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The Crystal Structure of Bis(acetylacetonato)platinum(II) Benzene Solvate

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Synopsis. The crystal structure of bis(acetylacetonato)platinum(II) benzene solvate has been determined by means of X-ray diffraction. The geometry around the platinum atom is square-planar. Acetylacetonato ligands are bonded to the Pt atom by the *O,O'*-chelation, the Pt–O bond lengths being 2.008 (15) and 1.979 (14) Å.

The transition metal complexes containing acetylacetonato (abbreviated as acac hereafter) ligands have been widely studied, and some of their structures have been reported hitherto. In the case of group VIII transition metal complexes, especially the nickel group transition metal complexes, molecular structures of $[Ni(acac)_2]$,[1,2] $[Ni(acac)_2]_3$,[3] and $[Pd(acac)_2]$[4,5] have been determined by means of diffraction methods. This paper will deal with the crystal structure analysis of bis(acetylacetonato)platinum(II) benzene solvate.

The yellow, prismatic crystals were obtained by recrystallization from a benzene solution. A well-shaped crystal with approximate dimensions of 0.40×0.43×0.25 mm was sealed in a glass capillary tube with a small amount of benzene in order to prevent its decomposition.

Crystal Data. $C_{10}H_{14}O_4Pt \cdot C_6H_6$, F.W.=471.4, $F(000)=452$, monoclinic, space group $P2_1/c$, $a=7.165(2)$, $b=12.836(2)$, $c=9.240(1)$ Å, $\beta=92.17(2)°$, $V=849.1(2)$ Å^3, $D_m=1.84$ g cm^{-3} (by flotation in $ZnBr_2$ aqueous solution), $D_c=1.85$ g cm^{-3} for $Z=2$, μ(Mo $K\alpha$)=87.0 cm^{-1}.

Intensity data were collected on a Rigaku automated four-circle diffractometer with graphite monochromatized Mo $K\alpha$ radiation employing the θ-2θ scan technique. The scan rate was 4° min^{-1}. A total of 1959 reflections were obtained, of which 1460 reflections were $F_o > 3\sigma(F_o)$. Lorentz and polarization corrections were made, but no absorption nor extinction correction was applied, which might limit the accuracy of the present structure determination.

TABLE 1. ATOMIC COORDINATES

Atom	*x*	*y*	*z*
Pt	0.	0.	0.
O(1)	0.2460(17)	−0.0703(11)	−0.0305(16)
O(2)	−0.0879(17)	−0.1072(11)	0.1349(15)
C(1)	0.290(3)	−0.1558(16)	0.027(3)
C(2)	0.188(3)	−0.2141(17)	0.118(3)
C(3)	0.006(3)	−0.1897(17)	0.167(3)
C(4)	0.478(4)	−0.195(3)	−0.018(4)
C(5)	−0.095(4)	−0.260(3)	0.266(4)
C(B1)	0.373(11)	−0.007(3)	0.392(7)
C(B2)	0.540(10)	−0.010(4)	0.361(6)
C(B3)	0.675(9)	−0.005(3)	0.451(10)

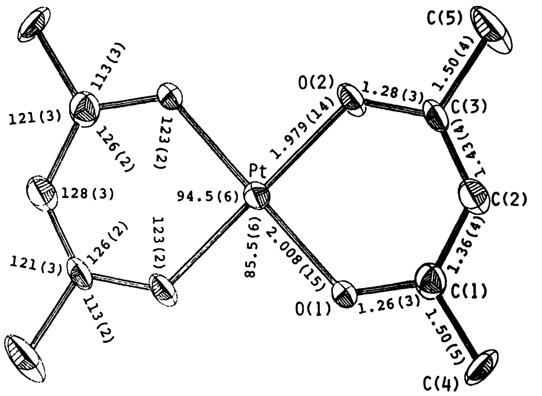

Fig. 1. An *ORTEP* drawing[9] of a $[Pt(acac)_2]$ molecule together with the atomic numbering system and selected bond lengths (l/Å) and angles (φ/°). The thermal ellipsoids correspond to 20% probability level.

The structure was solved by the heavy atom method, and refined anisotropically by the block-diagonal least-squares procedure using *HBLS*-V program.[6] The weighting scheme of Hughes,[7] $w=(50.0/|F_o|)^{-2}$ for $|F_o|>50.0$ and $w=1$ for $|F_o|\leq 50.0$, was employed. Atomic scattering factors used were taken from International Tables for X-Ray Crystallography.[8] The final R value is 0.086 for 1460 reflections.† Atomic coordinates are listed in Table 1.

