  Bull. Chem. Soc. Jpn., 53, 10—14 (1980) [Vol. 53, No. 1

The Crystal Structure of (Acetylacetonato)bis(diethylamine)palladium(II) Acetylacetonate at −170 °C

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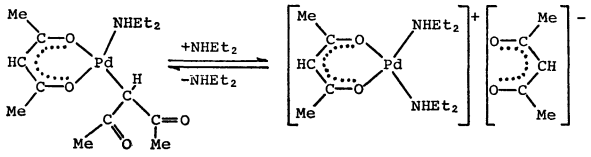
(Received February 22, 1979)

The crystal structure of $[\{Pd(acac)(NHEt_2)_2\}^+(acac)^-]$ at −170 °C was determined by means of X-ray diffraction. The crystal belongs to monoclinic system: $a=13.905(3)$, $b=12.901(4)$, $c=12.205(3)$ Å, $\beta=96.28(2)°$, space group I2/c with $Z=4$. The structure was established by the heavy atom method and refined anisotropically by the least-squares procedure; $R=0.044$ for 1558 non-zero reflections. Both the $\{Pd(acac)(NHEt_2)_2\}^+$ cation and $(acac)^-$ anion lie on the crystallographic two-fold axis. The cation and anion lying on the same two-fold axis are bound together by two hydrogen bonds [N–H···O(2)=N′–H′···O(2′)=2.871(4) Å] to form an ion-pair. Two ion-pairs mutually related by the crystallographic center of symmetry make a packing unit of the crystal.

Okeya *et al.*[1] obtained (acetylacetonato)bis(diethylamine)palladium(II) acetylacetonate (**2**) by the reaction between (acetylacetonatoacetylacetonyl)(diethylamine)palladium(II) (**1**) and diethylamine. They observed that ligand exchange and Pd–C bond formation take place when the complex is dissolved in dichloromethane.



1 **2**

Crystals of **2** are unstable at room temperature, and by liberating a diethylamine molecule, Pd–C bond formation takes place in the solid state. Since the spatial disposition of anions and cations in the crystal seemed to be of interest in relation to ligand exchange and Pd–C bond formation reactions, the crystal structure analysis of the present complex was undertaken.

Experimental

The crystals are unstable at room temperature and easily decompose in a few days. A crystal, *ca.* 0.25×0.23×0.25 mm, was mounted on a Rigaku automated, four-circle single crystal diffractometer. The unit-cell parameters were determined at 20 and −170 °C, respectively. Crystal data are given in Table 1.

Intensity data were collected at −170 °C on the Rigaku diffractometer. Low temperature was attained by the gas flow method using liquid N_2. Graphite-monochromatized Mo $K\alpha$ radiation was used, the θ-2θ scan technique, with scan rate 4° min^{-1} and asymmetric scan width $\Delta(2\theta)=(2.0+0.7\tan\theta_c)°$, where θ_c is the calculated value of the Bragg angle using λ(Mo $K\alpha_1$)(=0.70926 Å), being employed. Background count was obtained by averaging the values measured for 7.5 s at both ends of a scan. For weak reflections with $|F|<3\sigma(F)$ the peak scan was repeated up to four times depending on their intensities. Four standard reflections (404, 640, 314, and 080) were measured after every 60 reflections, no intensity decrease being observed during the course of experiment. Numbers of reflections scanned ($2\theta\leqq48°$), observed, and unobserved were 1804, 1558, and 246, respectively. Correction for the usual Lp effect was made, the absorption correction being ignored (μ(Mo $K\alpha$)=8.61 cm^{-1}).

