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X-Ray Study of the Compound Obtained by the Reaction of N^δ-Salicylidene-L-ornithine and Palladium(II) acetate. The Crystal Structure of (N^α-Salicylidene-D-ornithinato) (N^α-Salicylidene-L-ornithinato)dipalladium(II)-Dimethyl Sulfoxide

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X-Ray structure analysis has elucidated that the reaction of N^δ-salicylidene-L-ornithine and palladium(II) acetate in DMF results in the amine exchange and racemization of the ligand, yielding (N^α-salicylidene-D-ornithinato)(N^α-salicylidene-L-ornithinato)dipalladium(II). The yellow crystals are monoclinic, $a=15.15(2)$, $b=9.80(1)$, $c=15.67(2)$ Å, $\beta=111.3(1)°$, space group $P2_1/c$, and $Z=2$. The structure was solved by the Patterson and Fourier techniques and was refined by the least-squares method to $R=0.105$. The complex molecule has a center of symmetry by which D- and L-Schiff-base ligands are interrelated. Each Pd atom has a square-planar coordination by means of two O and N^α atoms of one ligand, and the N^δ atom of the other one, the two N atoms being in the *trans* position. The $H_2N^\delta{-}(CH_2)_3{-}\underset{|}{C}H{-}N^\alpha$ fragments of the two ligands bridge the two Pd atoms, giving a 14-membered ring.

The stereoselectivity of metal complex[1] is an important subject in the coordination chemistry. We planned to study the stereochemical behavior of the dissymmetric complexes of labile metal ions for some amino acids and attempted to prepare the optically active Ni(II), Cu(II), and Pd(II) complexes involving the quadridentate Schiff-base ligand N^δ-salicylidene-ornithine. However, none of the products obtained from the reactions of the acetates of these metal ions with the L-enantiomer of the ligand in DMF showed any optical activity. Since the Pd(II) complex was isolated as good crystals, an X-ray crystal structure analysis was undertaken in order to discover why the optical activity due to the dissymmetric ligand disappears during the reaction.

Experimental

Preparation. N^δ-Salicylidene-L-ornithine (sal-L-orn) was prepared following the procedure of Witkop *et al.*[2] The yellow crystals decompose at 201—202 °C; the temperature agrees well with the temperature reported by them. A suspension of equimolar amounts of sal-L-orn and palladium(II) acetate in DMF was stirred for several hours until they had been completely dissolved. Brownish yellow crystals were then precipitated by the addition of twice as many moles of dipyridyl as the sal-L-orn and subsequently recrystallized from hot DMSO. Since the compounds are efflorescent, the elemental analyses could not be carried out. The exact composition of the compound was determined by means of X-ray structure analysis, as will be described below.

X-Ray Measurement. Since the compound decomposes rapidly in air, the crystals were sealed in thin-walled Lindemann glass capillaries. Two well-formed specimens with the approximate dimensions of 0.12 × 0.27 × 0.23 and 0.12 × 0.25 × 0.43 mm were used for the intensity measurements, one mounted about the *b* axis and the other, about the *c* axis. The unit-cell dimensions were determined by a least-squares refinement of 45 independent measurements of the 2θ values from Weissenberg photographs calibrated by silicon powder ($a=5.4307$ Å). Crystal data: $Pd_2(C_{12}H_{14}N_2O_3)_2(C_2H_6SO)_4$, mol wt 993.7. Monoclinic, $a=15.15(2)$ Å, $b=9.80(1)$ Å, $c=15.67\,(2)$ Å, $\beta=111.3\,(1)°$, space group $P2_1/c$, $Z=2$ ($D_x=1.51$, $D_m=1.52$ g cm^{-3}), $F(000)=1008$, $V=2169$ Å^3, $\mu=90.7$ cm^{-1} (for Cu$K\alpha$).

Multiple film, equi-inclination Weissenberg photographs for the *h*0*l*-*h*6*l* and *hk*0-*hk*10 layers were taken with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). The intensities were estimated visually by the use of a calibrated intensity scale. After corrections for the usual *Lp*-factor and the spot shape, the structure amplitudes were placed on a common arbitrary scale by internal correlation. A total of 3641 independent reflections were collected. However, 622 of these were too weak to be observed, and so they were assumed to be zero. No correction for absorption was made.

