Acta Cryst. (1974). B30, 2451

The Crystal and Molecular Structure of μ-*N*,*N'*-Ethylenebis(salicylaldiminato)bis-[2-methylallylpalladium(II)]

By Bryan M. Gatehouse, Bernhard E. Reichert and Bruce O. West

Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

(*Received* 17 *June* 1974; *accepted* 19 *June* 1974)

The structure of the title compound, (2-methylallylPd)$_2$salen, has been determined by single-crystal X-ray analysis and refined by least-squares methods to an R of 0·078 with 985 counter intensities. The crystals are monoclinic, space group $P2_1/c$, with $Z=2$ and $a=9{\cdot}701$, $b=10{\cdot}060$, $c=11{\cdot}993$ Å, $\beta=99{\cdot}38°$. The molecule possesses a centre of symmetry bisecting the bridging ligand and planar coordination about each palladium atom. The Pd–Pd distance is 6·546 Å.

Introduction

Although there have been several compounds reported in which *N*,*N'*-ethylenebis(salicylaldimine)(salenH$_2$) appears to act as a bridging ligand (see, for example, Murray, Reichert & West, 1973, and references therein) there is only one report of a structure determination for such a binuclear complex (Calligaris, Nardin & Randaccio, 1970). This paper describes the crystal and molecular structure of (2-methylallylPd)$_2$salen which was prepared by reaction of [2-methylallyl-PdCl]$_2$ and Tl$_2$salen (Reichert & West, 1972). The interest in this structure was not only to confirm the formulation of the compound as a bridged derivative, but also to examine the symmetry of the molecule and the conformation of both the bridging ligand and the allyl groups.

Experimental

Crystals of the compound were grown by slow evaporation of a solution in dichloromethane/hexane. The diamond-shaped plates showed a strong tendency to crack along the short diagonal, which proved to be the crystallographic *b* axis, and to twin face-to-face. Eventually a very small crystal was found which was not cracked or twinned and this was used for the structural determination.

Crystal data

$C_{24}H_{28}N_2O_2Pd_2$, $M=589{\cdot}3$, monoclinic, $a=9{\cdot}701\,(5)$, $b=10{\cdot}060\,(5)$, $c=11{\cdot}993\,(6)$ Å, $U=1155$ Å^3, $D_m=1{\cdot}69\,(1)$ g cm^{-3} (by flotation in a mixture of carbon tetrachloride and 1,1,2,2-tetrabromoethane), $Z=2$, $D_c=1{\cdot}69$ g cm^{-3}. $F(000)=568$, $\mu=13{\cdot}7$ cm^{-1} for Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). Systematic absences indicate space group $P2_1/c$ (No. 14), which for $Z=2$ requires the molecule to possess a centre of symmetry. The cell parameters were obtained with a Philips PW 1100 computer-controlled X-ray diffractometer from 25 well spaced medium to strong reflexions.

Intensity measurements

Intensities were collected from a crystal of dimensions $0{\cdot}05\times0{\cdot}03\times0{\cdot}02$ mm with graphite-monochromated Mo $K\alpha$ radiation. A unique data set was collected out to 2θ (Mo $K\alpha$) $=50°$ by the ω-scan technique with a symmetric scan range of $\pm0{\cdot}5°$ in ω from the calculated scattering angle and a scan rate of $0{\cdot}025°$ s^{-1}; no reflexion was sufficiently strong to require the insertion of an attenuation filter.

The intensities of 2148 independent reflexions were measured; of these only 985 obeyed the condition $F_o^2>3\sigma(F_o^2)$ and were used in subsequent calculations. The large proportion of very weak reflexions may be attributed to the very small crystal used. Three standard reflexions, monitored at two-hourly intervals, showed no significant variations.

The intensities were processed with a program specifically designed for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). The standard devations for the background-corrected intensities were calculated from

$$\sigma(I)=[\mathrm{CT}+(t_c/t_b)^2(B_1+B_2)+(pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and

$$I=CT-(t_c/t_b)\,(B_1+B_2)\,.$$

The value of p was taken as 0·04 to allow for machine errors and to prevent unduly high weight being given to strong reflexions. Corrections for Lorentz and polarization effects were made to I and $\sigma(I)$. No extinction or absorption corrections were applied.

