HC(11)	12	-48	-522
HC(12)	143	-1	-533
HC(14)	247	74	-421
HC(16)	473	282	32
HC(17)	545	236	-305
HC(18)	494	144	-573
HC(19)	364	94	-495

Inclusion of H atoms, which were revealed in a difference map calculated with the final parameters, in their idealized positions (Table 1) with isotropic thermal parameters of  $5.0 \text{ \AA}^2$  gave  $R_1$  0.078 and  $R_2$  0.075.

#### (b) (ApoPd)<sub>2</sub>salophen

From the Patterson map a trial position for the two Pd atoms was found, and gave  $R_1$  0.264 when assigned thermal parameters of  $3.0 \text{ \AA}^2$ . All ligand non-hydrogen atoms were located from a difference synthesis and inclusion of these, all atoms being assigned an isotropic thermal parameter of  $3.0 \text{ \AA}^2$ , gave  $R_1$  0.131 and  $R_2$  0.165. Refinement was carried out by block-diagonal least squares to enable all positional and thermal parameters to be varied simultaneously. All variables converged to give  $R_1$  0.069 and  $R_2$  0.085.

A difference synthesis showed anisotropic thermal motion for each Pd atom which, when introduced into the refinement, gave  $R_1$  0.066 and  $R_2$  0.075. The subsequent difference synthesis revealed all H atoms, ex-

Table 2. (ApoPd)<sub>2</sub>salophen, idealized hydrogen-atom positions ( $\times 10^3$ )

	x	y	z
HO(2)	596	290	161
HC(2)	861	422	442
HC(3)	937	517	438
HC(4)	834	566	312
HC(5)	671	519	191
HC(10)	513	173	194
HC(11)	542	89	270
HC(12)	594	90	408
HC(13)	618	173	479
HC(15)	586	263	481
HC(17)	829	332	554
HC(18)	781	395	647
HO(2')	33	280	181
HC(2')	207	348	501
HC(3')	197	289	611
HC(4')	160	193	589
HC(5')	88	158	458
HC(10')	-83	380	63
HC(11')	-108	472	20
HC(12')	51	543	109
HC(13')	214	523	246
HC(15')	361	465	344
HC(17')	285	460	470
HC(18')	516	460	606

Table 3. Pd(salophen), final positional parameters ( $\times 10^4$ ) and isotropic thermal parameters

	x	y	z	B ( $\text{\AA}^2$ )
Pd	2154 (2)	1920 (2)	1564 (4)	*
O(1)	1746 (10)	2463 (10)	4535 (36)	2.8 (4)
O(2)	1131 (10)	1382 (10)	1465 (42)	3.6 (4)
N(1)	3186 (10)	2440 (10)	1478 (47)	2.1 (4)
N(2)	2586 (11)	1394 (11)	-1454 (45)	2.4 (4)
C(1)	2087 (14)	3073 (14)	5613 (44)	2.3 (4)
C(2)	1712 (16)	3383 (15)	7701 (55)	3.1 (6)
C(3)	2030 (17)	3992 (16)	8871 (60)	4.1 (6)
C(4)	2776 (17)	4272 (15)	8257 (65)	3.9 (6)
C(5)	3146 (16)	3974 (16)	6224 (65)	3.9 (6)
C(6)	2874 (18)	3314 (14)	4957 (54)	3.3 (6)
C(7)	3327 (14)	3016 (16)	2903 (52)	3.1 (6)
C(8)	908 (16)	913 (16)	-303 (58)	3.2 (6)
C(9)	146 (15)	578 (14)	-150 (55)	2.6 (6)
C(10)	-144 (14)	115 (13)	-1907 (54)	2.3 (5)
C(11)	335 (16)	-129 (16)	-3949 (60)	3.6 (6)
C(12)	1093 (16)	164 (16)	-4005 (60)	3.6 (6)
C(13)	1400 (15)	649 (14)	-2342 (50)	2.5 (5)
C(14)	2188 (16)	926 (13)	-2745 (47)	2.5 (5)
C(15)	3683 (14)	2196 (13)	-447 (50)	2.0 (5)
C(16)	4483 (14)	2458 (14)	-821 (49)	2.3 (6)
C(17)	4912 (16)	2169 (14)	-2752 (56)	2.9 (3)
C(18)	4615 (14)	1631 (14)	-4377 (51)	2.4 (6)
C(19)	3866 (15)	1344 (14)	-3897 (54)	2.8 (6)
C(20)	3399 (13)	1640 (12)	-1978 (48)	1.8 (4)

\* Pd anisotropic temperature factor of the form:

$\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ , with parameters ( $\times 10^5$ ):

