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The crystal and molecular structure of bis(salicylaldoximato)palladium(II).

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Bis(salicylaldoximato)palladium(II) is monoclinic, $a=10{\cdot}339$ (5), $b=4{\cdot}916$ (5), $c=14{\cdot}009$ (6) Å, $\beta=112°38'$ (5′), space group $P2_1/c$, and contains two centrosymmetric molecules in the unit cell. The atomic positions have been determined by the least-squares refinement of 1030 pieces of counter data and the resulting bond distances and angles are compared with those of the isomorphic nickel complex.

A three-dimensional structure determination of bis(salicylaldoximato)palladium(II) has recently been completed to update the two-dimensional study (Pfluger, 1958) so that a more accurate comparison between the nickel (Srivastava, Lingafelter & Jain, 1967) and palladium salicylaldoximes could be made. Although crystals of the two complexes are isomorphic (Cox, Pinkard, Wardlaw & Webster, 1935), a unit cell containing two molecules with space group $P2_1/c$, rather than $P2_1/n$, was selected. The cell parameters as determined from NaCl-calibrated rotation and Weissenberg films (Cu $K\alpha$) are: $a=10{\cdot}339(5), b=4{\cdot}916(5), c=14{\cdot}009(6)$ Å, $\beta=112°38'$ (5').

An experimental density of 1·912 g.cm^{-3} agrees very well with a calculated density of 1·913 g.cm^{-3}.

A Stoe Weissenberg camera equipped with a single-crystal counter attachment was used to collect Cu $K\alpha$ intensity data for 1030 reflections from $k=0$ through $k=3$. The stationary-crystal stationary-counter technique was used with each reflection being manually maximized before counting. Approximately 20 reflections in each layer were also scanned. A plot of integrated/peak height ratio for each of these reflections *versus* diffraction angle yielded an empirical curve for each layer by the application of which it was thus possible to convert all reflections in each layer to moving-crystal, integrated intensities. Standard reflections were counted every twenty reflections and the intensities corrected accordingly. Corrections were also made for background, filter factors, non-linearity of the counting system, and Lorentz-polarization. As the crystal had been ground into a cylindrical shape (radius = 0·12 mm, height = 0·92 mm), it was possible to make a relatively accurate absorption correction (Bradley, 1935), even though the compound has a very high linear absorption coefficient of $\mu=131{\cdot}7$ cm^{-1} for Cu $K\alpha$ radiation.

Using *ORFLS* (Busing, Martin & Levy, 1962), a three-dimensional least-squares refinement of the structure reduced R to 0·059 including all unobserved reflections as well as a few intense low-angle reflections suffering from

Table 1. *Atomic parameters* (× 10^4) *and thermal parameters* (× 10^4) *with their e.s.d.'s*

The thermal parameters are of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0000	0000	0000	0063 (01)	0116 (06)	0034 (00)	0005 (02)	0023 (01)	0006 (01)
O(2)	1013 (09)	2846 (23)	1014 (06)	0087 (08)	0160 (46)	0049 (09)	−0019 (14)	0037 (05)	−0006 (10)
C(3)	1998 (13)	4432 (35)	0952 (10)	0076 (10)	0054 (69)	0050 (06)	0052 (19)	0018 (06)	0024 (14)
C(4)	2641 (15)	6276 (38)	1788 (11)	0089 (11)	0089 (72)	0063 (07)	0004 (21)	0019 (07)	−0013 (16)
C(5)	3693 (16)	8064 (42)	1789 (12)	0092 (12)	0213 (79)	0076 (08)	0012 (24)	0024 (08)	0013 (20)
C(6)	4124 (16)	8111 (42)	0954 (12)	0083 (16)	0216 (79)	0081 (09)	−0008 (23)	0023 (08)	0024 (20)
C(7)	3496 (15)	6426 (39)	0140 (11)	0075 (11)	0117 (72)	0082 (08)	−0009 (21)	0030 (08)	0034 (19)
C(8)	2424 (14)	4497 (36)	0102 (10)	0092 (11)	0085 (71)	0056 (06)	0010 (20)	0027 (07)	0026 (15)
C(9)	1864 (14)	2843 (36)	−0808 (10)	0095 (11)	0064 (70)	0053 (06)	−0017 (20)	0033 (07)	0006 (15)
N(10)	0925 (11)	0994 (27)	−0938 (08)	0099 (10)	0119 (57)	0036 (04)	0039 (16)	0030 (05)	−0005 (11)
O(11)	0558 (10)	−0511 (25)	−1866 (07)	0141 (10)	0271 (52)	0047 (04)	−0035 (17)	0048 (05)	−0022 (11)