Structure Determination

In the beginning of the structure analysis we knew only that the crystal contains the palladium atoms, the salicylidene-ornithine ligand, and probably DMSO molecules. A trial calculation of the density indicated that there may be four Pd atoms in a unit cell. The initial coordinates for the Pd atom were determined from a three-dimensional Patterson map. Two sulfur and eight light atoms were located on a Fourier map phased by the heavy atom. The positions of all the remaining non-hydrogen atoms were found by successive Fourier syntheses. At this point it was revealed that the complex corresponded to dimeric(N^α-salicylidene-D-ornithinato) (N^α-salicylidene-L-ornithinato)-dipalladium(II)·4DMSO; the optically active N^δ-salicylidene-L-ornithine used initially seems to be isomerized to the N^α analogue and to be racemized during the reaction with palladium(II) acetate. Several cycles of block-diagonal least-squares refinement gave an R factor of 0.142, isotropic temperature factors being used for all the atoms. Five more cycles of the refinement with anisotropic temperature factors converged to $R=0.105$ for 3119 non-zero reflections. The weighting scheme employed was:

Table 1. Fractional positional parameters (× 10^4) and anisotropic temperature factors (× 10^4) with e. s. d. 's in parentheses

Temperature factors are of the form: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	460(1)	1856(1)	3996(1)	61(0)	72(1)	44(0)	−2(1)	45(1)	0(1)
C(1)	2343(10)	1120(12)	4060(9)	74(8)	99(13)	63(7)	15(17)	61(13)	14(16)
C(2)	3308(10)	1301(16)	4399(11)	69(9)	146(17)	76(9)	13(20)	52(15)	10(21)
C(3)	3900(12)	666(18)	3989(13)	78(10)	178(23)	105(12)	3(25)	73(19)	−12(28)
C(4)	3485(14)	−260(19)	3252(14)	123(15)	169(23)	122(15)	74(30)	129(25)	21(30)
C(5)	2524(11)	−493(15)	2913(12)	78(9)	125(17)	110(12)	22(21)	101(18)	6(24)
C(6)	1926(9)	185(11)	3310(9)	71(8)	88(12)	62(7)	10(15)	77(12)	12(15)
C(7)	952(9)	−150(12)	2871(8)	80(8)	89(12)	51(6)	25(16)	68(12)	25(14)
C(8)	−718(8)	52(12)	2603(8)	61(7)	100(13)	47(6)	−12(15)	31(11)	21(15)
C(9)	−1358(10)	1065(13)	2862(10)	74(8)	104(14)	63(8)	−1(18)	34(13)	2(17)
C(10)	−900(9)	−1417(11)	2863(8)	77(8)	87(11)	41(6)	−41(15)	38(11)	−19(13)
C(11)	−660(10)	−1602(11)	3883(8)	85(8)	70(11)	49(6)	−17(15)	53(12)	−12(13)
C(12)	992(10)	2994(12)	2906(8)	91(9)	97(13)	44(6)	−54(18)	59(12)	−18(15)
C(13)	7067(14)	4784(26)	5165(16)	99(14)	303(40)	137(18)	144(39)	76(26)	−73(44)
C(14)	7420(15)	2207(19)	4717(18)	111(15)	139(22)	171(21)	−66(29)	69(29)	5(34)
C(15)	3662(17)	1328(33)	7075(19)	99(16)	434(60)	149(22)	61(51)	2(30)	−149(63)
C(16)	4521(20)	−940(27)	8117(24)	161(25)	220(39)	234(34)	−46(49)	50(46)	84(60)
N(1)	292(7)	432(9)	3081(6)	73(6)	74(9)	44(5)	−8(12)	49(9)	17(11)
N(2)	492(6)	3332(8)	4928(6)	60(5)	63(9)	40(4)	−10(11)	42(8)	−6(10)
O(1)	1855(6)	1787(9)	4470(6)	61(5)	127(10)	57(5)	−16(12)	44(8)	−32(12)
O(2)	−942(6)	1960(8)	3479(6)	64(5)	84(8)	64(5)	7(11)	50(8)	−8(11)
O(3)	−2204(7)	980(11)	2491(8)	60(6)	162(14)	97(8)	0(14)	30(10)	−24(17)
O(4)	8746(7)	4012(9)	5272(7)	73(6)	109(10)	93(7)	−2(12)	82(11)	−15(14)
O(5)	5247(10)	1520(17)	8401(15)	78(9)	246(25)	228(19)	35(23)	20(20)	27(35)
S(1)	7716(3)	3882(4)	4626(3)	89(3)	141(5)	68(2)	−14(6)	52(4)	13(5)
S(2)	4308(4)	840(6)	8203(4)	85(3)	209(8)	130(4)	2(8)	56(6)	20(9)

