

may constitute evidence for what may be considered a weak hydrogen bond (Sutor, 1962). In this sense a certain measure of weak but not very specific interaction due to the lactone group may be considered to operate. However there is no clear distinction between the behaviour of the two oxygen atoms, O(1) and O(2), so that neither the lone pair of electrons or the partial charge appears to exert a specific bonding effect. The comparison of molecular packing in the two compounds therefore fails to reveal any direct evidence of the special states of O(1) and O(2) which would correlate with that suggested by the evidence of planarity of the lactone group and the dissymmetry of the C-O bond lengths.

We are grateful to Prof. G. W. K. Cavill of the University of New South Wales for his kindness in supplying a sample of iridomyrmecin. We also wish to thank Mr P. Jennings of the University of Western Australia for his assistance in constructing ball-on-spike models of the crystal structures of iridomyrmecin and isoiridomyrmecin.

Acta Cryst. (1964). **17**, 477

X-ray Studies of the Bis-*N*-alkylsalicylaldiminates of Bivalent Metals. III. Structure of Bis-*N*-butylsalicylaldimine-palladium

BY EDOARDO FRASSON, CARLO PANATTONI AND LUIGI SACCONI

Centro di Strutturistica Chimica del C.N.R.-Sezione di Padova, Italy
Istituto di Chimica Generale ed Inorganica dell'Universita, Firenze, Italy

(Received 18 March 1963)

Following the examination of the metal complexes of *N*-alkylsalicylaldimines the crystal structure of bis-*N*-butylsalicylaldimine-palladium was determined by two-dimensional Fourier methods.

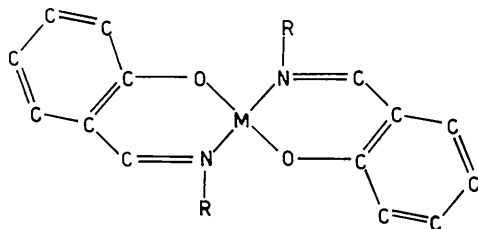
The unit cell is monoclinic with lattice constants

$$a = 10.99, b = 7.25, c = 14.72 \text{ \AA}; \beta = 120^\circ; Z = 2.$$

The space group is $P2_1/c$. The metal atoms are required to be at symmetry centers and the coordination bonds in a trans-planar arrangement. The form of the chelate ring in this compound will be discussed. The results of the structure determination of complexes of this series are compared.

Introduction

As a part of the study of the structures of complexes of *N*-alkylsalicylaldimines of bivalent metals with the general formula



the crystal structure of the palladium complex of the butyl derivative will be described in this paper.

The earlier studies of this series of complexes showed some curious features not only in the geometry of the coordination, but also in the shape of the chelate ring, exhibiting sensitivity to steric hindrance.

Complexes of the butyl derivative with nickel, copper and palladium have been previously described (Frasson & Panattoni, 1962). The crystals are practically isometric and hence the differences in the radii of the coordinating metals can have no influence on the volume occupied by the different molecules. These have virtually identical volumes.

References

- CAVILL, G. W. K. (1960). *Rev. Pure Appl. Chem.* **10**, 169.
CAVILL, G. W. K. & LOCKSLEY, H. D. (1957). *Austr. J. Chem.* **10**, 352.
DOLEJŠ, L., MIRONOV, A. & ŠORM, F. (1960). *Tetrahedron Letters*, No. 11, 18.
FRIDRICHSONS, J. (1959). *Amer. Min.* **44**, 200.
FRIDRICHSONS, J. & MATHIESON, A. McL. (1962). *Acta Cryst.* **15**, 119.
LIPSON, H. & TAYLOR, C. H. (1958). *Fourier Transforms and X-ray Diffraction*. London: Bell.
LÖFGREN, T. (1960). *Acta Cryst.* **13**, 156.
McCONNELL, J. F. & SCHOENBORN, B. P. (1962). *Acta Cryst.* **15**, 779.
McCONNELL, J. F., MATHIESON, A. McL. & SCHOENBORN, B. P. (1962). *Tetrahedron Letters*, No. 10, 445.
MATHIESON, A. McL. (1963). *Tetrahedron Letters*, No. 2, 81.
MATHIESON, A. McL. & TAYLOR, J. C. (1961). *Tetrahedron Letters*, No. 17, 590.
ROLLETT, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. p. 97. Symposium Publications Division, Pergamon Press.
SUTOR, D. J. (1962). *Nature, Lond.* **193**, 68.