Figure 1 represents an *ORTEP* drawing[9] of the $[Pt(acac)_2]$ molecule together with the atomic numbering system and selected bond lengths and bond angles.

Similar to $[Pd(acac)_2]$,[4,5] the $[Pt(acac)_2]$ molecule is centrosymmetric. The Pt atom is located on a crystallographic center of symmetry, and surrounded by four oxygen atoms of acac ligands. The geometry around the Pt atom is square-planar. Two Pt–O bond lengths are 2.008(15) and 1.979(14) Å, which are approximately

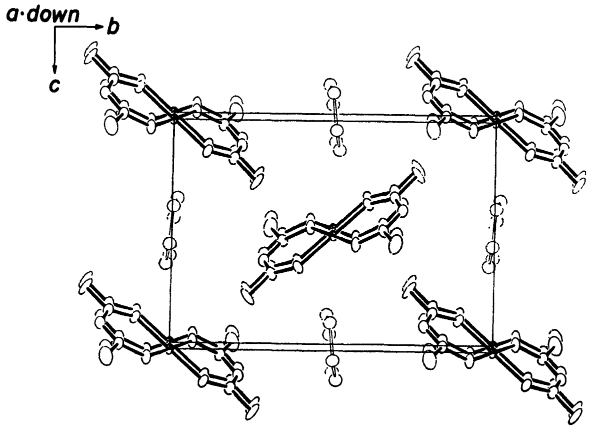

Fig. 2. Crystal structure(*ORTEP*[9]) projected along the c axis. Atoms in $[Pt(acac)_2]$ complex are drawn as thermal ellipsoids with 20% probability ,while those in benzene molecule as spheres with $B=5.0$ Å^2.

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† Complete F_o-F_c data and Tables of anisotropic thermal parameters are kept at the Chemical Society of Japan, Document No. 8113.

equal to the sum of the single bond radius of O atom (0.74 Å)[10] and the covalent bond radius of Pt(1.295 Å).[11]

The acac ligand is planar, the maximum atomic deviation from the least-squares plane being 0.02 Å. The dihedral angle between the acac plane and the plane defined by the Pt, O(1), and O(2) atom is 176.9°. Bond lengths and bond angles in the acac ligand are nearly equal to the values found for [Pd(acac)$_2$].[5]

Very recently, Onuma *et al.* reported the crystal structure analysis of the triclinic crystal of [Pt(acac)$_2$] which contains no crystalline benzene molecule.[12] The molecular structure of [Pt(acac)$_2$] in the present crystal is essentially identical with that obtained by Onuma *et al.*

Figure 2 shows an *ORTEP* drawing[9] of the crystal structure. The [Pt(acac)$_2$] molecules are piled up to form columns along the a axis. The crystalline benzene molecules lie, approximately parallel to the ac plane, in channels formed by piles of [Pt(acac)$_2$] molecules and are linked loosely with adjacent [Pt(acac)$_2$] and benzene molecules, which may explain the instability of the crystal.

All computations were carried out on an ACOS 700 computer at Crystallographic Research Center, Institute for Protein Research, Osaka University.

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References

1) M. Ota and S. Shibata, 41st National Meeting of the Chemical Society of Japan, Osaka, April 1980, Abstr. I, p. 432 (3L29).

2) S. Shibata, *Bull. Chem. Soc. Jpn.*, **30**, 753 (1975).

3) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

4) A. N. Knyazeva, E. A. Shugam, and L. M. Shkol'nikova, *Zh. Strukt. Khim.*, **11**, 938 (1970).

5) M. Sato, K. Miki, Y. Kai, N. Yasuoka, and N. Kasai, 38th National Meeting of the Chemical Society of Japan, Nagoya, October 1978, Abstr. III, p. 1039 (3F09).

6) T. Ashida, "The Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka University (1979), p. 53.

7) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

8) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 71.

9) C. K. Johnson, *ORTEP*-II, Report ORNL-5138. Oak Ridge National Laboratory, Tennessee (1976).

10) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, New York (1960).

12) S. Onuma, K. Horioka, H. Inoue, and S. Shibata, *Bull. Chem. Soc. Jpn.*, **53**, 2679 (1980).