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Redetermination of bis(2,4-pentanedionato)-palladium(II)

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Key indicators

Single-crystal X-ray study

$T = 100$ K

Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å

R factor = 0.024

wR factor = 0.068

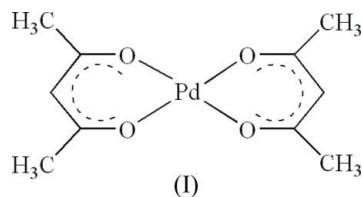
Data-to-parameter ratio = 22.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, $[\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2]$, has been redetermined at 100 K using modern equipment, resulting in improved precision compared to the previous study [Knyazeva *et al.* (1970). *Zh. Strukt. Khim.* **11**, 938–939]. The new measurements reveal that the plane of the 2,4-pentanedionate ligand is tilted by $3.4(1)^\circ$ with respect to the PdO_4 unit (Pd site symmetry = $\bar{1}$). Possible reasons for this bending are examined in terms of previously undiscussed intermolecular interactions.

Comment

The single-crystal structure of the title compound, (I), was first reported by Knyazeva *et al.* (1970) based on film intensity data. Anisotropic refinement was not attempted for the non-H atoms. Later, Siedle *et al.* (1980) reported a much higher quality structure of a 1:1 adduct of bis(2,4-pentanedionato)-palladium(II) and tetrathiofulvalene (TTF). On the basis of the Raman and X-ray data, the authors presented strong evidence that, in contrast to other complexes of TTF, this material seemed to contain only neutral tetrathiofulvalene. Nevertheless, with no good structural data for $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$ available at this time a small degree of charge transfer between the Pd complex and the TTF molecule could not be totally ruled out.



During our investigations into mixed metal complexes with, among others, 2,4-pentanedionate as the ligand we were able to isolate single crystals of (I) and redetermine its structure at 100 K. It was synthesized as described by Okeya *et al.* (1981) and single crystals were grown from a THF solution. The general findings are similar to those reported by Knyazeva *et al.* (1970), but the overall structure quality is significantly improved, with s.u. values for atom positions and structural parameters about a tenth of those reported previously, and the $R(F)$ value has been reduced from 0.129 to 0.026.

Compound (I) crystallizes in the space group $P2_1/n$ with two molecules in the unit cell. The Pd atom at the center of the molecule is located on an inversion center (Fig. 1), and each of the 2,4-pentanedionate ligands is very close to planar. The largest deviation from the mean plane is $0.030(2)$ Å for atom C3 and the r.m.s. deviation is 0.016 Å.

Knyazeva *et al.* (1970) stated that the Pd complex is planar, whereas in the isostructural copper compound (Starikova &

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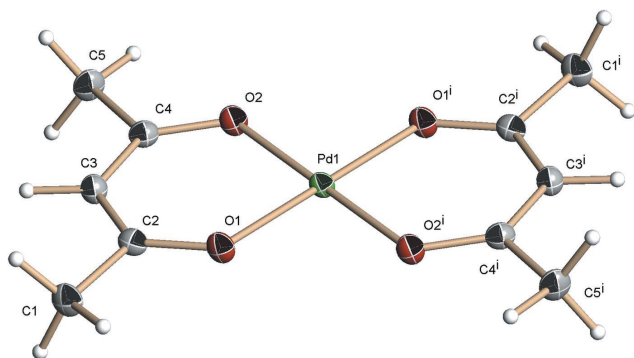


Figure 1
View of the title complex, with 50% probability displacement ellipsoids for the non-H atoms [symmetry code: (i) $-x, -y, -z$].

Shugam, 1969; Lebrun *et al.*, 1986; Berry *et al.*, 2004) a bend of 13.6° with respect to the $O \cdots O$ vector is found. A closer inspection of our data, those of Knyazeva *et al.* and those for the copper complex do not confirm this finding. For (I), the two 2,4-pentanedionate ligands are not located exactly in the same plane but are tilted with respect to the PdO_4 plane by $3.4(1)^\circ$. The separation of the two parallel 2,4-pentanedionate planes is $0.212(2) \text{ \AA}$, and the Pd atom is located half way between these planes. A reanalysis of the data of Knyazeva *et al.* (1970) [as deposited in the Cambridge Structural Database (CSD; Version 5.26 plus three updates; Allen, 2002)] gave, within the margin of error, the same values as found here. For the isostructural copper complex, Lebrun *et al.* (1986) reported a value of 7.05° for the angle between the planes of the 2,4-pentanedionate and the PdO_4 groups, and the corresponding values for the data sets of Berry *et al.* (2004) (CSD refcode ACACCU02) and Starikova & Shugam (1969) obtained from the CSD were 6.12 and 8.12° , respectively.