$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
155 (6)	177 (5)	2511 (66)	6 (6)	-53 (28)	-74 (27)

Table 4. (ApoPd)<sub>2</sub>salophen, final positional parameters ( $\times 10^4$ ) and isotropic thermal parameters

	x	y	z	B (Å <sup>2</sup> )
Pd	6396 (2)	3402 (1)	3001 (1)	*
Pd'	1391 (2)	3229 (1)	3182 (1)	*
N(1)	6066 (23)	3638 (7)	1911 (9)	4.4 (3)
N(2)	6134 (20)	3189 (6)	4054 (8)	3.3 (3)
O(1)	5598 (18)	2658 (5)	2554 (8)	4.5 (3)
O(2)	5456 (22)	3277 (6)	1295 (9)	5.9 (3)
C(1)	7217 (27)	4162 (8)	3189 (11)	3.8 (4)
C(2)	8191 (27)	4427 (8)	3874 (11)	3.8 (4)
C(3)	8613 (30)	4966 (9)	3852 (12)	5.0 (5)
C(4)	8049 (33)	5247 (9)	3134 (13)	5.3 (5)
C(5)	7118 (29)	4981 (8)	2453 (12)	4.7 (4)
C(6)	6742 (27)	4442 (7)	2467 (11)	3.6 (4)
C(7)	5935 (27)	4130 (8)	1759 (11)	4.1 (4)
C(8)	4994 (33)	4351 (9)	934 (14)	5.6 (5)
C(9)	5689 (29)	2234 (8)	2967 (12)	4.4 (4)
C(10)	5424 (32)	1737 (9)	2560 (13)	5.2 (5)
C(11)	5558 (34)	1265 (10)	2988 (13)	5.7 (5)
C(12)	5830 (33)	1265 (9)	3777 (13)	5.6 (5)
C(13)	6011 (31)	1735 (9)	4182 (13)	4.9 (4)
C(14)	5960 (29)	2239 (8)	3784 (12)	4.4 (4)
C(15)	5992 (26)	2695 (7)	4239 (10)	3.6 (4)
C(16)	5873 (25)	3569 (7)	4596 (10)	3.2 (3)
C(17)	7094 (28)	3587 (8)	5353 (11)	4.1 (4)
C(18)	6832 (30)	3953 (8)	5880 (12)	4.7 (4)
N(1')	386 (21)	2522 (6)	2770 (8)	3.6 (3)
N(2')	2917 (20)	3903 (6)	3603 (8)	3.2 (3)
O(1')	808 (17)	3481 (5)	2037 (7)	3.6 (2)
O(2')	-96 (20)	2404 (6)	1979 (8)	4.8 (3)
C(1')	1513 (25)	2865 (7)	4172 (10)	3.3 (3)
C(2')	1820 (27)	3066 (8)	4915 (11)	4.1 (4)
C(3')	1788 (31)	2732 (9)	5543 (12)	5.0 (5)
C(4')	1518 (30)	2193 (9)	5414 (12)	4.9 (4)
C(5')	1161 (30)	1995 (8)	4683 (12)	4.6 (4)
C(6')	1132 (26)	2317 (7)	4062 (11)	3.6 (4)
C(7')	657 (26)	2122 (8)	3245 (11)	3.7 (4)
C(8')	478 (32)	1551 (9)	2989 (13)	5.2 (5)
C(9')	737 (24)	3972 (7)	1833 (10)	3.2 (3)
C(10')	-193 (27)	4108 (8)	1043 (11)	3.9 (4)
C(11')	-324 (30)	4629 (8)	789 (11)	4.3 (4)
C(12')	571 (29)	5033 (8)	1298 (12)	4.7 (4)
C(13')	1508 (26)	4916 (8)	2068 (10)	3.7 (4)
C(14')	1647 (25)	4392 (7)	2356 (10)	3.1 (3)
C(15')	2762 (26)	4319 (7)	3164 (11)	3.5 (4)
C(16')	4299 (23)	3925 (7)	4366 (9)	2.8 (3)
C(17')	4045 (28)	4309 (8)	4881 (11)	4.1 (4)
C(18')	5333 (29)	4313 (8)	5651 (12)	4.5 (4)

\* Pd anisotropic temperature factors of the form:

$\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ , with parameters ( $\times 10^5$ ):

$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
2135 (35)	120 (2)	261 (5)	-8 (8)	260 (10)	-15 (3)
2099 (33)	91 (2)	188 (4)	-16 (7)	207 (9)	-3 (3)

cept those associated with the methyl groups, which were included in their idealized positions (Table 2) with fixed isotropic thermal parameters  $1 \text{ \AA}^2$  greater than the atom to which they are attached, and gave  $R_1$  0.062 and  $R_2$  0.070. At this point reflexions 021, 002 and 012 were marked as extinction affected and given zero weight. At convergence  $R_1 = 0.061$  and  $R_2 = 0.069$ .