Structure solution and refinement

The structure was solved by the heavy-atom method. In the least-squares refinement the function $\sum w(|F_o|-|F_c|)^2$ was minimized. The scattering factors used were those tabulated by Cromer & Waber (1965) for Pd^0, O^0, N^0 and C^0. Major programs used were *MONLS*, a modification of the full-matrix least-squares program of Busing, Martin & Levy (1962); *MONDLS*, a block-diagonal least-squares program based on that of Shiono (1968) and the Fourier synthesis program *MONFR* (White, 1965). The diagrams were drawn by the program *ORTEP* (Johnson, 1965). Calculations were all performed on the Monash University CDC 3200 and B 6700 computers.

Solution of the Patterson map located the palladium atoms in the $y=0$ and $y=\frac{1}{2}$ planes, and a structure-factor calculation based on the palladium position gave $R_1=0{\cdot}305$ and $R_2=0{\cdot}368$ where

$$R_1=\sum||F_o|-|F_c||/\sum|F_o|$$

and

$$R_2=(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2}.$$

The first difference synthesis displayed mirror symmetry about the $y=0$ plane; inclusion of another atom in the structure-factor calculation effectively removed the mirror symmetry and several further structure-factor calculations and difference syntheses enabled location of all the non-hydrogen atoms. A number of cycles of full-matrix least-squares refinement with isotropic temperature factors, varying first only the atom positions, then all parameters, led to convergence with $R_1=0{\cdot}085$, $R_2=0{\cdot}087$. A difference synthesis at this stage showed evidence of anisotropy in the thermal motion of the palladium atom. Further block-diagonal refinement with anisotropic temperature factors for palladium, and isotropic temperature factors for the other atoms, converged at $R_1=0{\cdot}078$, $R_2=0{\cdot}081$. Table 1 shows final positional and thermal parameters for the non-hydrogen atoms, with standard deviations derived from the inverse least-squares matrix.*

No attempt was made to locate hydrogen atoms because of the large temperature factors of some of the atoms and the relatively poor quality of the data. A final difference synthesis showed fluctuations no greater than 1·1 e Å^{-3}.

Discussion of the structure

The crystallographic centre of symmetry bisects the C(12)–C(12′) bond and the molecule consists of two essentially planar halves. Positional parameters of the second half of the molecule are generated by applying the transformation (x,y,z) to $(2-x,-y,1-z)$ to the data in Table 1. A stereoscopic view of the molecule is shown in Fig. 1, which also gives the labelling scheme.

Table 2. *Selected intramolecular distances* (Å) *and angles* (°)

Pd—O	2·06 (2)	C(6)—C(7)	1·37 (5)
Pd—N	2·08 (3)	C(7)—C(8)	1·43 (5)
Pd—C(1)	2·20 (5)	C(8)—C(9)	1·34 (5)
Pd—C(2)	2·10 (4)	C(9)—C(10)	1·46 (5)
Pd—C(3)	2·14 (4)	C(5)—C(10)	1·41 (5)
C(1)—C(2)	1·41 (7)	C(10)–C(11)	1·43 (5)
C(2)—C(3)	1·44 (6)	N—C(11)	1·31 (5)
C(2)—C(4)	1·50 (7)	N—C(12)	1·48 (5)
O—C(5)	1·30 (4)	C(12)–C(12′)	1·59 (5)
C(5)—C(6)	1·42 (5)	Pd—Pd′	6·546 (4)
O—Pd—N	90 (1)	C(7)—C(8)—C(9)	121 (4)
Pd—N—C(11)	124 (2)	C(8)—C(9)—C(10)	119 (3)
Pd—N—C(12)	120 (2)	C(5)—C(10)–C(9)	121 (3)
C(11)–N—C(12)	116 (3)	C(5)—C(10)–C(11)	126 (3)
N—C(12)–C(12′)	108 (3)	C(9)—C(10)–C(11)	114 (3)
Pd—O—C(5)	126 (2)	N—C(11)–C(10)	127 (3)
O—C(5)—C(10)	125 (3)	C(1)—Pd—C(3)	66 (2)
O—C(5)—C(6)	117 (3)	C(1)—C(2)—C(3)	112 (4)
C(6)—C(5)—C(10)	118 (3)	C(1)—C(2)—C(4)	124 (4)
C(5)—C(6)—C(7)	122 (3)	C(3)—C(2)—C(4)	124 (4)
C(6)—C(7)—C(8)	120 (3)		

