Acta Cryst. (1985). C**41**, 192–194

Synthesis and Structure of Bis[*N*-(4-butylphenyl)salicylideneaminato]palladium(II), $[Pd(C_{17}H_{18}NO)_2]$

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(*Received* 23 *February* 1984; *accepted* 1 *October* 1984)

Abstract. $M_r = 611{\cdot}1$, orthorhombic, *Pbca*, $a = 32{\cdot}023\,(10)$, $b = 11{\cdot}064\,(5)$, $c = 7{\cdot}934\,(2)$ Å, $V = 2811\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}44$ g cm^{-3}, Mo $K\alpha$, $\bar{\lambda} = 0{\cdot}71069$ Å, $\mu = 6{\cdot}83$ cm^{-1}, $F(000) = 1264$, room temperature, $R = 0{\cdot}034$ for 1857 independent observed reflections. The structure consists of discrete complexes in which the palladium atom has a strictly planar square coordination involving the N and O atoms, in *trans* position, from two chelating ligands. The conformation of the molecules is markedly 'stepped': the 'step' separating the mean planes of the salicylideneamine groups of a complex is 1·33 (3) Å and each of these planes is tilted by 27·3 (1)° with respect to the planar square coordination group. No plane-to-plane molecular stacks are present in the title compound.

Introduction. The reactions between palladium(II) and Schiff bases formed from salicylaldehyde and aliphatic amines afford square-planar complexes of the type PdL_2 (Yamada, 1966; Holm & O'Connor, 1971). The crystal structures of these compounds, generally in a *trans* PdN_2O_2 configuration, consist of both unstepped (Pachler & Stackelberg, 1960; Frasson, Panattoni & Sacconi, 1964; Jain & Lingafelter, 1967) and stepped (Braun & Lingafelter, 1967; Day, Glick & Hoard, 1968) isolated molecules. Moreover, complexes of Pd with other N_2O_2 donor atom ligands such as $Pd(qnl)_2$ (qnl = 8-quinolinolato) display stacked structures in the crystalline state (Prout & Wheeler, 1966). Stacked metal complexes exhibit a broad range of interesting properties (Ibers, Pace, Martinsen & Hoffman, 1982), so we have determined the crystal structure of bis[*N*-(4-butylphenyl)salicylideneaminato]palladium(II) in order to examine the effect of aromatic rings near to the metal center in determining such a possible feature.

Experimental. The ligand (*L*H) was prepared by reacting salicylaldehyde and 4-butylaniline (1:1 molecular ratio, 1 h in boiling ethanol), purified by chromatography (SiO_2/CH_2Cl_2) and characterized by IR, NMR and mass spectroscopy.

Preparation of the complex PdL_2: To an ethanolic solution (10 ml) containing 1 mmol of *L*H was added an ethanolic solution (5 ml) containing the stoichiometric amount of potassium hydroxide and stirred at room temperature for 10 min. To the resulting solution was then added a dichloromethane solution (10 ml) containing 1 mmol of $(PhCN)_2PdCl_2$. The mixture was stirred at room temperature for 2 h. After filtration the solution was concentrated under reduced pressure until a yellow microcrystalline solid formed. The solid was collected, washed with petroleum ether and dried under vacuum (yield 80%). Analysis: calc. for $C_{34}H_{36}N_2O_2Pd$: C 66·83; H 5·93; N 4·58; found: C 66·45; H 5·85; N 4·89.

Crystals suitable for X-ray analysis by recrystallization from ethanol–chloroform. Yellow irregularly shaped crystal 0·30 × 0·45 × 0·60 mm, Siemens AED diffractometer, Nb-filtered Mo $K\alpha$, 15 reflections for lattice-parameter measurements; 3730 independent reflections with $2\theta < 58°$ ($0 \le h \le 42$, $0 \le k \le 14$, $0 \le l \le 10$), 1858 with $I > 2\sigma(I)$, no significant intensity deterioration of standard reflection (15,1,3). Lp correction, absorption ignored; Patterson and Fourier methods; full-matrix least-squares refinement, anisotropic for non-hydrogen atoms (*SHELX*76, Sheldrick, 1976); H (from ΔF synthesis) isotropically refined; $\sum w|\Delta F|^2$ minimized, final $R = 0{\cdot}034$, $wR = 0{\cdot}040$, unit weights; $(\Delta/\sigma)_{\max} = 0{\cdot}08$, final $\Delta\rho$ excursions $\le |0{\cdot}8|$ e Å^{-3}; atomic scattering factors (anomalous dispersion of Pd atom) from *International Tables for X-ray Crystallography* (1974); calculations performed on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Casalecchio (Bologna) with financial support from the University of Parma.*