Table 2. *Comparison of interatomic distances*

	SLJ*	P*	PHS*	LB*
Pd —O(2)		1·99 Å	1·982 (10) Å	
O(2)—C(3)	1·326 Å	1·32	1·312 (18)	1·312 Å
C(3)—C(4)	1·401	1·40	1·426 (21)	1·415
C(4)—C(5)	1·375	1·40	1·398 (26)	1·388
C(5)—C(6)	1·382	1·41	1·404 (23)	1·384
C(6)—C(7)	1·376	1·40	1·356 (24)	1·367
C(7)—C(8)	1·391	1·39	1·444 (24)	1·423
C(8)—C(3)	1·420	1·41	1·421 (19)	1·415
C(8)—C(9)	1·418	1·41	1·433 (21)	1·430
C(9)—N(10)	1·343	1·28	1·291 (20)	1·295
N(10)-Pd		1·94	1·961 (11)	
N(10)-O(11)	1·363	1·36	1·415 (15)	
O(2′) -O(11), H-bond	2·520	2·68	2·621 (15)	
O(2)—N(10), 'Bite'	2·692	2·85	2·850 (14)	

* See footnote to Table 3.

extinction. The following weights were applied: 1·0 for F_o between 5·0 and 30; 0·9 for F_o between 2·0 and 5·0; 0·8 for $F_o < 2·0$; and 0·7 for $F_o > 30$. The final atomic and thermal parameters and their estimated standard deviations are given in Table 1. Because of the predominant contribution of the palladium atom to the structure factors, the thermal parameters of the light atoms are of dubious value. The resulting bond distance and angles with estimated standard deviations are given in Tables 2 and 3 and Fig. 1. In Table 2, the bond distances are compared with those of the nickel complex, the two-dimensional palladium structure, and a set of average bond distances for various salicylaldiminate structures (Lingafelter & Braun, 1966); the bond angles are compared with those of the nickel complex in Table 3. The atom numbering system follows that used by Merritt, Guare & Lessor (1956) in their original determination of the nickel complex. Table 4 lists the calculated and observed structure factors.