Cromer & Waber (1965) was used as the source for Pd, O, N and C scattering factors and Ibers (1962)

for H, for both structures. Final positional and thermal parameters for all non-hydrogen atoms are given in Table 3\* for Pd(salophen) and Table 4 for (ApoPd)<sub>2</sub>salophen, with their estimated standard deviations derived from the inverse least-squares matrix.

The major calculations were carried out with modified versions of the full-matrix least-squares refinement program of Busing, Martin & Levy (1962), the block-diagonal least-squares program of Shiono (1968) and the Fourier summation program of White (1965). All diagrams were drawn with ORTEP (Johnson, 1965). All major calculations were performed on the Monash University CDC 3200 computer.

## Results and discussion

### (a) Pd(salophen)

Montgomery & Morosin (1961) reported space groups and unit-cell dimensions for the isomorphous complexes, Ni(salophen) ( $P2_12_12_1$ ;  $a = 17.41$ ,  $b = 5.45$ ,  $c = 16.72 \text{ \AA}$ ) and Cu(salophen) ( $P2_12_12_1$ ;  $a = 17.79$ ,  $b = 5.34$ ,  $c = 16.87 \text{ \AA}$ ). These cell dimensions, being similar to those of the present compound, suggest that Ni and Cu(salophen) are isomorphous and probably isostructural with Pd(salophen), which is in contrast to the salen complexes where Ni(salen) ( $Pbca$ ,  $a = 13.82$ ,  $b = 26.13$ ,  $c = 7.48 \text{ \AA}$ ), a centrosymmetric dimer with Ni-Ni bonding (Shkol'nikova, Yumal', Shugam & Voblikova, 1970), is not isostructural with its Cu analogue. Cu(salen) (Hall & Waters, 1960) is monoclinic,  $Cc$ ,  $a = 26.55$ ,  $b = 6.93$ ,  $c = 14.60 \text{ \AA}$ ,  $\beta = 97.5^\circ$ , with Cu-O-Cu-O bonding forming the central unit of the centrosymmetric dimer. The crystal class and cell dimensions of Pd(salen) (monoclinic,  $a = 14.04$ ,  $b = 7.35$ ,  $c = 27.42 \text{ \AA}$ ,  $\beta = 104.7^\circ$ ) determined on a very small, poorly formed crystal, suggest that it is isomorphous with its Cu analogue.

Crystals of Pd(salophen) consist of discrete molecules separated by normal van der Waals contacts, the packing arrangement being shown in Fig. 1. A stereoscopic view and labelling scheme of the molecule are shown in Fig. 2. Relevant bond lengths and angles are given in Table 5. The molecule is almost planar, the Schiff-base moieties, which in themselves are planar (Table 6), being inclined at  $8.9^\circ$  to each other, in a shallow umbrella form which is very common in salen derivatives (Calligaris, Nardin & Randaccio, 1972). The greatest deviant from the molecular mean plane is C(5) being  $0.26 (3) \text{ \AA}$  out of the plane (Table 6).

The O coordination lengths, Table 5, are similar to, but marginally shorter than, those found in Pd bis-bidentate Schiff-base complexes; bis(*N*-butylsilylaldiminato)palladium(II),  $2.00 (2) \text{ \AA}$  (Frasson,

\* A list of observed and calculated structure factors for both structures has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31778 (31 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Panattoni & Sacconi, 1964); bis(*N*-isopropyl-3-ethylsalicylaldiminato)palladium(II), 1·991 (2) Å (Braun & Lingafelter, 1967); and the tetragonal and

monoclinic forms of bis(*N*-isopropyl-3-methylsalicylaldiminato)palladium(II), 1·987 (3) and 1·988 (3) Å respectively (Jain & Lingafelter, 1967), which may be the result of decreased electron density on the coordination atoms due to increased electron delocalization in the ligand through the phenylene bridge.

This delocalization should manifest itself in a shortening of the N(1)–C(15) and N(2)–C(20) lengths.