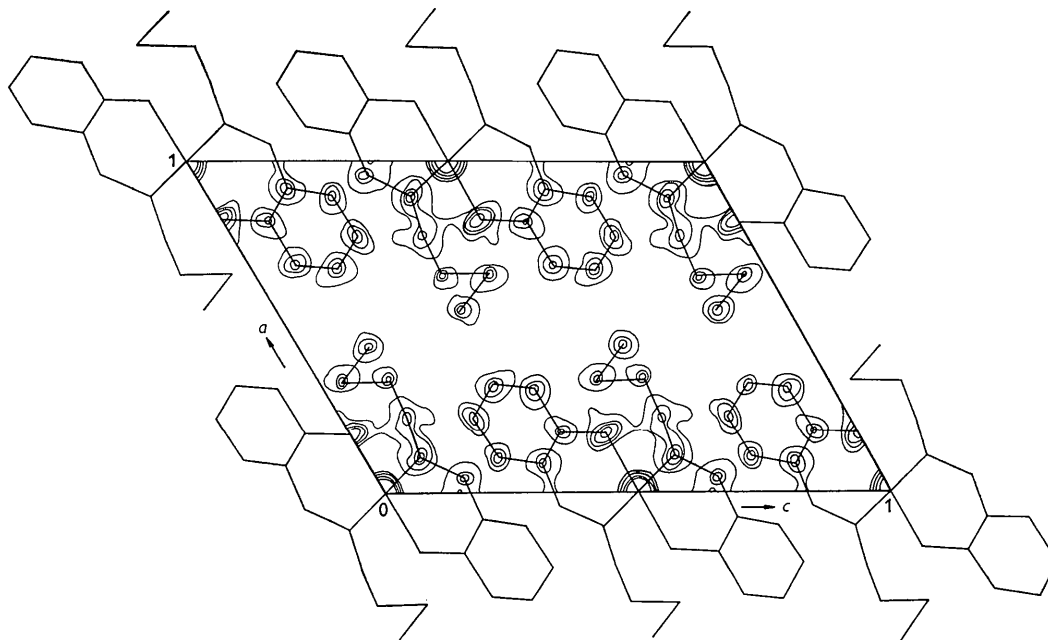


Fig. 1. Electron density projection on (010). Contours at 2, 4, 6, 8 e.Å⁻².

lengths and the supposed inclination of the molecule.

Experimental data were put on an absolute scale by comparison of the experimental and calculated structure factors F_o and F_c . The thermal factor was calculated with the same procedure. This calculation was repeated at successive refinement steps. The final value for the Debye-Waller factor is $B=2.88$ for all atomic species. For the refinement of the atomic coordinates Cochran's method of difference synthesis (1951) was followed. The refinement procedure yielded the following values for the reliability indices: $R=0.11$ for the $h0l$ reflexions and $R=0.08$ for the $0kl$ reflexions. Observed and calculated structure factors for bis-*N*-butylsalicylaldimine-palladium are listed in Table 1. The final atomic coordinates are listed in Table 2. The projection of electron density on (010) is shown in Fig. 1.

The corrections of the intensities and the calculation

of structure factors and Fourier series were made on the Olivetti-Elea 9000 electronic computer with programs elaborated by Panattoni, Frasson & Mammi (1960*a, b*) and Panattoni & Frasson (1961).