A closer analysis of the packing and molecular interactions for (I) and the Cu complex gives a possible explanation for the observed bending of the metallacycles. The bis(2,4-pentanedionate) complexes of palladium and copper are arranged in stacks of parallel molecules along the b axis. Each complex within those stacks is offset by half a molecule with respect to their nearest neighbor up or down the b axis, resulting in atom C3 of each molecule coming into close contact with the Pd atom of the next molecule along the stack (Fig. 2). For (I), the $Pd1 \cdots C3^j$ distance is $3.310(2) \text{ \AA}$, and $Pd1 \cdots H3^j$ is 3.171 \AA [symmetry code (j): $x, y - 1, z$; the equivalent metal-carbon distance in the copper complex is 3.017 \AA (Berry *et al.* 2004)]. Atom C3 is the most nucleophilic C atom of the 2,4-pentanedionate ligand, and thus an attractive and stabilizing interaction between this carbon center and the metal cation can be proposed, formally augmenting the coordination plane of the cation to a very distorted octahedron. Such an attractive interaction would be maximized by slightly bending the ligand of the complex towards a neighboring molecule so that the $Pd \cdots C3^j$ distance is minimized, without the need to also minimize the less attractive interactions of the other atoms of the ligand.

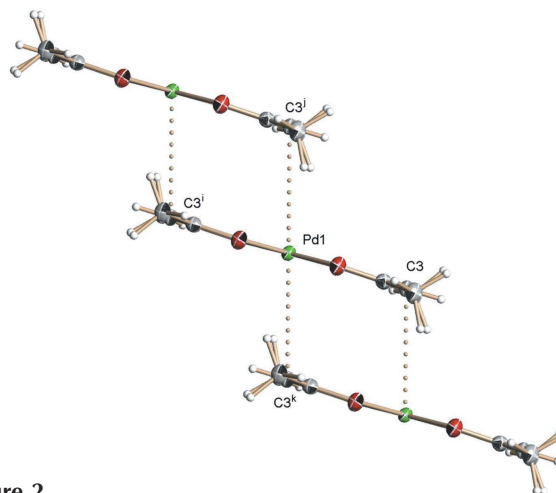


Figure 2
Illustration of the intermolecular interactions (dotted lines) between the Pd atom and atoms C3 up and down the stacks along the b axis. The b axis is aligned along the Pd atoms displayed [50% probability level displacement ellipsoids; symmetry codes: (i) $-x, -y, -z$; (j) $x, y - 1, z$; (k) $-x, -y + 1, -z$].

This assumption seems to be further verified by comparing (I) with its 1:1 tetrathiofulvalene (TTF) adduct (Siedle *et al.*, 1980). In the latter structure, no stacks of Pd complexes are present and also no intermolecular close contacts for the Pd atom can be found. In agreement with the above assumption, no significant bending of the metallacycle is found for the mixed crystal, and the angle between the two ligand planes is less than 1° . All these observations, together with the similar type of bending for the isostructural Cu and Pd complexes, point towards the attractive intermolecular interaction between the metal atom and the nucleophilic C atom as the main cause for the non-planarity observed for the metallacycles.

All other bond distances and angles are in the expected range, and are in good agreement with those reported previously for (I) and its adduct with tetrathiofulvalene. Selected bond lengths and angles are listed in Table 1.

Experimental

A 5 M solution (5 ml) of sodium hydroxide was added to a stirred mixture of 2,4-pentanedione (2.5 ml) and a 0.5 M solution (10 ml) of disodium tetrachloropalladate(II), $Na_2[PdCl_4]$, to give a yellow precipitate (Okeya *et al.*, 1981). The precipitate was filtered off, washed with water, then with methanol and finally with diethyl ether, and dissolved in a minimum amount of tetrahydrofuran to give orange crystals of (I) (yield 85%), some of which were suitable for single-crystal X-ray diffraction.

Crystal data

$[Pd(C_5H_7O_2)_2]$
 $M_r = 304.61$
Monoclinic, $P2_1/n$
 $a = 9.9119(10) \text{ \AA}$
 $b = 5.2232(5) \text{ \AA}$
 $c = 10.3877(10) \text{ \AA}$
 $\beta = 95.807(2)^\circ$
 $V = 535.03(9) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.891 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4907 reflections
 $\theta = 3.0\text{--}30.2^\circ$
 $\mu = 1.73 \text{ mm}^{-1}$
 $T = 100(2) \text{ K}$
Block, orange
 $0.60 \times 0.55 \times 0.25 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer	1581 independent reflections
ω scans	1457 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 2003)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.453$, $T_{\text{max}} = 0.65$	$\theta_{\text{max}} = 30.2^\circ$
5832 measured reflections	$h = -14 \rightarrow 13$
	$k = -7 \rightarrow 7$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.24P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 1.23 \text{ e } \text{\AA}^{-3}$
1581 reflections	$\Delta\rho_{\text{min}} = -1.73 \text{ e } \text{\AA}^{-3}$
72 parameters	
H-atom parameters constrained	

Table 1Selected geometric parameters (\AA , $^\circ$).

Pd1–O2	1.9815 (10)	Pd1–O1	1.9837 (10)
O2–Pd1–O1	95.19 (4)	O2–Pd1–O1 ¹	84.81 (4)

Symmetry code: (i) $-x, -y, -z$.

All H atoms were placed in calculated positions ($C-H = 0.95-0.98 \text{ \AA}$) and were refined with an isotropic displacement parameter of 1.5 (methyl) or 1.2 times U_{eq} of the adjacent C atom. Methyl H atoms were allowed to rotate to best fit the experimental electron density. The highest peak and deepest hole are located 0.78 and 0.75 \AA , respectively, from atom Pd1.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE-Plus* (Bruker, 2003); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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