TABLE 1. CRYSTAL DATA OF $[\{Pd(acac)(NHEt_2)_2\}^+(acac)^-]$ ($C_{18}H_{36}N_2O_4Pd$, *F.W.* 450.9)

	−170 °C	20 °C
Crystal system	Monoclinic	Monoclinic
Space group	I2/c	I2/c
a/Å	13.905 (3)	14.455 (3)
b/Å	12.901 (4)	12.863 (3)
c/Å	12.205 (3)	12.210 (2)
β/°	96.28 (2)	95.56 (2)
V/Å^3	2176.2 (8)	2259.3 (7)
Z	4	4
D_c/g cm^{-3}	1.376	1.325
μ(Mo $K\alpha$)/cm^{-1}	8.61	8.30

Structure Determination and Refinement

The structure was solved by the heavy atom method. Since the space group is I2/c (No. 15) and the number of formula units per unit-cell is four, both the $\{Pd(acac)(NHEt_2)_2\}^+$ and $(acac)^-$ ions should lie on a two-fold axis. The coordinates of the Pd atom were determined from a three-dimensional Patterson function. Locations of all the remaining non-hydrogen atoms were determined by the Fourier synthesis. All the H atoms were located from the subsequent difference Fourier map.

The structure was refined by the block-diagonal least-squares procedure (*HBLS* V)[2] minimizing $\Sigma w\cdot(\Delta F)^2$. Anisotropic thermal parameters were considered for Pd, C, O, and N and isotropic ones for H. The final R value is 0.044 for 1558 observed (0.057 for all) reflections. The weighting scheme used was $w=(\sigma_{cs}+a|F_o|+b|F_o|^2)^{-1}$ for $|F_o|>0$ and $w=c$ for $|F_o|=0$, where σ_{cs} is the standard deviation obtained from the counting statistics, the values of a, b, and c used in the final refinement being −0.0162, 0.0037, and 2.7537, respectively. All the atomic scattering factors used were taken from International Tables for X-Ray Crystallography, Vol. IV.[3] The final atomic parameters are given in Table 2.†

TABLE 2. FINAL ATOMIC PARAMETERS (e.s.d.'s in parentheses)

Positional parameters in fraction of cell edges and anisotropic and isotropic thermal parameters in the form of $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$ and $\exp\{-B(\sin\theta/\lambda)^2\}$, respectively.