Table 5. Pd(salophen), bond lengths (Å) and selected angles (°)

Pd–O(1)	1·97 (2)	Pd–N(1)	1·96 (2)
Pd–O(2)	1·96 (2)	Pd–N(2)	2·00 (2)
O(1)–C(1)	1·35 (3)	O(2)–C(8)	1·31 (4)
C(1)–C(2)	1·39 (4)	C(8)–C(9)	1·41 (4)
C(2)–C(3)	1·35 (4)	C(9)–C(10)	1·34 (4)
C(3)–C(4)	1·39 (4)	C(10)–C(11)	1·42 (4)
C(4)–C(5)	1·36 (5)	C(11)–C(12)	1·37 (4)
C(5)–C(6)	1·42 (4)	C(12)–C(13)	1·34 (4)
C(1)–C(6)	1·43 (4)	C(8)–C(13)	1·44 (4)
C(6)–C(7)	1·43 (4)	C(13)–C(14)	1·43 (4)
N(1)–C(7)	1·29 (4)	N(2)–C(14)	1·27 (3)
N(1)–C(15)	1·39 (3)	N(2)–C(20)	1·46 (3)
C(15)–C(16)	1·43 (3)	C(18)–C(19)	1·38 (4)
C(16)–C(17)	1·36 (4)	C(19)–C(20)	1·39 (4)
C(17)–C(18)	1·38 (4)	C(20)–C(15)	1·36 (3)
O(1)–Pd–O(2)	87·4 (8)	Pd–O(1)–C(1)	125·7 (15)
O(1)–Pd–N(1)	95·6 (8)	Pd–N(1)–C(7)	121·1 (17)
O(2)–Pd–N(2)	94·0 (8)	O(1)–C(1)–C(6)	121·7 (22)
N(1)–Pd–N(2)	83·0 (8)	C(1)–C(6)–C(7)	124·5 (24)
		N(1)–C(7)–C(6)	129·9 (25)
Pd–O(2)–C(8)	125·2 (18)	Pd–N(2)–C(20)	110·8 (14)
Pd–N(2)–C(14)	123·5 (17)	Pd–N(1)–C(15)	113·7 (15)
O(2)–C(8)–C(13)	125·7 (25)	N(2)–C(20)–C(15)	115·3 (20)
C(8)–C(13)–C(14)	122·2 (23)	N(1)–C(15)–C(20)	117·1 (21)
N(2)–C(14)–C(13)	129·1 (24)		
C(1)–C(2)–C(3)	120·2 (26)	C(8)–C(9)–C(10)	123·1 (25)
C(2)–C(3)–C(4)	122·1 (28)	C(9)–C(10)–C(11)	121·2 (25)
C(3)–C(4)–C(5)	117·7 (28)	C(10)–C(11)–C(12)	115·2 (26)
C(4)–C(5)–C(6)	123·4 (28)	C(11)–C(12)–C(13)	125·7 (27)
C(5)–C(6)–C(1)	115·1 (24)	C(12)–C(13)–C(8)	119·1 (25)
C(6)–C(1)–C(2)	119·7 (23)	C(13)–C(8)–C(9)	115·2 (24)
C(15)–C(16)–C(17)	118·7 (23)		
C(16)–C(17)–C(18)	123·0 (25)		
C(17)–C(18)–C(19)	117·8 (24)		
C(18)–C(19)–C(20)	120·8 (24)		
C(19)–C(20)–C(15)	121·0 (23)		
C(20)–C(15)–C(16)	118·5 (22)		

Table 6. Pd(salophen), equations of mean planes and deviations (Å) of individual atoms from the planes

*X, Y, Z* are orthogonal coordinates and are related to the fractional coordinates *x, y, z* in the crystal system by the matrix equation

$$\begin{pmatrix} 16\cdot79 & 0 & 0 \\ 0 & 17\cdot68 & 0 \\ 0 & 0 & 5\cdot34 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$

(I) Molecular mean plane

$$-0\cdot3466X + 0\cdot7004Y - 0\cdot6239Z - 0\cdot7536 = 0$$

Pd	-0·151 (3)	O(1)	-0·23 (2)	O(2)	-0·19 (2)
N(1)	-0·08 (2)	N(2)	-0·05 (2)	C(1)	-0·03 (2)
C(2)	-0·12 (3)	C(3)	0·05 (3)	C(4)	0·17 (3)
C(5)	0·26 (3)	C(6)	0·03 (3)	C(7)	0·08 (3)
C(8)	-0·05 (3)	C(9)	-0·07 (3)	C(10)	0·11 (3)
C(11)	0·21 (3)	C(12)	0·15 (3)	C(13)	0·02 (3)
C(14)	0·03 (2)	C(15)	-0·03 (2)	C(16)	-0·05 (3)
C(17)	-0·01 (3)	C(18)	0·04 (3)	C(19)	-0·04 (3)
C(20)	-0·04 (2)				

(II) Plane through O(1), N(1), C(1)–C(7)

$$-0\cdot4422X + 0\cdot6245Y - 0\cdot6438Z + 0\cdot1457 = 0$$

O(1)	0·01 (2)	N(1)	-0·03 (2)	C(1)	0·06 (2)
C(2)	-0·04 (3)	C(3)	0·00 (3)	C(4)	-0·04 (3)
C(5)	0·06 (3)	C(6)	-0·03 (3)	C(7)	0·01 (3)

