The Crystal and Molecular Structure of (Acetylacetonato)-(diacetylmethyl)(diethylamine)palladium(II)

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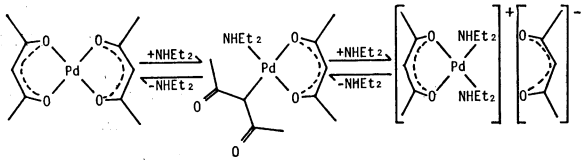
The molecular structure of $[Pd(acac)_2(NHEt_2)]$ was determined by means of X-ray diffraction. The crystal belongs to the monoclinic system: $a=14.166(1)$, $b=8.209(1)$, $c=14.764(2)$ Å, $\beta=100.75(1)°$, space group $P2_1/n$, with $Z=4$. The structure was solved by the heavy-atom method and refined anisotropically by the least-squares procedure; $R=0.067$ for 3149 non-zero reflections. The geometry around the Pd atom is square-planar: one of the two (acac) ligands coordinates to the Pd atom by O,O'-chelation, and the other, by σ-bonding of the γ-carbon atom, while the diethylamine occupies the fourth coordination site. A weak intramolecular N–H···O hydrogen bond [2.962(10) Å] is observed.

With relation to the reactions shown below,[1] the molecular structures of $[Pd(acac)_2]$[2] (**1**) and $[\{Pd(acac)(NHEt_2)_2\}^+(acac)^-]$[3] (**3**) have been determined. This paper will deal with the molecular structure of $[Pd(acac)_2(NHEt_2)]$ (**2**).



1 **2** **3**

Experimental

Yellow platelet crystals of $[Pd(acac)_2(NHEt_2)]$ were provided by Professor Seichi Okeya and Professor Shinichi Kawaguchi. A toluene–hexane mixture was used for the recrystallization. Efforts to cut out a crystal of a size suitable for an X-ray experiment was unsuccessful. A rather large crystal with dimensions of *ca.* $0.5\times0.18\times0.4$ mm was, therefore, used for the X-ray experiments, though it may limit the accuracy of the results.

Crystal Data: $C_{14}H_{25}NO_4Pd$, *F.W.* 377.8, monoclinic, $a=14.166(1)$, $b=8.209(1)$, $c=14.764(2)$ Å, $\beta=100.75(1)°$, $V=1686.7(3)$ Å^3, space group $P2_1/n$(No. 14), $D_m=1.46$(flotation), $D_c=1.488$ g cm^{-3}, $Z=4$.

The unit-cell dimensions were determined by the least-squares fit of 2θ values of 18 strong reflections measured precisely on a Rigaku automated four-circle diffractometer. The intensity data were collected using graphite-monochromatized Mo $K\alpha$ radiation on the diffractometer. The θ-2θ scan technique was applied. The scan width was $\Delta 2\theta=(2.0+0.7\tan\theta)°$, and the scan rate was 4° min^{-1}. Backgrounds were measured for 7.5 s before and after the measurement of each peak. The intensity measurements were repeated up to three times for weak reflections. A total of 3694(3149 non-zero) reflections were measured up to $2\theta=54°$. Usual Lp corrections were made, but absorption corrections were ignored [μ(Mo $K\alpha$)$=10.7$ cm^{-1}].

Structure Solution and Refinement

The structure was solved by using Patterson and Fourier methods. The block-diagonal least-squares refinement (*HBLS* V)[4] with isotropic temperature factors reduced R to 0.096. The final R value was 0.066 ($R_w=0.089$) for non-zero reflections, allowing anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms, except H(3) and H(6), could not be located reasonably, so they were not included in the refinement. The weighting schemes used at the final stage were $w=\{\sigma_{cs}^2(F_o)+0.0011\cdot|F_o|+0.0726|F_o|^2\}^{-1}$ for $|F_o|>0$ and $w=0$ for $|F_o|=0$, where σ_{cs} is the standard deviations obtained by the counting statistics. The final atomic positional and thermal parameters are given in Table 1.†††

Table 1. Fractional atomic coordinates, with estimated standard deviations in parentheses

(a) Non-hydrogen atoms with equivalent temperature factors.[10]