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39789 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/85/020192-03$01.50

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with equivalent isotropic thermal parameters for the non-hydrogen atoms, with e.s.d.'s in parentheses*

$B_{eq} = \frac{8}{3}\pi^2 \text{ trace } \tilde{\mathbf{U}}$.

	x	y	z	B_{eq}(Å^2)
Pd	$\frac{1}{2}$	0	$\frac{1}{2}$	2·12 (1)
O	4570 (1)	389 (4)	3287 (5)	2·73 (10)
N	5362 (1)	−780 (4)	3223 (6)	2·19 (10)
C(1)	5223 (2)	−1166 (5)	1809 (8)	2·18 (13)
C(2)	4796 (2)	−1101 (5)	1239 (7)	2·35 (14)
C(3)	4497 (2)	−334 (5)	2000 (7)	2·28 (12)
C(4)	4095 (2)	−310 (6)	1296 (8)	2·73 (15)
C(5)	3993 (2)	−1017 (6)	−75 (10)	3·40 (15)
C(6)	4287 (2)	−1756 (6)	−809 (9)	3·32 (19)
C(7)	4681 (2)	−1784 (5)	−186 (8)	2·87 (16)
C(8)	5805 (2)	−963 (5)	3501 (8)	2·46 (13)
C(9)	6048 (2)	−35 (7)	4147 (7)	2·83 (14)
C(10)	6471 (2)	−205 (6)	4361 (9)	3·28 (18)
C(11)	6660 (2)	−1288 (6)	3989 (9)	3·40 (17)
C(12)	6416 (2)	−2206 (7)	3356 (10)	3·63 (19)
C(13)	5989 (2)	−2061 (6)	3114 (9)	3·27 (16)
C(14)	7128 (2)	−1464 (8)	4257 (12)	4·24 (22)
C(15)	7393 (3)	−680 (10)	3143 (15)	5·66 (29)
C(16)	7864 (2)	−874 (8)	3396 (14)	4·96 (24)
C(17)	8020 (3)	−2047 (9)	2728 (15)	5·82 (29)

Table 2. *Bond distances* (Å) *and angles* (°) *involving the heavy atoms*

Pd—N	2·019 (4)	N—C(8)	1·450 (7)
Pd—O	1·982 (4)	C(8)—C(9)	1·386 (9)
N—C(1)	1·280 (8)	C(8)—C(13)	1·385 (9)
C(1)—C(2)	1·442 (9)	C(9)—C(10)	1·378 (9)
C(2)—C(3)	1·415 (8)	C(10)—C(11)	1·374 (9)
C(2)—C(7)	1·409 (8)	C(11)—C(12)	1·376 (9)
C(3)—O	1·318 (7)	C(11)—C(14)	1·526 (9)
C(3)—C(4)	1·403 (9)	C(12)—C(13)	1·390 (9)
C(4)—C(5)	1·379 (9)	C(14)—C(15)	1·501 (12)
C(5)—C(6)	1·376 (9)	C(15)—C(16)	1·537 (11)
C(6)—C(7)	1·355 (9)	C(16)—C(17)	1·488 (12)