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.0	0.00329(3)	0.25	0.00249(2)	0.00128(2)	0.00351(3)	0.0	0.00078(4)	0.0
O(1)	0.0876(2)	−0.1024(2)	0.1935(2)	0.0031(1)	0.0025(2)	0.0049(2)	0.0008(3)	−0.0000(3)	−0.0023(3)
O(2)	0.0744(2)	0.2889(2)	0.3461(2)	0.0034(2)	0.0017(2)	0.0039(2)	0.0004(2)	−0.0005(3)	−0.0005(3)
N	0.0905(2)	0.1153(2)	0.2020(2)	0.0022(2)	0.0019(2)	0.0027(2)	0.0003(3)	0.0007(3)	−0.0001(3)
C(1)	0.0732(3)	−0.1999(3)	0.1992(3)	0.0051(3)	0.0024(2)	0.0038(3)	0.0029(4)	−0.0027(5)	−0.0002(4)
C(2)	0.0	−0.2467(4)	0.25	0.0081(5)	0.0008(3)	0.0042(4)	0.0	−0.0045(7)	0.0
C(3)	0.1412(4)	−0.2641(3)	0.1404(4)	0.0081(4)	0.0030(3)	0.0054(4)	0.0058(5)	−0.0023(6)	−0.0021(5)
C(4)	0.0600(3)	0.3839(3)	0.3353(3)	0.0019(2)	0.0025(2)	0.0037(3)	−0.0002(3)	0.0012(4)	−0.0012(4)
C(5)	0.0	0.4321(4)	0.25	0.0030(3)	0.0009(3)	0.0048(4)	0.0	−0.0002(6)	0.0
C(6)	0.1117(3)	0.4545(3)	0.4235(3)	0.0035(2)	0.0020(2)	0.0042(3)	−0.0006(4)	−0.0001(4)	−0.0004(4)
C(7)	0.1935(2)	0.0927(3)	0.2438(3)	0.0017(2)	0.0027(2)	0.0054(2)	0.0005(3)	0.0007(3)	0.0006(4)
C(8)	0.0765(3)	0.1283(3)	0.0796(3)	0.0028(2)	0.0035(2)	0.0026(3)	0.0003(4)	0.0008(4)	0.0012(4)
C(9)	0.2060(3)	0.0698(3)	0.3656(4)	0.0024(2)	0.0035(3)	0.0054(3)	−0.0001(4)	−0.0016(4)	0.0020(5)
C(10)	0.1296(3)	0.2203(3)	0.0397(4)	0.0033(2)	0.0056(2)	0.0050(3)	−0.0006(3)	0.0014(5)	0.0040(5)
H(2)	0.0	−0.314(5)	0.25	5.8(17)					
H(3A)	0.141(3)	−0.322(4)	0.158(3)	3.6(10)					
H(3B)	0.128(3)	−0.267(3)	0.066(4)	3.4(9)					
H(3C)	0.204(3)	−0.234(4)	0.153(4)	5.3(11)					
H(5)	0.0	0.505(3)	0.25	1.2(10)					
H(6A)	0.180(3)	0.427(3)	0.454(3)	2.8(9)					
H(6B)	0.074(3)	0.459(3)	0.488(3)	2.7(8)					
H(6C)	0.117(3)	0.505(2)	0.406(3)	1.4(8)					
H(7A)	0.216(3)	0.037(3)	0.203(3)	0.9(7)					
H(7B)	0.224(2)	0.146(2)	0.223(3)	0.8(7)					
H(8A)	0.098(2)	0.057(3)	0.054(3)	2.1(8)					
H(8B)	0.006(3)	0.140(3)	0.055(3)	2.2(8)					
H(9A)	0.176(2)	0.003(2)	0.368(3)	1.3(8)					
H(9B)	0.265(3)	0.066(4)	0.389(3)	4.2(11)					
H(9C)	0.180(2)	0.127(3)	0.404(3)	2.3(9)					
H(10A)	0.199(2)	0.206(3)	0.052(3)	2.3(8)					
H(10B)	0.110(3)	0.279(4)	0.069(4)	4.9(12)					
H(10C)	0.117(3)	0.218(3)	−0.046(3)	2.8(9)					
H(N1)	0.075(2)	0.168(3)	0.231(3)	1.7(8)					

Results and Discussions

An *ORTEP*[4] drawing of an ion-pair of the present complex and the numbering scheme of the atoms are shown in Fig. 1. The bond lengths and bond angles are given in Table 3. Some least-squares planes, deviations of atoms from the plane, and dihedral angles are given in Table 4. The most remarkable feature of the structure is that both the $\{Pd(NHEt_2)_2(acac)\}^+$ cation and $(acac)^-$ anion lie on the crystallographic two-fold axis.

In the cation the geometry around the Pd atom is square-planar. The Pd, N, O(1), N′, and O(1′) atoms lie on nearly the same plane, the maximum deviation being 0.054 Å. The Pd–O(1) distance [2.000(3) Å] is almost equal to that in $Pd(acac)_2$ at −170 °C [1.991(3) and 1.988(3) Å].[7] However, it is shorter than in mono-β-diketonate complexes.[5,6] The