Table 3. *Comparison of interatomic angles*

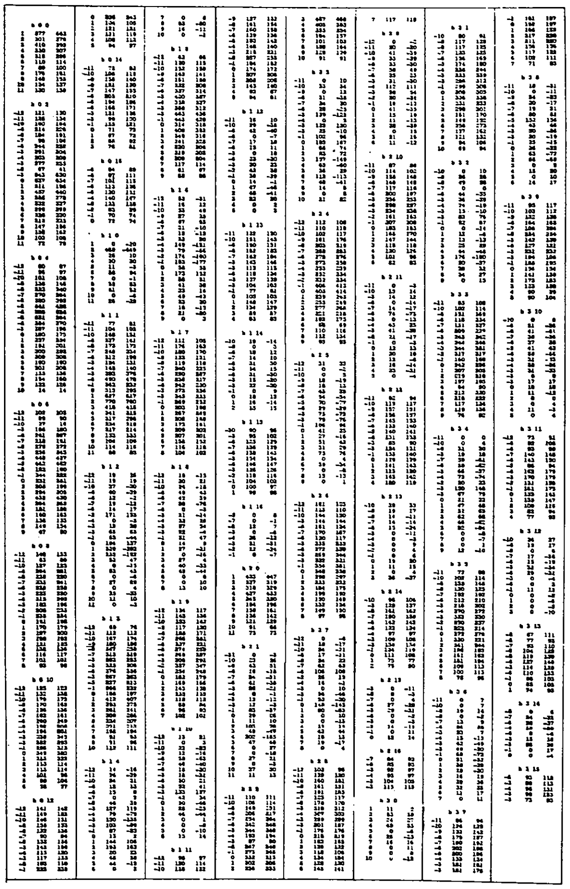
	PHS*	SLJ*†
N(10)–M——O(2)	92·5 (0·7)°	94·0°
M——O(2)—C(3)	125·6 (1·2)	129·2
O(2)—C(3)—C(8)	124·6 (1·8)	123·3
C(8)—C(3)—C(4)	118·5 (1·8)	117·6
C(3)—C(4)—C(5)	121·2 (2·2)	121·2
C(4)—C(5)—C(6)	120·3 (2·2)	121·2
C(5)—C(6)—C(7)	119·2 (2·1)	118·7
C(6)—C(7)—C(8)	123·0 (2·2)	121·7
C(7)—C(8)—C(3)	117·7 (1·9)	119·6
C(3)—C(8)—C(9)	125·8 (1·8)	121·5
C(8)—C(9)—N(10)	123·3 (1·9)	124·7
C(9)—N(10)–M	128·0 (1·3)	126·8
O(11)–N(10)–M	117·3 (0·9)	120·9

* SLJ Values of Srivastava, Lingafelter & Jain (1967) for nickel complex.
P Values of Pfluger (1958) for two-dimensional study of Pd complex.
PHS Values of this three-dimensional study of Pd complex.
LB Mean values from three-dimensional determinations of salicylaldiminate structures (Lingafelter & Braun, 1966).
† Calculated from SLJ's atomic coordinates.

In general, the determined bond distances agree very well with the other three sets of distances, particularly with the average values. Only the N(10)–O(11) bond deviates somewhat from that in the nickel complex; however the 1·415 Å distance found agrees very well with distances 1·413 and 1·409 Å found by Groth (1968) in cyclohexa-1,4-dionedioxime. As expected for an atom of larger size, the 'bite' and hydrogen-bonding distances for the palladium complex are much larger than for the nickel complex. Infrared spectra of the two complexes showed a higher OH-stretching frequency for the palladium complex, in agreement with the structural findings. The angles, too, in spite of their rather large standard deviations, show an expected trend for the accommodation of a larger atom, *i.e.* the angles that the functional groups make with the benzene ring have opened up somewhat, while the other angles have either remained about the same or have decreased.

Similar to the nickel complex, the carbon atoms and the phenolic oxygen atom of the palladium complex form a plane having the equation $-0·568X + 0·690Y - 0·196Z = 0·076$ (X, Y, Z are in Å units in an axis system parallel to the unit-cell axes), with deviations from the plane being on the order of 0·01 Å. The metal atom, the oxime nitrogen atom, and the oxime oxygen atom are out of this plane by 0·08, 0·03 and 0·07 Å respectively, compared with 0·12, 0·06 and 0·08 Å for the nickel complex, indicating the palladium complex to be somewhat more planar than the nickel complex but still exhibiting the 'chair' type structure typically found in complexes of this type.

Table 4. *Observed and calculated structure factors* (× 10)



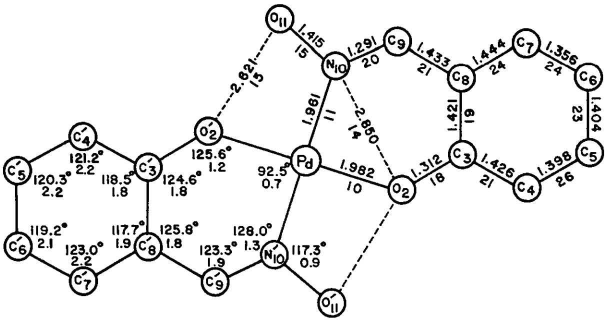


Fig. 1. Bond distances and angles. Estimated standard deviations are given below each value.