Table 2 gives selected intramolecular distances and angles with their estimated standard deviations. The standard deviations for all but the Pd–Pd′ distance are rather high and reflect the low precision of the positional parameters for the other atoms (Table 1). Because of the large uncertainties comparison of the various lengths and angles is difficult, as apparent differences are not really significant.

Table 1. *Final positional and thermal parameters*

Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. The B values are the parameters in the isotropic temperature-factor expression $\exp[-B\sin^2\theta/\lambda^2]$. The atomic scattering factor for palladium is expressed as $f=f_o\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl]$.

(*a*) Isotropic temperature factors (fractional coordinates × 10^3 and B × 10)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
O	735 (3)	158 (2)	170 (2)	25 (5)	C(6)	586 (4)	339 (3)	162 (3)	29 (8)
N	845 (3)	66 (3)	400 (2)	27 (6)	C(7)	526 (4)	441 (4)	212 (3)	33 (8)
C(1)	862 (5)	−113 (4)	81 (4)	48 (10)	C(8)	555 (4)	458 (4)	331 (3)	35 (9)
C(2)	840 (5)	−202 (4)	168 (4)	47 (10)	C(9)	641 (4)	375 (3)	397 (3)	26 (7)
C(3)	949 (5)	−194 (4)	264 (4)	46 (10)	C(10)	707 (4)	267 (4)	344 (3)	29 (8)
C(4)	714 (6)	−288 (5)	163 (5)	73 (14)	C(11)	788 (4)	179 (3)	422 (3)	27 (8)
C(5)	681 (3)	250 (3)	226 (3)	21 (7)	C(12)	918 (3)	−8 (5)	499 (3)	34 (7)

(*b*) Anisotropic temperature factors (fractional coordinates × 10^4 and U_{ij} × 10^3)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	8391 (3)	−98 (3)	2381 (2)	42 (1)	32 (1)	38 (1)	10 (2)	7 (1)	0 (2)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30536 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Nevertheless, the bond lengths and angles within the salen molecule are very similar to those found in complexes where salen is tetradentate on a single metal atom (Calligaris, Nardin & Randaccio, 1972), although the C–C bond of the ethylene bridge does appear to be marginally longer. Comparison with the previous structure determination of a bridged salen complex (Calligaris, Nardin & Randaccio, 1970) cannot be made, as virtually no detailed parameters were given. From the diagram these authors gave, however, it appears that the general conformation of the ligand is the same as that found here. The Pd–O distance and O–Pd–N angle are also similar to those found in the only previous structure determination for a palladium Schiff-base complex (Fallon & Gatehouse, 1974). The distance between the palladium atoms of 6·546 Å may be regarded as a metal–metal separation to be expected for bridging salen complexes. This would be relevant to magnetic or e.s.r. studies if paramagnetic derivatives were to be synthesized.

Several least-squares planes of interest have been calculated by the method of Blow (1960). Equations of these, with distances of relevant atoms from them, are shown in Table 3. The benzene ring is planar as expected, and the chelate ring including the palladium atom shows only very small deviations from planarity. However, these two sets of atoms are not coplanar, the atoms C(6)–C(9) all lying significantly below the plane of the 6-membered chelate ring. C(12) is not significantly displaced from this latter plane. The coordination plane of palladium is probably best defined by Pd, O and N, and the carbon atoms of the chelate ring lie somewhat below this. The allyl group has C(1) and C(3) just above the plane, and C(2) about 0·66 Å below it.