(III) Plane through O(2), N(2), C(8)–C(14)

$$-0\cdot3484X + 0\cdot7607Y - 0\cdot5476Z - 0\cdot7683 = 0$$

O(2)	0·00 (2)	N(2)	0·02 (2)	C(8)	0·02 (3)
C(9)	-0·03 (3)	C(10)	0·03 (3)	C(11)	0·02 (3)
C(12)	-0·02 (3)	C(13)	-0·03 (3)	C(14)	0·00 (3)

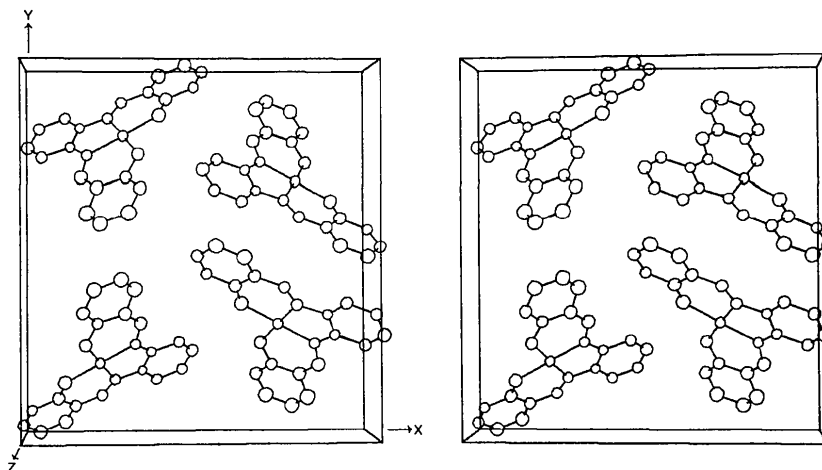


Fig. 1. Pd(salophen). Stereo view of contents of unit cell.

Comparison of N(1)–C(15), 1.39 (3) and N(2)–C(20), 1.46 (3) Å with the individual and average [1.481 (3) Å] analogous N–C distances found in several salen complexes (Calligaris, Nardin & Randaccio, 1972) suggests that this bond may be marginally shorter in the salophen complex. Bond lengths within the rest of the Schiff-base moiety of Pd(salophen) (Table 5) compare favourably with those documented for bidentate Schiff-bases by Lingafelter & Braun (1966) and qua-

dridentate Schiff-bases by Calligaris, Nardin & Randaccio (1972).

(b) (ApoPd)<sub>2</sub>salophen

An illustration of the molecular conformation is shown in Fig. 3, with the labelling scheme for the atoms; the unit-cell contents are shown in Fig. 4. Bridging by the salophen ligand is achieved by twisting the two sal moieties [N(2), O(2), C(9)–C(15) and N(2'),

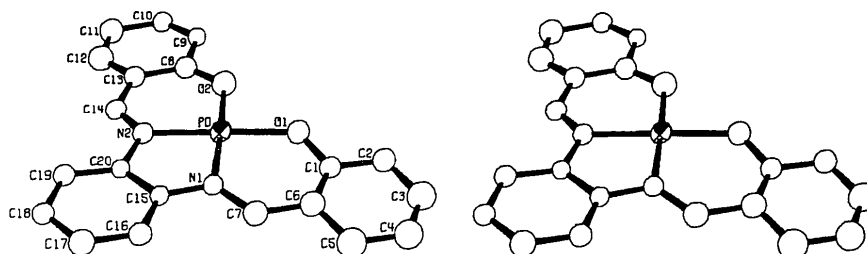


Fig. 2. Pd(salophen). Molecular geometry and labelling scheme.

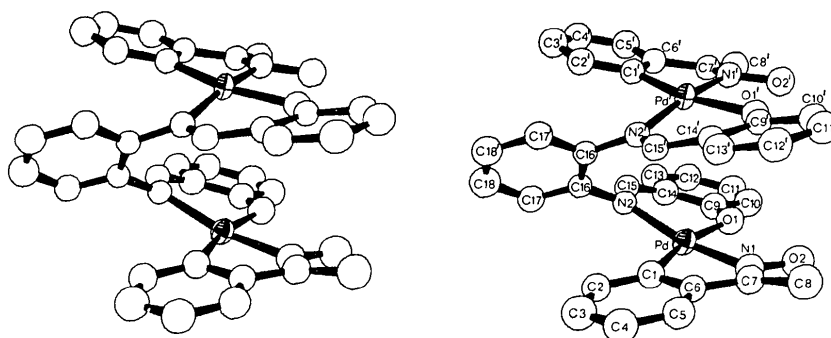


Fig. 3. Stereo view and labelling scheme of (ApoPd)<sub>2</sub>salophen, omitting hydrogen atoms for clarity.