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A refinement of the crystal structure of β-isoprene sulfone.

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The crystal structure of β-isoprene sulfone, determined by Cox & Jeffrey and refined by Jeffrey has been re-refined. The crystals are monoclinic ($P2_1/m$) with $a=6{\cdot}709$ (5), $b=7{\cdot}67$ (1), $c=6{\cdot}707$ (5) Å, $\beta=110{\cdot}266$ (6)°, $Z=4$. Three-dimensional counter data were collected using silicon monochromatized Mo $K\alpha$ radiation. The structure was refined by full-matrix least squares to an R index of 0·069.

Introduction

The crystal structure of β-isoprene sulfone [Fig. 1(*a*)] was first determined by Cox & Jeffrey (1942) and later refined by Jeffrey (1951) using Fourier methods and the original data. Jeffrey (1951) reported the C(2)–C(3) bond length to be 1·37 (2) Å. This is considerably longer than one would expect for a carbon–carbon double bond. A related compound, butadiene [Fig. 1(*b*)] has been studied by Sands & Day (1967) and they report the C(2)–C(3) bond length to be 1·299 (8) Å. As part of a study of cyclic sulfones in our laboratory we also have determined the structure of butadiene sulfone. Our results confirm those of Sands & Day. Because of this discrepancy in the C(2)–C(3) bond length between the two compounds, we have collected a set of three-dimensional data and have re-refined the structure of β-isoprene sulfone by full-matrix least squares.

Table 1. *Final atomic parameters and their e.s.d.'s*

The values in the Table have been multiplied by 10^4.

The temperature factors are of the form: $T=\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	2621 (2)	2500	298 (2)	146 (3)	103 (2)	159 (3)	0	55 (3)	0
C(1)	1140 (7)	2500	2097 (7)	154 (15)	145 (9)	237 (17)	0	108 (14)	0
C(2)	2866 (10)	2500	4218 (8)	383 (24)	213 (11)	155 (19)	0	135 (17)	0
C(3)	4860 (8)	2500	4362 (7)	260 (18)	106 (9)	188 (17)	0	−17 (15)	0
C(4)	5267 (7)	2500	2297 (8)	109 (15)	173 (10)	273 (20)	0	12 (14)	0
C(5)	6732 (15)	2500	6356 (11)	443 (34)	283 (20)	315 (31)	0	−122 (23)	0
O	2266 (3)	912 (3)	−0871 (3)	237 (7)	170 (5)	273 (9)	−13 (5)	96 (7)	−68 (5)
				B					
H(1)	180 (38)	1522 (33)	2063 (40)	6·0					
H(2)	2413 (64)	2500	5037 (58)	6·0					
H(3)	5950 (39)	1448 (32)	2300 (42)	6·0					
H(4)	6395 (83)	2500	7247 (70)	6·0					
H(5)	7426 (44)	1661 (34)	6126 (45)	6·0					

Table 2. *A comparison of the bond distances and angles of β-isoprene and butadiene sulfone*

I		II	
S—O	1·424 (2) Å	S—O	1·440 (4) Å
S—C(1)	1·809 (6)	S—C(1)	1·795 (6)
S—C(4)	1·816 (4)	S—C(4)	1·792 (7)
C(1)–C(2)	1·491 (6)	C(1)–C(2)	1·475 (9)
C(2)–C(3)	1·307 (9)	C(2)–C(3)	1·299 (8)
C(3)–C(4)	1·501 (8)	C(3)–C(4)	1·482 (8)
C(3)–C(5)	1·482 (8)		