$$w = 0.2 \text{ for } F_o < 7.2$$

$$w = 1.0 \text{ for } 7.2 \leqq F_o \leqq 43.0$$

$$w = (43.0/F_o)^2 \text{ for } F_o > 43.0$$

The scattering factors for the zerovalent Pd, S, N, C, and O atoms were taken from "International Tables for X-ray Crystallography." In the final cycle, the shifts in the atomic parameters were less than their standard deviations. A difference Fourier synthesis computed at this stage did not show the peaks corresponding to any of the hydrogen atoms. The final atomic parameters and their estimated standard deviations are listed in Table 1. A table of the observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7516).

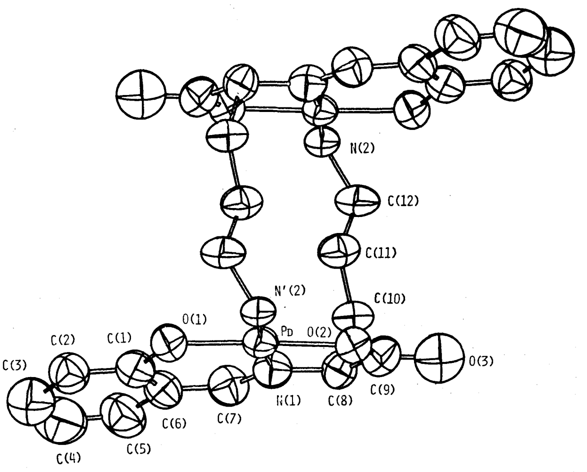


Fig. 1. Perspective view of (N^{α}-sal-D-orn) (N^{α}-sal-L-orn) dipalladium (II). The thermal ellipsoids are drawn at the 48% probability level.

Results and Discussion

A perspective view of the complex, which shows the coordination geometry and the numbering of the atoms, is given in Fig. 1. The complex assumes a dimeric structure. The two halves of this dimer are related by a crystallographic center of symmetry: thus, the molecule is of an inactive *meso* form, with two enantiomeric Schiff-base ligands. The H_2N^{δ}–$(CH_2)_3$–$\overset{|}{C}H$–N^{α} fragments of the two ligands bridge the two Pd atoms, giving the 14-membered ring, as is shown in Fig. 2. The two Pd atoms are separated by 5.31 Å. Each Pd atom has a square-planar coordination and is bonded to the phenolic oxygen, O(1); the carboxylate oxygen, O(2); and the imino nitrogen, N(1), of one salicylidene-ornithine ligand, and to the terminal amino nitrogen N(2) of the enantiomeric one. One of the hydrogen atoms attached to C(11) lies close to the Pd atom, as is shown in Fig. 2. (The coordinates of the H atoms were calculated by assuming the C–H distance to be 1.08 Å.) The Pd···H distance (2.93 Å) seems to be slightly shorter than the sum of the van der Waals radii (3.1 Å);[3)] this suggests that there is a weak interaction between the Pd and H atoms, giving a distorted square-pyramidal coordination of the Pd atom. It is,