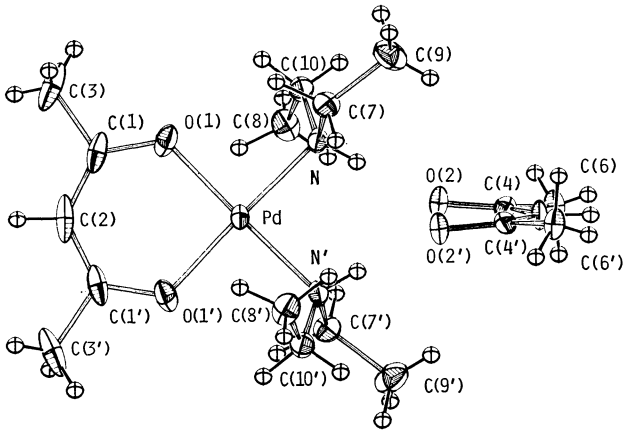


Fig. 1. An *ORTEP* drawing of the $\{Pd(acac)(NHEt_2)_2\}^+(acac)^-$ ion-pair with the numbering scheme of non-hydrogen atoms.
Non-hydrogen atoms are drawn as thermal ellipsoids with 50% probability level, and hydrogen atoms are drawn as spheres with 0.1 Å radius.

† The Tables of structure factors are kept in the Chemical Society of Japan as Document No. 8014.

TABLE 3. BOND LENGTHS, BOND ANGLES, AND HYDROGEN BONDS IN $[\{Pd(NHEt_2)_2(acac)\}^+(acac)^-]$ (e.s.d.'s in parentheses)

Bond length [l/Å]					
$\{Pd(NHEt_2)_2(acac)\}^+$					
Pd	-O(1)	2.000(3)	Pd	-N	2.044(3)
C(1)	-O(1)	1.277(5)	C(1)	-C(2)	1.386(7)
C(1)	-C(3)	1.498(7)	N	-C(7)	1.497(5)
N	-C(8)	1.494(5)	C(7)	-C(9)	1.506(6)
C(8)	-C(10)	1.507(6)			
C(2)	-H(2)	0.86(7)	C(3)	-H(3A)	0.78(5)
C(3)	-H(3B)	0.91(4)	C(3)	-H(3C)	0.95(5)
C(7)	-H(7A)	0.95(4)	C(7)	-H(7B)	0.86(3)
C(8)	-H(8A)	1.03(4)	C(8)	-H(8B)	1.01(4)
C(9)	-H(9A)	0.97(4)	C(9)	-H(9B)	0.85(5)
C(9)	-H(9C)	0.98(4)	C(10)	-H(10A)	0.97(4)
C(10)	-H(10B)	0.89(5)	C(10)	-H(10C)	1.04(4)
N	-H(N)	0.81(4)			
$(acac)^-$					
C(4)	-C(5)	1.406(6)	C(4)	-C(6)	1.528(6)
O(2)	-C(4)	1.246(5)			
C(5)	-H(5)	0.95(4)	C(6)	-H(6A)	1.04(4)
C(6)	-H(6B)	1.00(4)	C(6)	-H(6C)	0.69(4)
Bond angle [ϕ/°]					
$\{Pd(NHEt_2)_2(acac)\}^+$					
O(1)	-Pd -N	88.1(2)	N	-Pd -N'	90.0(2)
O(1)	-Pd -O(1')	94.0(2)	Pd	-O(1) -C(1)	123.2(3)
Pd	-N -C(7)	111.1(2)	Pd	-N -C(8)	110.4(2)
O(1)	-C(1) -C(2)	125.4(5)	O(1)	-C(1) -C(3)	114.1(4)
C(1)	-C(2) -C(1')	128.4(5)	C(2)	-C(1) -C(3)	120.5(4)
N	-C(7) -C(9)	112.2(3)	N	-C(8) -C(10)	113.4(3)
C(7)	-N -C(8)	112.2(3)			
C(1)	-C(2) -H(2)	116(5)	C(1)	-C(3) -H(3A)	112(3)
C(1)	-C(3) -H(3B)	116(3)	C(1)	-C(3) -H(3C)	108(3)
H(3A)	-C(3) -H(3B)	103(4)	H(3A)	-C(3) -H(3C)	112(5)
H(3B)	-C(3) -H(3C)	105(4)			
Pd	-N -H(N)	106(3)	N	-C(7) -H(7A)	109(2)
N	-C(7) -H(7B)	103(2)	N	-C(8) -H(8A)	101(2)
N	-C(8) -H(8B)	109(2)	C(7)	-C(9) -H(9A)	101(2)
C(7)	-C(9) -H(9B)	111(3)	C(7)	-C(9) -H(9C)	109(2)
C(8)	-C(10) -H(10A)	108(2)	C(8)	-C(10) -H(10B)	111(3)
C(8)	-C(10) -H(10C)	105(2)	C(7)	-N -H(N)	108(3)
C(8)	-N -H(N)	109(3)	C(9)	-C(7) -H(7A)	112(2)
C(9)	-C(7) -H(7B)	116(2)	C(10)	-C(8) -H(8A)	116(2)
C(10)	-C(8) -H(8B)	106(2)			
H(7A)	-C(7) -H(7B)	104(3)	H(8A)	-C(8) -H(8B)	111(3)
H(9A)	-C(9) -H(9B)	110(4)	H(9A)	-C(9) -H(9C)	118(3)
H(9B)	-C(9) -H(9C)	107(4)	H(10A)	-C(10) -H(10B)	116(4)
H(10A)	-C(10) -H(10C)	102(3)	H(10B)	-C(10) -H(10C)	114(4)
$(acac)^-$					
O(2)	-C(4) -C(6)	117.0(3)	C(5)	-C(4) -C(6)	116.9(4)
O(2)	-C(4) -C(5)	126.1(4)	C(4)	-C(5) -C(4')	127.5(4)
C(4)	-C(5) -H(5)	116(2)	C(4)	-C(6) -H(6A)	113(2)
C(4)	-C(6) -H(6B)	110(2)	C(4)	-C(6) -H(6C)	114(4)
H(6A)	-C(6) -H(6B)	106(3)	H(6A)	-C(6) -H(6C)	107(4)
H(6B)	-C(6) -H(6C)	106(4)			
Hydrogen bonding [l/Å and ϕ/°]					
H(N)·····O(2)		2.10(4)			
N·····O(2)		2.871(4)			
N-H(N)···O(2)		160(4)			