N—Pd—O	90·7 (2)	N—C(8)—C(9)	120·1 (5)
Pd—N—C(1)	123·7 (4)	N—C(8)—C(13)	120·3 (5)
Pd—O—C(3)	121·5 (3)	C(9)—C(8)—C(13)	119·5 (6)
N—C(1)—C(2)	126·0 (5)	C(8)—C(9)—C(10)	119·7 (6)
C(1)—C(2)—C(3)	122·5 (5)	C(9)—C(10)—C(11)	121·7 (6)
C(2)—C(3)—O	125·1 (5)	C(10)—C(11)—C(12)	118·1 (6)
C(3)—C(2)—C(7)	119·2 (6)	C(10)—C(11)—C(14)	120·9 (6)
C(2)—C(3)—C(4)	117·5 (5)	C(12)—C(11)—C(14)	120·9 (6)
C(3)—C(4)—C(5)	121·4 (6)	C(11)—C(12)—C(13)	121·6 (7)
C(4)—C(5)—C(6)	120·6 (6)	C(12)—C(13)—C(8)	119·3 (6)
C(5)—C(6)—C(7)	119·7 (6)	C(11)—C(14)—C(15)	113·5 (7)
C(6)—C(7)—C(2)	121·6 (6)	C(14)—C(15)—C(16)	113·4 (8)
Pd—N—C(8)	121·0 (4)	C(15)—C(16)—C(17)	113·9 (7)
C(1)—N—C(8)	115·3 (5)		

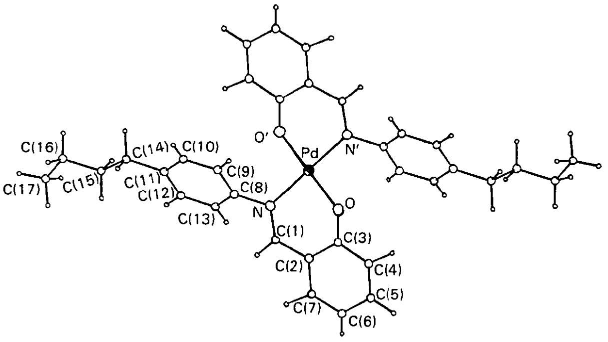

Fig. 1. Perspective view of the complex with the atomic numbering scheme.

Discussion. The refined atomic coordinates are listed in Table 1.

The crystal structure consists of discrete molecules (Fig. 1) in which the palladium atom, lying on a center of symmetry, is square-planar coordinated by N and O atoms from two chelating organic ligands. Bond distances and angles involving the heavy atoms are shown in Table 2. The Pd—N and Pd—O bond lengths agree well with the values found in similar *trans*-PdN_2O_2 configurations (Braun & Lingafelter, 1967) and the C—C bond lengths of the salicylideneamine moieties show the same trend found in the salicylideneamine chelates (Lingafelter & Braun, 1966), in which the C—C bonds not adjacent to the C—C bonds involved in the six-membered chelate ring are shorter than the others.

The strictly planar coordination, by contrast, is accompanied by a marked departure from the planarity of the overall configuration of the bis(salicylideneaminato)palladium(II) skeleton; in fact the dihedral angle between the PdN_2O_2 coordination plane and the mean planes of the two salicylideneamine moieties is 27·3 (1)° with a significant ruffling of the six-membered chelate ring as shown by the torsion angles Pd—N—C(1)—C(2) 0·8 (8), N—C(1)—C(2)—C(3) 16·2 (9), C(1)—C(2)—C(3)—O −0·2 (9), C(2)—C(3)—O—Pd −29·3 (7), C(3)—O—Pd—N 34·2 (4), O—Pd—N—C(1) −20·9 (5)°. The present complex can be considered as markedly 'stepped', the height of the step being the distance between the mean planes of the parallel salicylideneamine moieties [1·33 (3) Å] with the palladium atom lying halfway between. Stepped conformations of the bis(salicylideneaminato)metal(II) skeleton have been found in the structures of bis(*N*-isopropyl-3-ethylsalicylideneaminato)palladium(II) (Braun & Lingafelter, 1967), bis(*N*-isopropyl-3-methylsalicylideneaminato)nickel(II) (Braun & Lingafelter, 1966) and in bis(*N*-*tert*-butylsalicylideneaminato)palladium(II) (Day, Glick & Hoard, 1968) where the steps are 0·42, 0·76 and 1·72 Å, respectively: in particular, the last compound shows a 'step' between the salicylideneamine portions comparable to that found in the present structure.