TABLE 2. DEVIATIONS OF THE ATOMS FROM LEAST-SQUARES PLANES (d/Å) AND DIHEDRAL ANGLES BETWEEN THEM

(A) Plane through N(1), N′(2), O(1), and O(2) (plane A)					
Pd	−0.01	N(1)	−0.03	N(2)	−0.03
O(1)	0.03	O(2)	0.03		
(B) Plane through Pd, C(8), C(9), N(1), and O(2) (plane B)					
Pd	−0.04	C(8)	−0.05	C(9)	0.01
N(1)	0.06	O(2)	0.03	O(3)	0.03
(C) Plane through Pd, C(1), C(6), C(7), N(1), and O(1) (plane C)					
Pd	0.06	C(1)	0.03	C(6)	0.04
C(7)	−0.02	N(1)	−0.03	O(1)	−0.08
(D) Plane through C(1), C(2), C(3), C(4), C(5), and C(6) (plane D)					
C(1)	0.01	C(2)	−0.02	C(3)	0.02
C(4)	−0.00	C(5)	−0.00	C(6)	−0.00
Dihedral angles between the planes (φ/°)					
A and B	3.9	A and C	5.6	A and D	10.7
B and C	7.4	B and D	12.3	C and D	5.2

Equations of planes

(A) $0.289X + 0.698Y - 0.655Z + 3.005 = 0$

(B) $0.288X + 0.650Y - 0.703Z + 3.329 = 0$

(C) $0.197X + 0.728Y - 0.657Z + 2.878 = 0$

(D) $0.114X + 0.758Y - 0.642Z + 2.847 = 0$

where X, Y, and Z are coordinates in Å units relative to a, b, and c^* axes, respectively.

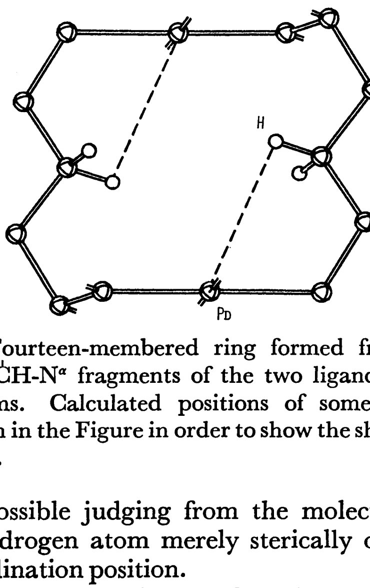


Fig. 2. Fourteen-membered ring formed from H_2N^δ-$(CH_2)_3$-$\dot{C}H$-N^α fragments of the two ligands and two Pd atoms. Calculated positions of some H atoms are given in the Figure in order to show the short Pd···H contacts.

however, possible judging from the molecular models that the hydrogen atom merely sterically occupies the apical coordination position.

The least-squares planes of various parts of the complex and the dihedral angles between them are listed in Table 2. The Pd atom lies on the best least-squares plane (Plane A) defined by the four ligator atoms (Fig. 3). The salicylidene moiety is bent away from Plane A in the opposite direction of another salicylidene-glycinato Pd moiety, while the glycinato residue is bent in its direction.

The bond distances and angles are summarized in Table 3. The Pd–N(2) distance (2.04 Å) is in good agreement with the value found for that in bisethylenediamine palladium(II) (2.04 Å).[4] The Pd–O(2) and Pd–O(1) distances (1.98 and 1.97 Å) are approximately in agreement with the values found for those (2.02 and 1.99 Å) in bis(L-prolinato)palladium(II)[5] and bis(N-isopropyl-3-methylsalicylaldiminato)palladium(II)[6] respectively. The Pd–N(1) distance (1.95 Å) is shorter than those of 2.02 and 2.03 Å in bis(N-isopropyl-3-methylsalicylaldiminato)palladium(II).[6] The other bond distances and angles in the salicylidene-glycinato moiety are similar to those found in (N-salicylideneglycinato)copper(II).[7]

The stereoview along the b axis and the numbering of the atoms of DMSO molecules are shown in Fig. 4. The crystal is composed of the dimeric Pd(II) complexes and the DMSO molecules. All the intermolecular atomic contacts are of the van der Waals type except for the N(2)–H···O(4) hydrogen bond (2.90 Å), which is shown by a dotted line in Fig. 4. The DMSO molecules are normal in their dimensions,[8] but the relatively large thermal motion suggests that there is some disorder in the molecular arrangement.