Atom	x	y	z	B_{eq}/Å^2
Pd	0.51248(4)	0.54100(7)	0.29614(4)	3.79
O(1)	0.5847(4)	0.3299(7)	0.3182(4)	4.5
C(1)	0.6748(6)	0.3223(10)	0.3506(5)	4.0
C(2)	0.7125(6)	0.1471(11)	0.3639(7)	5.3
C(3)	0.7371(6)	0.4508(10)	0.3739(6)	4.4
C(4)	0.7166(5)	0.6164(10)	0.3658(5)	3.9
C(5)	0.7971(6)	0.7384(11)	0.3941(6)	5.0
O(2)	0.6351(4)	0.6771(6)	0.3379(4)	4.2
C(6)	0.3905(6)	0.3986(10)	0.2532(6)	4.3
C(7)	0.3675(6)	0.4181(10)	0.1523(6)	4.5
O(3)	0.3125(6)	0.5180(9)	0.1125(5)	6.2
C(8)	0.4190(8)	0.2983(15)	0.0978(7)	7.2
C(9)	0.3185(6)	0.4470(11)	0.3088(6)	5.0
O(4)	0.2621(5)	0.5581(9)	0.2875(5)	6.2
C(10)	0.3253(9)	0.3491(15)	0.3998(7)	7.4
N	0.4344(5)	0.7538(8)	0.2746(5)	4.6
C(11)	0.4715(9)	0.8697(17)	0.2115(9)	8.3
C(12)	0.4834(11)	0.8080(18)	0.1248(9)	9.5
C(13)	0.4411(10)	0.8539(14)	0.3613(10)	8.2
C(14)	0.4162(11)	0.775(2)	0.4377(9)	9.8

(b) Hydrogen atoms with isotropic temperature factors.

Atom	x	y	z	B/Å^2
H(3)	0.795(5)	0.420(9)	0.395(5)	1.4(14)
H(6)	0.412(6)	0.299(10)	0.272(5)	2.2(16)

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††† Tables of observed and calculated structure factors and anisotropic thermal parameters are kept at the Chemical Society of Japan. Document No. 8201.

TABLE 2. LEAST-SQUARES PLANES AND DIHEDRAL ANGLES

The 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.

$0.3393X+0.0252Y-0.9404Z+1.7443=0$.

	Pd	O (1)	O (2)	C (6)	N
Δ[a)]	0.003	−0.014	0.012	0.014	−0.014

2) O,O'-Chelated acac ligand.

$0.3628X+0.0031Y-0.9319Z+1.6150=0$.

	O (1)	C (1)	C (2)	C (3)	C (4)	C (5)	O (2)	Pd[b)]	H (3)[b)]
Δ[a)]	0.009	0.002	−0.001	−0.013	0.004	0.008	−0.010	−0.004	−0.003

Dihedral angles between 1) and 2) planes[ϕ/°]. 1.9(2)

a) Deviation of atoms from the plane [l/Å]. b) Not included in the least-squares plane calculation.

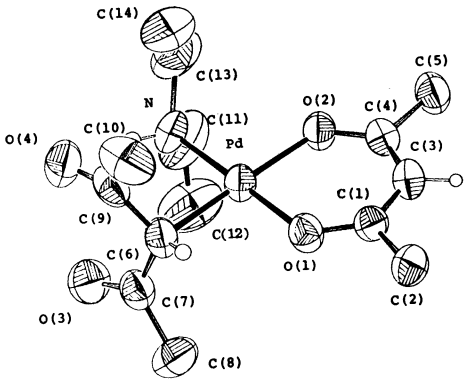

Fig. 1. Perspective view of the molecule. Non-hydrogen atoms are represented by thermal ellipsoids at 50% probability levels.

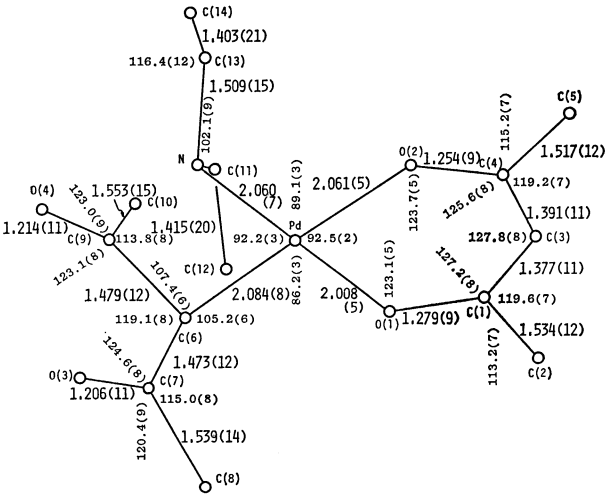

Fig. 2. Bond lengths [l/Å] and bond angles [ϕ/°] with estimated standard deviations in parentheses. The followings are bond lengths and bond angles which could not be shown in the figure.