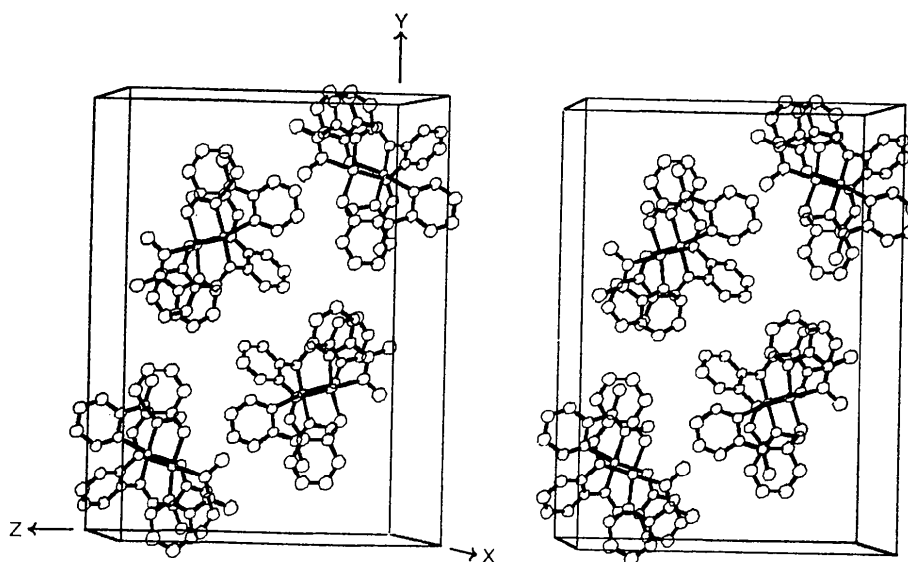


Fig. 4. (ApoPd)<sub>2</sub>salophen. Molecular packing arrangement.

Table 7. (ApoPd)<sub>2</sub>salophen, bond lengths (Å) and selected angles (°)