In the synthesis of the complex, we used only N^δ-salicylidene-L-ornithine as the ligand. Nevertheless, the product contained both the enantiomeric N^α-salicylidene-L- and -D-ornithinate anions. This means that, in the ligand, the amine-exchange reaction

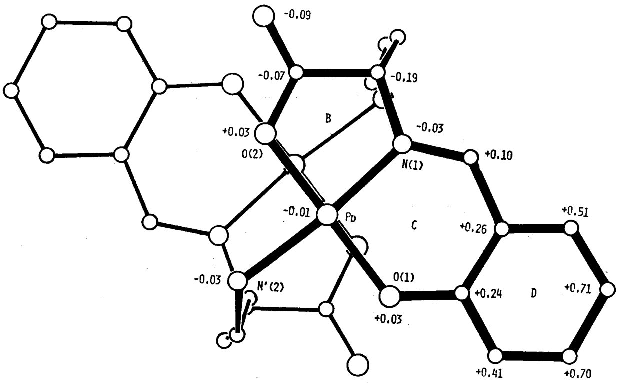


Fig. 3. Projection of (N^α-sal-D-orn) (N^α-sal-L-orn)-dipalladium(II) on the plane through N(1), N′(2), O(1), and O(2) and deviations (Å) of the atoms from the plane.

Table 3. Bond distances (d/Å) and bond angles (φ/°)
E. s. d. 's are in parentheses

Pd-N(1)	1.95(1)	Pd-N(2)	2.04(1)	Pd-O(1)	1.97(1)
Pd-O(2)	1.98(1)	O(1)-C(1)	1.32(2)	C(1)-C(2)	1.38(2)
C(2)-C(3)	1.42(3)	C(3)-C(4)	1.42(3)	C(4)-C(5)	1.38(3)
C(5)-C(6)	1.44(2)	C(1)-C(6)	1.44(2)	C(6)-C(7)	1.42(2)
C(7)-N(1)	1.29(2)	N(1)-C(8)	1.49(2)	C(8)-C(9)	1.54(2)
C(9)-O(2)	1.29(2)	C(9)-O(3)	1.20(2)	C(8)-C(10)	1.55(2)
C(10)-C(11)	1.52(2)	C(11)-C(12)	1.53(2)	C(12)-N(2)	1.48(2)
O(1)-Pd-N(1)	95.0(4)	N(1)-Pd-O(2)	84.4(4)		
O(2)-Pd-N′(2)	90.0(3)	O(1)-Pd-N′(2)	90.6(3)		
Pd-O(1)-C(1)	123.3(9)	O(1)-C(1)-C(2)	117.1(13)		
O(1)-C(1)-C(6)	123.7(13)	C(2)-C(1)-C(6)	119.2(14)		
C(1)-C(2)-C(3)	121.7(16)	C(2)-C(3)-C(4)	118.7(18)		
C(3)-C(4)-C(5)	120.9(20)	C(4)-C(5)-C(6)	120.1(17)		
C(5)-C(6)-C(1)	119.3(13)	C(1)-C(6)-C(7)	127.7(13)		
C(5)-C(6)-C(7)	113.0(13)	C(6)-C(7)-N(1)	122.5(11)		
C(7)-N(1)-C(8)	120.7(11)	C(7)-N(1)-Pd	126.6(10)		
Pd-N(1)-C(8)	112.7(8)	N(1)-C(8)-C(9)	109.6(11)		
N(1)-C(8)-C(10)	110.5(10)	C(9)-C(8)-C(10)	109.9(11)		
C(8)-C(9)-O(2)	117.0(12)	C(8)-C(9)-O(3)	119.3(14)		
O(2)-C(9)-O(3)	123.7(14)	C(9)-O(2)-Pd	115.5(9)		
Pd-N′(2)-C′(12)	116.9(10)	C(8)-C(10)-C(11)	113.1(11)		
C(10)-C(11)-C(12)	111.3(11)	C(11)-C(12)-N(2)	109.8(11)		
S(1)-O(4)	1.53(1)	S(1)-C(13)	1.75(3)	S(1)-C(14)	1.72(3)
S(2)-O(5)	1.50(3)	S(2)-C(15)	1.75(3)	S(2)-C(16)	1.79(4)
O(4)-S(1)-C(13)	104.9(10)	O(4)-S(1)-C(14)	105.0(11)		
C(13)-S(1)-C(14)	103.5(13)	O(5)-S(2)-C(15)	103.3(15)		
O(5)-S(2)-C(16)	105.4(16)	C(15)-S(2)-C(16)	103.9(16)		