Estimation of accuracy

The accuracy of the proposed coordinates has been calculated by the method of Cruickshank (1949). The values of the standard error have been calculated for the well resolved maxima neglecting some overlapped atoms on the projection on (100). The values of the standard deviations along x , y , and z for the oxygen and nitrogen atoms do not exceed 0.015 Å, while that for the carbon atoms has a mean value of 0.02 Å with a maximum of 0.05 Å.

Description of the structure

As has been done for the other complexes of this series, the mean plane of this molecule has been calculated with the exclusion from the least-squares equation of the atoms of the alkyl chain and of the atoms of the adjacent side of the chelate ring, which are not coplanar with the other part of the molecule.

The equation of the mean plane is:

$$0.14701x - 1.22583y + z = 0.$$

Atomic coordinates have been calculated with respect to three orthogonal axes ξ , η , ζ with origin on the palladium atom; ξ and η lie in the mean plane of the molecule, ζ being normal to this plane.

Table 3 lists the atomic coordinates of the atoms

Table 2. Atomic coordinates for bis-*N*-butylsalicylaldimine-palladium

	x/a	y/b	z/c
Pd	0.0000	0.5000	0.5000
O	0.1808	0.5153	0.4980
N	-0.1077	0.2999	0.3944
C(1)	0.1828	0.4026	0.4069
C(2)	0.3090	0.4306	0.4080
C(3)	0.3253	0.3500	0.3303
C(4)	0.2246	0.2341	0.2585
C(5)	0.1008	0.2016	0.2600
C(6)	0.0800	0.2838	0.3360
C(7)	-0.0457	0.2414	0.3350
C(8)	-0.2228	0.1863	0.3722
C(9)	-0.2000	0.1166	0.4667
C(10)	-0.3365	0.0741	0.4584
C(11)	-0.4451	-0.0051	0.3589

Table 3. Atomic coordinates referred to the orthogonal axes ξ , η , and ζ

	ξ	η	ζ
Pd	0.0000 Å	0.0000 Å	0.0000 Å
O	2.0007	-0.1005	0.0836
N	-0.5762	-1.9222	0.2344
C(1)	2.5909	-1.5664	0.0471
C(2)	3.9841	-1.5311	0.0269
C(3)	4.6602	-2.7221	-0.0761
C(4)	3.9861	-3.9152	-0.0574
C(5)	2.5962	-3.9448	0.0095
C(6)	1.8848	-2.7605	0.0864
C(7)	0.4839	-2.8595	0.1885
C(8)	-1.7681	-2.5743	0.5898
C(9)	-2.2700	-1.9206	1.6967
C(10)	-3.7355	-2.0877	1.7348
C(11)	-4.2617	-3.3974	1.3368

Table 4. Bond lengths and angles

Bond	Bond	Bond	
Pd-O	2.00 ± 0.02 Å	C(6)-C(1)	1.39 ± 0.04 Å
Pd-N	2.01 ± 0.02	C(6)-C(7)	1.40 ± 0.03
O-C(1)	1.58 ± 0.03	N-C(7)	1.42 ± 0.03
C(1)-C(2)	1.39 ± 0.03	N-C(8)	1.41 ± 0.02
C(2)-C(3)	1.38 ± 0.03	C(8)-C(9)	1.39 ± 0.03
C(3)-C(4)	1.38 ± 0.05	C(9)-C(10)	1.48 ± 0.04
C(4)-C(5)	1.39 ± 0.04	C(10)-C(11)	1.47 ± 0.04
C(5)-C(6)	1.38 ± 0.04		
Angle	Angle	Angle	
O-Pd-N	104°	C(3)-C(4)-C(5)	120°
C(1)-O-Pd	115	C(4)-C(5)-C(6)	120
C(6)-C(1)-O	127	C(5)-C(6)-C(1)	119
C(1)-C(6)-C(7)	124.5	C(6)-C(1)-C(2)	122
C(6)-C(7)-N	134	N-C(8)-C(9)	106
C(7)-N-Pd	115	C(8)-C(9)-C(10)	105.5
C(1)-C(2)-C(3)	118	C(9)-C(10)-C(11)	116
C(2)-C(3)-C(4)	121		

referred to the axes ξ , η , ζ . Bond lengths and angles in bis-*N*-butylsalicylaldimine-palladium are shown in