Pd-N-C(11)	113.3(7),	C(6)-H(6)	0.90(8),
Pd-N-C(13)	112.5(7),	Pd-C(6)-H(6)	102(5),
N-C(11)-C(12)	116.8(11),	C(7)-C(6)-H(6)	114(5),
C(3)-H(3)	0.86(7),	C(9)-C(6)-H(6)	108(5).
C(1)-C(3)-H(3)	113(5),		
C(4)-C(3)-H(3)	119(5),		

The atomic scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. IV.[5] The computations were done on an ACOS Series 77 NEAC System 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

A perspective view (*ORTEP* II)[6] of the molecule is shown in Fig. 1, while the bond lengths and bond angles are given in Fig. 2. The geometry around the Pd atom is square-planar: one of the two (acac) ligands coordinates to the Pd atom by the O,O'-chelation, and the other, by σ-bonding of the γ-carbon atom, while the diethylamine occupies the fourth coordination site.

The two Pd–O lengths are unequal, Pd–O(1)= 2.008(5) and Pd–O(2)=2.061(5) Å. The *trans*-influence is observed. The former is equal to the Pd–O length *trans* to the diethylamine [2.000(3) Å],[7] and the latter, to that *trans* to the acetylacetonyl ligand [2.06(1) Å].[8]

The planarity of the acetylacetonato ligand is good (Table 2). This plane is approximately parallel to the coordination plane (Fig. 1.), the dihedral angle between these planes being 1.9(2)°. The bond lengths and bond angles in the acetylacetonato ligand in the present complex are normal, like those in $Pd(acac)_2$[2] or $[\{Pd(acac)(NHEt_2)_2\}^+(acac)^-]$.[3]

The diacetylmethyl ligand is approximately perpendicular to the coordination plane. The bond angles around the γ-carbon atom are considerably distorted. The C(7)–C(6)–C(9) angle [119.1(8)°] is larger than the tetrahedral angle, whereas the Pd–C(6)–C(7) angle [105.2(6)°] is slightly smaller. The C_β–C_γ and C_β=O bond lengths and C_β–C_γ–C_β bond angles are normal compared with the corresponding values in $[(PPh_3)Pd(acac)_2]$,[7] $[Me_3Pt(acac)(bipy)]$,[8] and $[K^+\cdot\{Pt(acac)_2Cl\}^-]$.[9] The two carbonyl groups are parallel in $[K^+\cdot\{Pt(acac)_2Cl\}^-]$ and in the present complex, whereas they are not parallel in $[(PPh_3)Pd(acac)_2]$. In the pottasium salt, the dihedral angle between the two C_α–C_β–C_γ moieties is 9.5°, while in the present complex it is 27.4(3)°. It was suggested that interactions between two carbonyl oxygen atoms and the K^+ cation in the crystalline state affect the parallel position of the two carbonyl groups and the small dihedral angle. In the present complex,

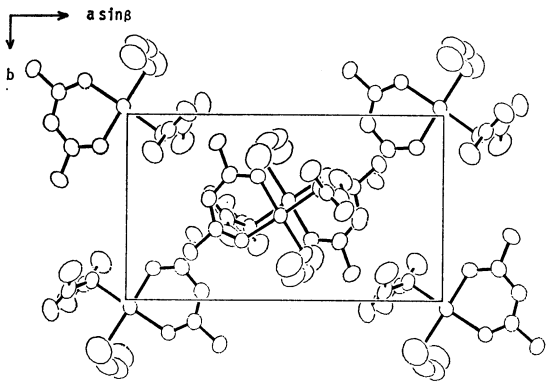

Fig. 3. Crystal structure projected along the c axis.

a weak intramolecular hydrogen bond, N–H···O(4) [2.958(10) Å], and a rather close N–H···O(3) contact [3.304(10) Å] between the two carbonyl groups and the N–H of the diethylamine ligand are observed.

The diethylamine ligand is also approximately perpendicular to the coordination plane. The two N–C bond lengths are equal [1.494(15) and 1.509(15) Å], comparable with those in $[\{Pd(acac)(NHEt_2)_2\}^+(acac)^-]$ [1.497(5) and 1.498(5) Å]. The two methyl groups are in a stable *trans* conformation.

The crystal structure projected along the c axis is shown in Fig. 3. The intermolecular atomic contacts are usual van der Waals distances, the closest being $C(10)(x,y,z)\cdots O(3)(0.5-x, -0.5+y, 0.5-z)$ [3.331(14) Å].

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