Pd—O(1)	2.06 (1)	Pd'—O(1')	2.07 (1)
Pd—C(1)	2.01 (2)	Pd'—C(1')	1.98 (2)
Pd—N(1)	1.99 (2)	Pd'—N(1')	1.99 (2)
Pd—N(2)	2.03 (2)	Pd'—N(2')	2.04 (1)
Within the oxime ligand			
N(1)—O(2)	1.40 (2)	N(1')—O(2')	1.39 (2)
C(1)—C(2)	1.39 (3)	C(1')—C(2')	1.38 (3)
C(2)—C(3)	1.40 (3)	C(2')—C(3')	1.42 (3)
C(3)—C(4)	1.42 (3)	C(3')—C(4')	1.39 (3)
C(4)—C(5)	1.38 (3)	C(4')—C(5')	1.36 (3)
C(5)—C(6)	1.39 (3)	C(5')—C(6')	1.38 (3)
C(1)—C(6)	1.43 (3)	C(1')—C(6')	1.42 (3)
C(6)—C(7)	1.46 (3)	C(6')—C(7')	1.49 (3)
C(7)—C(8)	1.54 (3)	C(7')—C(8')	1.51 (3)
C(7)—N(1)	1.27 (3)	C(7')—N(1')	1.30 (2)
Within the salophen ligand			
O(1)—C(9)	1.30 (3)	O(1')—C(9')	1.29 (2)
C(9)—C(10)	1.44 (3)	C(9')—C(10')	1.41 (2)
C(10)—C(11)	1.41 (3)	C(10')—C(11')	1.39 (3)
C(11)—C(12)	1.37 (3)	C(11')—C(12')	1.39 (3)
C(12)—C(13)	1.38 (3)	C(12')—C(13')	1.37 (3)
C(13)—C(14)	1.46 (3)	C(13')—C(14')	1.42 (3)
C(9)—C(14)	1.42 (3)	C(9')—C(14')	1.44 (2)
C(14)—C(15)	1.41 (3)	C(14')—C(15')	1.44 (2)
N(2)—C(15)	1.31 (2)	N(2')—C(15')	1.30 (2)
N(2)—C(16)	1.42 (2)	N(2')—C(16')	1.42 (2)
C(16)—C(17)	1.37 (2)	C(16')—C(17')	1.39 (3)
C(17)—C(18)	1.38 (3)	C(17')—C(18')	1.41 (2)
C(16)—C(16')	1.40 (2)		
C(18)—C(18')	1.37 (3)		
O(1)—Pd—N(1)	87.4 (6)	O(1')—Pd'—N(1')	88.1 (6)
O(1)—Pd—N(2)	91.6 (6)	O(1')—Pd'—N(2')	92.0 (5)
N(1)—Pd—C(1)	79.6 (7)	N(1')—Pd'—C(1')	80.1 (7)
N(2)—Pd—C(1)	101.7 (7)	N(2')—Pd'—C(1')	100.6 (7)
Within the oxime ligand			
Pd—N(1)—C(7)	118.9 (14)	Pd'—N(1')—C(7')	119.6 (13)
Pd—C(1)—C(6)	110.3 (13)	Pd'—C(1')—C(6')	112.1 (13)
N(1)—C(7)—C(6)	111.1 (17)	N(1')—C(7')—C(6')	109.4 (16)
C(1)—C(6)—C(7)	116.5 (17)	C(1')—C(6')—C(7')	116.1 (16)
Pd—N(1)—O(2)	119.9 (12)	Pd'—N(1')—O(2')	121.6 (11)
O(2)—N(1)—C(7)	119.0 (17)	O(2')—N(1')—C(7')	116.4 (15)
N(1)—C(7)—C(8)	123.1 (18)	N(1')—C(7')—C(8')	124.3 (18)
C(8)—C(7)—C(6)	125.8 (18)	C(8')—C(7')—C(6')	126.3 (17)
C(1)—C(2)—C(3)	120.1 (18)	C(1')—C(2')—C(3')	120.8 (18)
C(2)—C(3)—C(4)	120.6 (20)	C(2')—C(3')—C(4')	119.3 (20)
C(3)—C(4)—C(5)	119.3 (20)	C(3')—C(4')—C(5')	120.1 (20)
C(4)—C(5)—C(6)	120.4 (19)	C(4')—C(5')—C(6')	121.1 (20)
C(5)—C(6)—C(1)	120.7 (18)	C(5')—C(6')—C(1')	120.9 (18)
C(6)—C(1)—C(2)	118.8 (17)	C(6')—C(1')—C(2')	117.6 (17)
Within the salophen ligand			
Pd—O(1)—C(9)	125.1 (13)	Pd'—O(1')—C(9')	123.8 (11)
Pd—N(2)—C(15)	122.0 (12)	Pd'—N(2')—C(15')	121.0 (12)
O(1)—C(9)—C(14)	123.5 (19)	O(1')—C(9')—C(14')	123.7 (16)
N(2)—C(15)—C(14)	128.5 (18)	N(2')—C(15')—C(14')	129.5 (17)
C(15)—C(14)—C(9)	125.5 (19)	C(15')—C(14')—C(9')	124.4 (16)
C(9)—C(10)—C(11)	119.1 (20)	C(9')—C(10')—C(11')	121.7 (18)
C(10)—C(11)—C(12)	122.1 (22)	C(10')—C(11')—C(12')	120.7 (19)
C(11)—C(12)—C(13)	120.3 (22)	C(11')—C(12')—C(13')	119.3 (19)
C(12)—C(13)—C(14)	120.8 (20)	C(12')—C(13')—C(14')	121.9 (18)
C(13)—C(14)—C(9)	118.3 (19)	C(13')—C(14')—C(9')	119.1 (16)
C(14)—C(9)—C(10)	119.2 (19)	C(14')—C(9')—C(10')	117.2 (16)
Pd—N(2)—C(16)	121.8 (11)	C(16)—C(17)—C(18)	121.8 (19)
Pd'—N(2')—C(16')	121.5 (11)	C(17)—C(18)—C(18')	119.8 (20)
N(2)—C(16)—C(16')	119.6 (15)	C(18)—C(18')—C(17')	120.4 (19)
N(2')—C(16')—C(16)	121.0 (15)	C(18')—C(17')—C(16')	118.8 (18)
		C(17')—C(16')—C(16)	120.6 (16)
		C(16')—C(16)—C(17)	118.6 (17)

O(2'), C(9')—C(15')] out of the plane of the phenylene bridge, about the N(2)—C(16) bonds; the sal units being inclined at 48.3 and 50.1° respectively to the phenylene bridge. This distortion of the ligand probably limits the degree of electron delocalization through the phenylene bridge, although no evidence for this is obtained from significant changes in bond lengths within the salophen ligand between (ApoPd)<sub>2</sub>salophen and Pd(salophen) (Tables 7 and 5).