Table 4. Least-squares planes and dihedral angles

Equation of the plane is of the form $AX+BY+CZ+D=0$,
where X, Y, Z, and D are measured in Å units; $X=ax+cz\cos\beta$, $Y=by$ and $Z=cz\sin\beta$.

(1) Coordination plane (Pd, O(1), O(1′), N(1), N(1′))
$-0.4360X-0.9000Z+2.5848=0$

	Pd	O(1)	O(1′)	N(1)	N(1′)
Δ[a]	0.001	0.054	−0.054	−0.051	0.053

(2) (acac) ligand (C(1), C(2), C(3), C(1′), C(3′), O(1), O(1′))
$-0.5127X+0.0038Y-0.8586Z+2.4434=0$

	C(1)	C(2)	C(3)	C(1′)	C(3′)	O(1)	O(1′)
Δ[a]	−0.026	−0.001	0.057	0.028	−0.062	−0.069	0.080

(3) $(acac)^-$ ion (C(4), C(5), C(6), C(4′), C(6′), O(2), O(2′))
$0.8187X+0.0155Y-0.5740Z+1.9572=0$

	C(4)	C(5)	C(6)	C(4′)	C(5′)	O(2)	O(2′)
Δ[a]	0.016	0.030	−0.092	0.024	0.030	0.074	−0.072

Dihedral angles [ϕ/°]

between planes		
	(1) & (2)	5.0
	(1) & (3)	80.8
	(2) & (3)	85.8

a) Δ: Deviations of atoms [l/Å] from the plane.

O(1)–Pd–O(1′) angle [94.0(2)°] is slightly smaller than that in $Pd(acac)_2$ [95.04(10)°]. The Pd–N bond length is 2.044(3) Å. The N–Pd–N′ and O(1)–Pd–N angles are 90.0(2)° and 88.2(2)°, respectively. All the bond lengths and bond angles for the acac ligand in the cation are equal within the limits of errors to the corresponding values in $Pd(acac)_2$ (Fig. 2).