Within the allyl group, although the C(2)–C(4) bond length does appear to be somewhat longer than the others, the difference is not really significant and all the bonds are virtually equal within the errors. This is contrary to previous structural determinations (Mason & Russell, 1966; Mason & Wheeler, 1968) where the bond to the methyl group was found to be appreciably longer, and probably merely reflects the large uncertainties here. The bond lengths are, within the errors, similar to those found in the previous 2-

Tables 3. *Equations of least-squares and distances of individual atoms from the planes* (Å)

X,Y,Z are coordinates in Å referred to the set of Cartesian axes a,b,c^*. These are related to fractional coordinates in the monoclinic crystal system by the matrix equation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} 9\cdot701 & 0 & -1\cdot955 \\ 0 & 10\cdot060 & 0 \\ 0 & 0 & 11\cdot674 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

The sign of displacements given as zero refers to the sign of the calculated displacement, although the value is zero when truncated to two decimal places.

(1) Plane through C(5), C(6), C(7), C(8), C(9), C(10)

$$0\cdot7949X + 0\cdot5988Y - 0\cdot0973Z - 6\cdot1338 = 0$$

C(5)	0·01 (3)	C(7)	0·00 (4)	C(9)	−0·00 (4)
C(6)	−0·01 (4)	C(8)	0·00 (4)	C(10)	−0·00 (4)

(2) Plane through Pd, O, C(5), C(10), C(11), N

$$0\cdot8663X + 0\cdot4964Y - 0\cdot0560Z - 6\cdot4877 = 0$$

Pd	−0·046 (3)	C(11)	0·03 (4)	C(8)	−0·32 (4)
O	0·08 (2)	N	0·01 (3)	C(9)	−0·16 (4)
C(5)	−0·05 (3)	C(6)	−0·25 (4)	C(12)	0·01 (4)
C(10)	−0·02 (4)	C(7)	−0·37 (4)		

(3) Plane through Pd, O, N

$$0\cdot8975X + 0\cdot4374Y - 0\cdot0557Z - 6\cdot6880 = 0$$

Pd	0·000 (3)	C(10)	−0·19 (4)	C(2)	−0·66 (5)
O	0·00 (2)	C(11)	−0·06 (4)	C(3)	0·09 (5)
N	0·00 (3)	C(12)	0·07 (4)		
C(5)	−0·21 (3)	C(1)	0·12 (5)		

(4) Plane through C(1), C(2), C(3)

$$0\cdot5814X - 0\cdot7108Y - 0\cdot3959Z - 5\cdot2023 = 0$$

C(1)	0·00 (5)	C(3)	0·00 (4)
C(2)	0·00 (5)	C(4)	−0·06 (6)

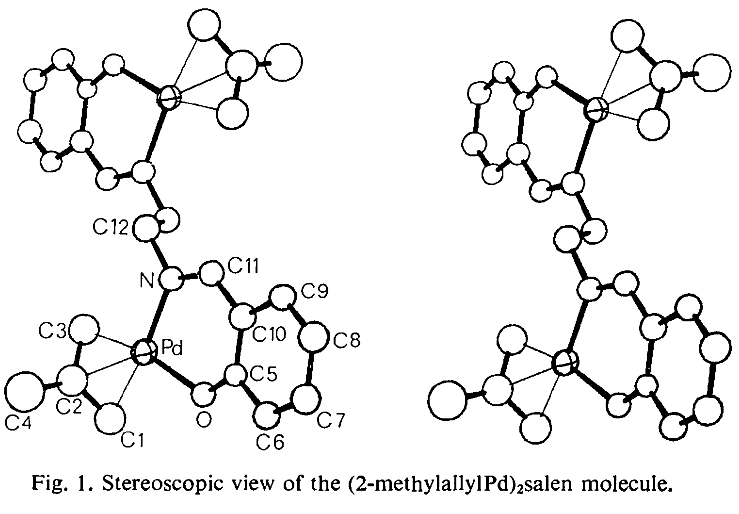

Fig. 1. Stereoscopic view of the (2-methylallylPd)$_2$salen molecule.