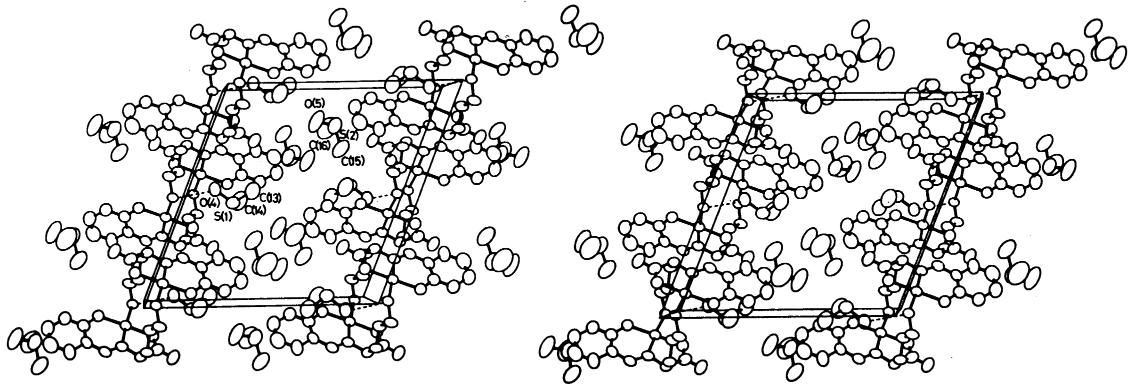
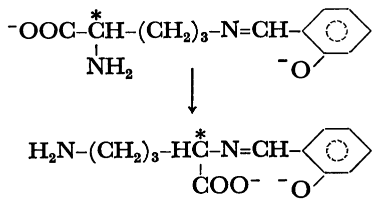


Fig. 4. Stereoscopic view of (N^{α}-sal-D-orn)(N^{α}-sal-L-orn)dipalladium(II)·4DMSO, looking down along the b axis. Dotted lines show the N(2)–H···O(4) hydrogen bonds.

proceeds thus:



$$\begin{array}{l} {}^{-}OOC\text{-}\overset{*}{C}H\text{-}(CH_2)_3\text{-}N{=}CH\text{-}C_6H_4\text{-}O^{-} \\ \quad\;\; NH_2 \\ \qquad\qquad\downarrow \\ H_2N\text{-}(CH_2)_3\text{-}H\overset{*}{C}\text{-}N{=}CH\text{-}C_6H_4\text{-}O^{-} \\ \qquad\qquad\quad COO^{-} \end{array}$$

Furthermore, the recemization reaction apparently takes place during the reaction of N^{δ}-salicylidene-L-ornithine and palladium(II) acetate in DMF and the subsequent recrystallization from DMSO.

So far several studies have been made of the mechanisms of amine-exchange and racemization reactions in the metal chelates of some Schiff bases. Verter and his co-workers proposed the mechanism of amine-exchange reaction in bis[N-(phenyl derivatives)-salicylaldimine]copper(II) [9] whereas Weinstein *et al.* presented that of the racemization reaction in (N-pyridoxylidene-L-valinato)copper(II).[10] The former may be applicable to the present complex, though whether the reaction occurs by means of an intra- or an intermolecular mechanism is unknown. The latter is different in situation from the present case.

Most of the calculations were made by using a local version of the UNICS programs.[11] The authors wish to express their thanks to Dr. Ken Hirotsu and Dr.

Fusao Takusagawa, who adapted these programs to a FACOM 270-30 computer at Osaka City University. Figure 4 was drawn by using the TECS program written by Dr. Takusagawa.

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