The plane through the *N*-substituent benzene group is tilted with respect to the coordination plane by 58·6 (2)°. Even if from the projection of the structure along **b** (Fig. 2) overlap of palladium complexes can be suggested, no stacking interaction can be recognized, the metal–metal separations being greater than 5 Å (Ibers *et al.*, 1982) and the shortest distances between the salicylideneamine atoms from complexes symmetry-related along **b** being C(7)···N(x, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$) = 3·690 (7) and C(7)···C(2)(x, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$) = 3·695 (8) Å. The lack of planarity of the overall bis(salicylideneaminato)palladium(II) skeleton and the steric demand of the bulky *N* substituent in the packing of the molecules seem to be responsible for the lack of

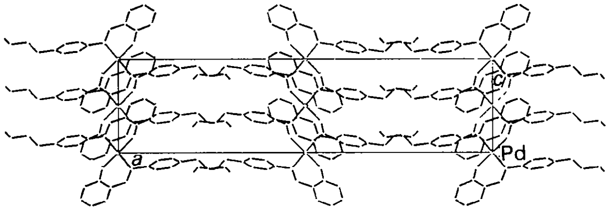

Fig. 2. Projection of the structure along **b**.

plane-to-plane stacks involving the metal complexes and/or the organic portions. Stacks of these two types have been found in [2-(4-methoxyphenylazo-N^2)-5-methoxyphenyl](8-quinolinolato)palladium(II) (Manotti Lanfredi, Ugozzoli, Ghedini & Licoccia, 1984).

The stepped molecules are connected by centrosymmetric Pd···H interactions involving palladium and hydrogen atoms from adjacent complexes [Pd···H(7)$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$ and Pd···H(7)$(1-x, \frac{1}{2}+y, \frac{1}{2}-z) = 2\cdot86\ (6)$ Å] in slices parallel to (100) at $x = 0$ and $x = \frac{1}{2}$ (Fig. 2).

Packing of the slices is determined by van der Waals contacts involving hydrogen atoms of the *n*-butyl groups.

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Acta Cryst. (1985). C**41**, 194–197

Structure of Copper(II) Distrontium(II) Formate Octahydrate, $CuSr_2(HCOO)_6.8H_2O$

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(*Received* 2 *November* 1983; *accepted* 12 *July* 1984)

Abstract. $M_r = 652\cdot5$, triclinic, $P\bar{1}$, $a = 6\cdot61\ (1)$, $b = 8\cdot84\ (2)$, $c = 8\cdot90\ (2)$ Å, $\alpha = 104\cdot5\ (1)$, $\beta = 96\cdot0\ (1)$, $\gamma = 88\cdot5\ (1)°$, $U = 500\cdot7\ (7)$ Å^3, $Z = 1$, $D_m = 2\cdot19$ (pycnometric), $D_x = 2\cdot17$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu(\text{Cu } K\alpha) = 100$ cm^{-1}, $\mu(\text{Mo } K\alpha) = 70$ cm^{-1}, $F(000) = 323$, final $R = 0\cdot092$ for 1458 independent reflexions. The structure consists of layers parallel to (010), linked to each other by only one type of H bond. Coordination around the heavy atoms is normal.

Introduction. During a survey on possible ferroelectric materials related to the well known ferroelectric $Cu(HCOO)_2.4H_2O$, we came across the mixed salt $CuSr_2(HCOO)_6.8H_2O$, which we tested for its electrical properties.

Although ferroelectricity tests proved negative in the range of stability of the compound, some intriguing features were observed regarding the dehydration of single crystals (a shape-preserving process, with the appearance of new, single-crystal-like diffraction spots). This fact encouraged further work on the subject and, as part of this more general work, we report here the crystal structure of the hydrated species $CuSr_2(HCOO)_6.8H_2O$.

Experimental. Crystals obtained at room temperature by slow evaporation of a 20% formic acid solution of $CuCO_3$ and $SrCO_3$ in 1:2 molar ratio. Predominant habit: light-blue (010) plates. Some batches showed ⟨100⟩ and ⟨001⟩ needles as well. Typical well developed faces: {010}, {100}, {001}, {110}. Cell

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