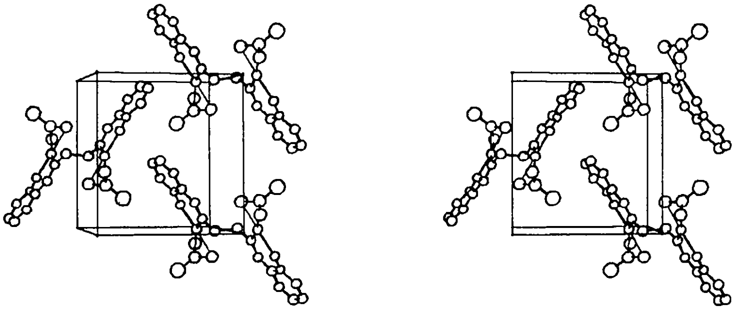

Fig. 2. Stereoscopic view illustrating the packing in the crystal. Direction of view is 15° from negative **c*** with **b** vertical.

methylallyl structures, and also those found for [π-allylPdCl]$_2$ (Smith, 1965), although the C(1)–C(2) and C(2)–C(3) bonds in the salen complex here may, in common with the phosphine complex (Mason & Russell, 1966), be slightly longer than those in the chloro-bridged dimers. Pd–C bond lengths are also similar to previous observations. The angle C(1)–C(2)–C(3) of 112° is the same as that found in [2-methylallylPdCl]$_2$ (Mason & Wheeler, 1968). A major difference between the structure here and those previously determined for 2-methylallyl palladium compounds is the planarity of the allyl group. In this salen complex the displacement of the methyl carbon C(4) from the plane of the allylic carbons is hardly significant, while in [2-methylallylPdCl]$_2$ it is displaced 0·29 Å and in 2-methylallylPdCl(PPh$_3$) 0·5 Å towards the metal, giving angles of bend of 11·8 and 17·7° respectively. There seems to be no obvious explanation for this difference, which does however indicate that the previously observed bend is not a universal feature of 2-methylallyl-palladium complexes. The plane of the group makes an angle of 103·9° with the Pd–O–N plane, so that C(2) is tilted away from Pd, as in other structures.

The large temperature factors for the carbon atoms of the allyl group, particularly C(4), indicate that this group is not very rigidly bound and capable of considerable thermal motion.

A stereoscopic view of the packing of the molecules is given in Fig. 2. The molecules form stacks along **b**, each molecule being at an angle to this direction, so that cleavage would be relatively easy between the stacks, but more difficult across them since the stacks are staggered. This helps to explain the observed tendency of the crystals to crack along **b**.

We thank Mr G. D. Fallon of this department for his invaluable assistance.

References

Blow, D. M. (1960). *Acta Cryst.* **13**, 168.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *OFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Calligaris, M., Nardin, G. & Randaccio, L. (1970). *Chem. Commun.* pp. 1079–1080.

Calligaris, M., Nardin, G. & Randaccio, L. (1972). *Coord. Chem. Rev.* **7**, 385–403.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Fallon, G. D. & Gatehouse, B. M. (1974). *J. Chem. Soc. Dalton.* In the press.

Hornstra, J. & Stubbe, B. (1972). PW 1100 *Data Processing Program.* Philips Research Laboratories, Eindhoven, The Netherlands.

Johnson, C. K. (1965). *ORETP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Mason, R. & Russell, D. R. (1966). *Chem. Commun.* p. 26.

Mason, R. & Wheeler, A. G. (1968). *J. Chem. Soc.* (*A*), pp. 2549–2554.

Murray, K. S., Reichert, B. E. & West, B. O. (1973). *J. Organometal. Chem.* **63**, 461–466.

Reichert, B. E. & West, B. O. (1972). *J. Organometal. Chem.* **36**, C29–C31.

Shiono, R. (1968). *SF. Block-diagonal least-squares refinement program.* Univ. of Pittsburgh, U.S.A.

Smith, A. E. (1965). *Acta Cryst.* **18**, 331–340.

White, J. C. B. (1965). Melbourne University Fourier Program *MUFR*3. See J. S. Rollett (1961). in *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. Pepinsky, J. M. Robertson & J. C. Speakman, p. 87. Oxford: Pergamon Press.