Two diethylamines *cis*-coordinated to the Pd atom are mutually related by the two-fold axis. The N–C bond lengths are equal [1.497(5) and 1.498(7) Å], comparable with those in $RhCl(CO)(C_2H_4)(NHEt_2)$[8] [1.507 and 1.508 Å]. One of the methyl groups in a diethylamine group takes the most stable *trans* conformation, the other being in a *gauche* conformation. This seems to be caused by the steric hindrance between the $C(9)H_3$ and $C(8')H_3$ or the $C(8)H_3$ and $C(9')H_3$ methyl groups.

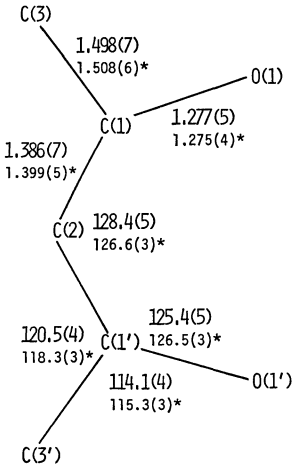


Fig. 2. Structure of the (acac) moiety *O,O′*-chelated to the Pd atom (−170 °C).
Average values the corresponding bond lengths and bond angles in $Pd(acac)_2$[7] are also given with asterisks.

In the $(acac)^-$ anion the O(2)–C(4) bond length of 1.246(5) Å is *ca.* 0.03 Å shorter than the corresponding length [1.277(5) Å] for the (acac)-*O,O′*-chelate. On the other hand, the C(4)–C(5) and C(4)–C(6) bond lengths [1.406(6) and 1.528(6) Å] are respectively equal to the corresponding lengths in the *O,O′*-chelate.

The cation and the anion lying on the same two-fold axis are bound together by hydrogen bonds, N–H···O(2) and N′–H′···O(2′) [both 2.871(4) Å], to form a ion-pair. The other two N–H···O(2′) and N′–H′···O(2) distances [both 3.213(4) Å] are rather short, and comparable with the largest value of the N–H···O hydrogen bond distances determined by means of neutron diffraction.[9]

An *ORTEP* drawing of the crystal structure is given in Fig. 3. Two ion-pairs mutually related by the crystallographic center of symmetry make a packing

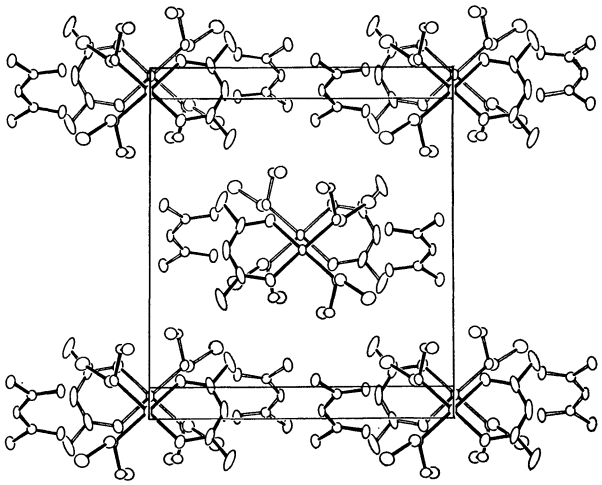


Fig. 3. Crystal structure of $[\{Pd(acac)(NHEt_2)_2\}^+(acac)^-]$ projected onto the ab plane.

unit of the crystal. No close atomic contact was found between these ion-pairs. No anion is located above or below the Pd atom of the cation. No explanation can be obtained for the ligand exchange reaction from **2** to **1**.

The authors wish to express their thanks to Prof. Shinichi Kawaguchi, Osaka City University, and Prof. Seichi Okeya, Wakayama University, for their valuable discussions and the supply of crystals. Computations were carried out on an ACOS Series 77 NEAC System 800 computer at Osaka University.

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