The <sup>1</sup>H NMR spectrum of (ApoPd)<sub>2</sub>salophen (Reichert, 1974) showed the aromatic *ortho*-protons of the metallated ligand to be shifted ~0.5 p.p.m. upfield from the normal aromatic proton resonances by the anisotropic shielding due to the ring current of the adjacent benzene ring, similar to that found for (dmba)PdSal=N-Ph (Reichert & West, 1973). As stated above the phenylene bridge is inclined at *ca* 50° to the sal moieties, which is similar to the angle of inclination of the phenyl ring (55.1°) in (dmba)PdSal=N-Ph (Fallon & Gatehouse, 1974), and this inclination places the affected *ortho*-protons HC(2) and HC(2') of the acetophenone oxime ligand over, and 2.61 and 2.44 Å from, the phenylene bridge.

The bridging arrangement (Fig. 3) gives an intramolecular Pd—Pd distance of 3.696 (4) Å which is considerably greater than twice the covalent radius of Pd<sup>II</sup>, 1.31 Å, and greater than other reported Pd—Pd bonding contact distances: Browth, Bursh, Interrante & Kasper (1972), 2.790 (2) Å in the ethylene-1,2-dithiolenene complex, [PdS<sub>4</sub>C<sub>4</sub>H<sub>4</sub>]<sub>2</sub>; Churchill & Mason (1964), 2.94 (1) Å in  $\pi$ -allyl palladium acetate; Miller (1960, 1961), in [Pd(NH<sub>3</sub>)<sub>4</sub>][PdCl<sub>4</sub>], 3.25 Å; [Pd(NH<sub>3</sub>)<sub>4</sub>][PdBr<sub>4</sub>], 3.33 Å and [Pd(NH<sub>3</sub>)<sub>4</sub>][Pd(SCN)<sub>4</sub>], 3.35 Å, thus excluding any metal—metal bonding interaction.

Coordination bond distances, Pd—N(2), 2.03 (2) and Pd—N(2'), 2.04 (1) Å (Table 7) are the same, within experimental error, as those in Pd(salophen) (Table 5) and several related bidentate Pd Schiff-base complexes (Frasson *et al.*, 1964; Braun & Lingafelter, 1967; Jain & Lingafelter, 1967). The bonds between Pd and the imine N of the oxime ligand, Pd—N(1), 1.99 (2) and Pd—N(1'), 1.99 (2) Å are typical of this bond reported for [Pd(acetoxime)acetate]<sub>3</sub>, 1.97 (av.) Å (Mawby & Pringle, 1971); Pd(dimethylglyoxime)<sub>2</sub>, 1.96 Å (Williams, Wohlauer & Rundle, 1959) and Pd(glyoxime)<sub>2</sub>, 1.97 Å (Calleri, Ferraris & Viterbo, 1967).

The significant lengthening of the Pd—O(1) and Pd—O(1') bonds, 2.06 (1) and 2.07 (1) Å respectively, in (ApoPd)<sub>2</sub>salophen, in comparison with Pd(salophen) 1.97 (2) and 1.96 (2) Å, and other related Pd Schiff-base complexes (Frasson *et al.*, 1964; Braun & Lingafelter, 1967; Jain & Lingafelter, 1967), is similar to that found for (dmba)PdSal=N-Ph, 2.094 (6) Å (Fallon & Gatehouse, 1974), and is due to the *trans*-effect of the  $\sigma$ -carbon bond (Reichert & West, 1973; Churchill, 1970; Bombieri, Caglioti, Cattalini, Forcellini, Gasparrine, Graziani & Vigato, 1971).

Pd— $\sigma$ -carbon bond lengths (Table 7) are similar to

those of other Pd metallated systems, 1.981 (7) Å in (dmba)PdSal=N-Ph (Fallon & Gatehouse, 1974); 1.94 (2) Å in diacetylbis(*N*-methyl-*N*-phenyl)osazone-palladium(II) (Bombieri *et al.*, 1971); and 1.998 (13) Å found by Siekman & Weaver (1968) in *trans*-Pd(PEt<sub>3</sub>)(C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>)Cl.

Hydrogen bonding of the hydroxyl group, O(2), O(2'), was inferred by Reichert (1974) from IR data, which gave a weak broad ν(O-H) around 3200 cm<sup>-1</sup>. This bonding is confirmed by the present structural analysis, HO(2) and HO(2') being 1.89 and 1.78 Å from the intramolecular Schiff-base O(1) and O(1') respectively.

Bond lengths within the oxime functional group, C-N and N-O, (Table 7) are similar to those found for several oximes (Chakravorty, 1974), the averages for C-N and N-O being 1.27 (2) and 1.40 (2) Å respectively.

There are no unusual intermolecular contact distances, the shortest being 3.01 Å between O(2) and C(4').

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