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

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Synopsis. The crystal structure of $Pt(acac)_2$ has been determined by means of X-ray diffraction. The molecule is monomeric, the coordination geometry being square-planar. The average Pt–O distance is 1.991(8) Å. The bond lengths and angles of the chelating ligands are almost the same as those for other acetylacetone complexes.

The acac ligand in $Pt(acac)_2$ is thought to be bidentate (Hacac=acetylacetone). However, some anomalous modes of ligation have been found in platinum complexes; *e.g.*, in $K[Pt(acac)_2Cl]$,[1] one of the β-diketones is unidentate and linked to the metal through the methylene carbon; in $[Me_3Pt(acac)]_2$,[2] the β-diketone is linked to one platinum atom *via* γ-carbon atom and to the other platinum *via* oxygen atoms to yield a binuclear complex. The present study has been undertaken to elucidate the crystal structure of $Pt(acac)_2$.

Experimental

The crystals were prepared by the method of Werner.[3] Crystal Data: $Pt(C_5H_7O_2)_2$, Mol. wt. 393.3, triclinic, space group $P\bar{1}$ $a=7.13(2)$, $b=5.75(2)$, $c=7.957(4)$ Å, $\alpha=70.0(1)$, $\beta=98.9(1)$, $\gamma=113.2(2)°$, $V=282(1)$ Å^3; $D_m=2.32$, $D_c=2.31$ g cm^{-3} for $Z=1$. Found: C, 30.57; H, 3.56%. Calcd for C, 30.54; H, 3.59%. Crystal dimensions: $0.08\times0.14\times0.20$ mm^3.

Intensity data were collected on a Rigaku diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Reflections were measured with the ω-scan ($2\theta\leqq30°$) and ω-2θ scan ($30°<2\theta<70°$) techniques. The scan rate was 4° min^{-1} and the scan width $(1.8+0.5\tan\theta)°$. The number of reflections with $F>3\sigma$ was 2342. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The space group $P\bar{1}$ was assumed at the outset and verified by successful refinement of the crystal structure. Compliance to the centrosymmetric space group requires that the monomer possesses a crystallographic center of symmetry. The structure was solved by the heavy atom method. The positional and anisotropic thermal parameters of the eight non-hydrogen atoms were refined by the block-diagonal least-squares method. The final R value was 0.059 for 2342 reflections. The atomic scattering factors were taken from Ref. 4. Anomalous dispersion correction for platinum atom was taken into account. The resulting difference Fourier map shows no significant peaks or troughs. The final positional and thermal parameters are given in Table 1. The complete F_o-F_c data are kept at the Chemical Society of Japan (Document No. 8029).

Results and Discussion

The complex was found to be monomeric, the platinum atom having a square-planar coordination by four oxygen atoms of the acetylacetonato ligands.

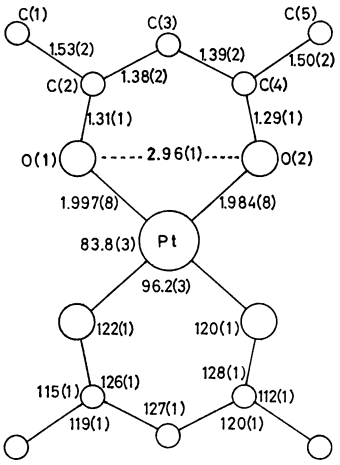

Fig. 1. Bond lengths (l/Å) and angles (ϕ/°) with their estimated standard deviations in parentheses.

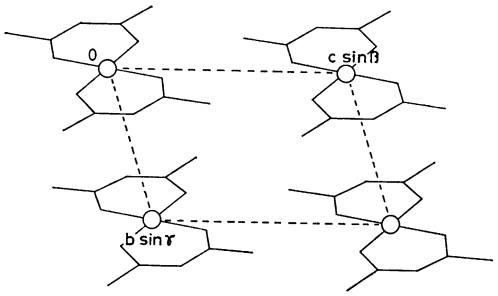

Fig. 2. Projection of the crystal structure along the a axis.

Table 1. The final positional and thermal parameters ($\times10^4$)
The anisotropic thermal parameters are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0	0	0	181(1)	326(2)	96(1)	315(2)	−26(1)	−125(2)
O (1)	−1735(11)	1805(15)	−1709(8)	298(19)	564(35)	96(9)	587(46)	−58(21)	−160(29)
O (2)	−596(11)	572(14)	2150(8)	263(18)	488(33)	136(11)	487(42)	−64(22)	−199(31)
C (1)	−3876(18)	4257(24)	−2675(14)	326(32)	611(59)	168(18)	681(77)	−128(39)	−179(53)
C (2)	−2716(15)	2894(19)	−1147(12)	230(23)	402(40)	148(15)	405(53)	−33(30)	−132(40)
C (3)	−2791(15)	2914(20)	570(12)	238(24)	448(43)	136(15)	409(55)	−20(30)	−151(41)
C (4)	−1757(15)	1850(20)	2080(12)	251(25)	414(41)	131(14)	360(54)	22(30)	−176(40)
C (5)	−1989(19)	2142(24)	3837(14)	354(35)	579(57)	148(17)	548(76)	27(39)	−202(51)

Table 2. The average bond lengths (l/Å) and angles (ϕ/°) in $Pt(acac)_2$ and the related chelates

	Present work	$K[Pt(acac)_2Cl]$[1]	$PtCl(acac)\text{-}(H_2CCHOH)$[6]
Pt-O	1.99	2.02	2.02
C-O	1.30	1.31	1.29
C-C	1.39	1.41	1.39
$C\text{-}CH_3$	1.51	1.49	1.49
CCC	127	129	128
OCC	127	125	126
$OCCH_3$	114	116	114
OPtO	96	95	94

The molecular structure is shown in Fig. 1, atom numbering and bond lengths and angles also being given with their esd values in parentheses. The chelate ring was found to be planar, the deviations of atoms from the least-squares plane being: Pt 0.0, O(1) 0.02, O(2) 0.02, C(1) −0.03, C(2) 0.01, C(3) 0.02, C(4) 0.00, C(5) −0.02 Å. The average values of the chemically equivalent bond lengths and angles are given in Table 2, those of other β-diketonato complexes being given for the sake of comparison. They agree with each other.

The molecules are well separated. The arrangement viewed along the a axis is shown in Fig. 2. The intermolecular distances are normal, the shortest distance between methyl carbon atoms being 4.00 Å.

Most of the calculations were carried out by using the UNICS programs[5] at the Computer Center of the University of Tokyo.

References

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