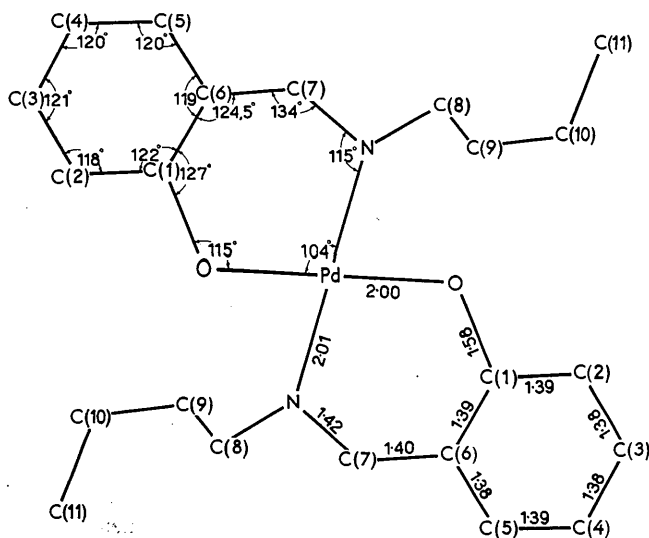


Fig. 2. Bond lengths and angles in bis-*N*-butylsalicylaldimine-palladium.

Fig. 2. In Table 4 bond lengths and angles are listed, together with the standard errors.

Discussion of the structure

This complex, like the others, shown the non-planarity of the six-membered chelate ring. It is therefore concluded that the normal alkyl group bonded to the nitrogen is able to move a part of the chelate ring out of the mean plane of the molecule in its direction.

But this is not the only noteworthy characteristic of this structure. Table 5 shows the bond lengths and angles of the chelate rings of similar compounds that we have found in the literature. The values of the bond lengths of the complexes (a), (b), (c), and (d) are almost the same, the differences being of the same order as the standard errors. The second group of complexes (e and f) shows almost identical values for the N-C(7) and C(7)-C(6) bond distances. In both complexes (e and f) we note a little shortening of the C(7)-C(6) distance in comparison with the previous group (a), (b), (c) and (d), and a relatively great increase (0.1 Å) in the N-C(7) distance. The O-C(1) distances in (e) and (f) are both greater than those found in the other group of complexes. In the other structures the shortening of the O-C(1) bonds has been interpreted as a contribution of the chelate ring to the aromatic character of the benzene ring (Merritt, Guare & Lessor, 1956). In this butyl complex the oxygen side of the chelate ring does not show aromatic character. However, the bond distances on the nitrogen side of the chelate ring may be influenced by the aromatic ring. The sequence of atoms departing from the benzene ring, *viz.* C(6)-C(7)-N-C(8)-C(9)-C(10)-C(11), shows the bond distances 1.40, 1.42, 1.41, 1.39, 1.48, 1.47 Å. The values for the most distant bonds in the butyl group approach the normal value for a single bond, but a noticeable shortening is present

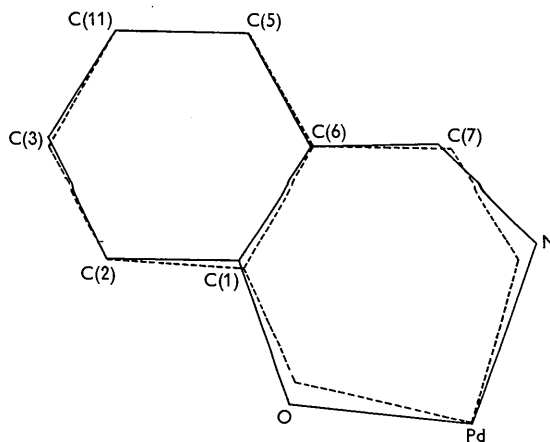


Fig. 3. Comparison of the form of the molecules of bis-*N*-ethylsalicylaldimine-Pd (dashed lines) and bis-*N*-butylsalicylaldimine-Pd (full lines). Alkyl chains omitted.

Table 5. *Interatomic distances and angles in the chelate ring of some metal (M) complexes of salicylaldimine and salicylaldoxime*

	(a)	(b)	(c)	(d)	(e)	(f)
M-O	1.94 Å	1.80 Å	1.90 Å	1.84 Å	1.83 Å	2.00 Å
M-N	1.86	1.90	1.99	1.84	1.86	2.01
N-C(7)	1.31	1.30	1.31	1.29	1.40	1.42
C(7)-C(6)	1.49	1.46	1.44	1.44	1.40	1.42
C(1)-O	1.32	1.28	1.32	1.32	1.40	1.58
N-M-O	91°	96°	91°	94°	96°	104°
M-N-C(7)	133	125	126	130.3	124	115
N-C(7)-C(6)	121	122	126	121.5	126	134
C(7)-C(6)-C(1)	122.5	124	123	122.8	121	124.5
C(6)-C(1)-O	123	126	119	124	127	127
C(1)-O-M	129	127	131	127.5	126	115

(a) Bis-*N*-ethylsalicylaldimine-palladium (Frasson, Panattoni & Sacconi, 1964).

(b) Bis-*N*-methylsalicylaldimine-nickel (Frasson, Panattoni & Sacconi, 1959).

(c) Bis-*N*-methylsalicylaldimine-copper (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961).

(d) Bis-salicylaldimine-nickel (Stewart & Lingafelter, 1959).

(e) Bis-salicylaldoxime-nickel (Merrit *et al.*, 1956).

(f) Bis-*N*-butylsalicylaldimine-palladium (Frasson *et al.*, present work).

in the distances of the bonds nearest to the benzene ring.

In Table 5 bond angles are also listed, but it is difficult to find any regularities in their variations. With respect to bond angles the butyl complex of palladium presents an additional odd feature: the smallness of the bond angles at the nitrogen and oxygen. Fig. 3 compares the forms of the molecules of the ethyl and butyl complexes. The coordination bonds in the latter complex are significantly about 0.1 Å longer than in the ethyl complex. A casual convergence of errors increased the C-O bond, but in any case it is a single bond. Nevertheless we can note that both benzene rings are in the same position with respect to the metal atom. In other words the increase in the Pd-N, Pd-O and O-C bonds that occurs in this structure does not influence the length of the molecule, but the N-O distance in the chelate ring. Almost certainly this is a steric phenomenon due to the possibility of expansion of the molecule within the crystal.

References

- COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 FRASSON, E. & BEZZI, S. (1959). *Acta Cryst.* **12**, 536.
 FRASSON, E., PANATTONI, C. & SACCONI, L. (1959). *J. Phys. Chem.* **63**, 1908.
 FRASSON, E., PANATTONI, C. (1962). Proc. 7th I.C.C.C. Stockholm, 88.
 FRASSON, E., PANATTONI, C. & SACCONI, L. (1964). *Acta Cryst.* **17**, 85.
 LINGAFELTER, E. C., SIMMONS, G. L., MOROSIN, B., SCHERINGER, C. & FREIBURG, C. (1961). *Acta Cryst.* **14**, 1222.
 MERRIT, L. L., GUARE, C. & LESSOR, A. E. (1956). *Acta Cryst.* **9**, 253.
 PANATTONI, C., FRASSON, E. & MAMMI, M. (1960a). *Ric. Sci.* **30**, 2099.
 PANATTONI, C., FRASSON, E. & MAMMI, M. (1960b). *Ric. Sci.* **30**, 2474.
 PANATTONI, C. & FRASSON, E. (1961). *Ric. Sci.* **31**, 120.
 SACCONI, L., CIAMPOLINI, M., MAGGIO, F. & DEL RE, G. (1960). *J. Amer. Chem. Soc.* **82**, 815.
 STEWART, J. M. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 842.