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Redetermination of potassium benzilate

Loguard S. Rojas, Belkis M. Ramírez,* Asiloé J. Mora, Gerzon E. Delgado and Graciela Díaz de Delgado

Laboratorio de Cristalografía, Facultad de Ciencias, Departamento de Química, Universidad de Los Andes, Apdo. Postal 40 La Hechicera, Mérida 5251, Venezuela

Correspondence e-mail: belkis@ula.ve

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Key indicators

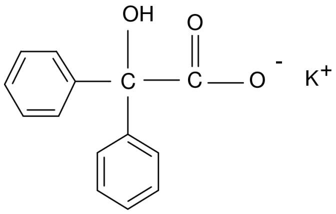
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.119
Data-to-parameter ratio = 17.1

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

The structure of potassium benzilate, $K^+\cdot C_{14}H_{11}O_3^-$, previously determined from visually estimated intensities, has been redetermined from CCD data. The K^+ ion is five-coordinate and the distribution of O atoms around the metal is a flattened square-base pyramid. Pairs of edge-sharing polyhedra join to form corrugated layers parallel to ab, which stack along the c axis. The K^+ ion is in contact with the π electrons of one phenyl ring at a perpendicular distance of 3.0899 (4) Å and is displaced laterally by 0.252 Å with respect to the ring centroid. This interaction and an intramolecular hydrogen bond account for the rigidity of this ring compared to the second ring. The two intramolecular hydrogen bonds present have graph-set motif $S(5)$. An intermolecular hydrogen bond, which also involves the hydroxyl group, has graph-set motif $C_1^2(4)$.

Comment

The structure of potassium benzilate, (I), was described previously by Vyas *et al.* (1978), determined from visually estimated intensities collected on Weissenberg photographs. The crystal used in that study was a colorless needle obtained by reaction of benzilic acid with KOH. For our study, we carried out one synthesis using KOH and another using K_2CO_3, both with benzilic acid in a 1:1 molar ratio. Colorless plates were obtained from the synthesis with KOH, while the reaction with K_2CO_3 produced elongated plates. However, data collection on both types of crystals produced the same unit cell and structural results. For the present study, the crystals obtained from K_2CO_3 appeared to be of better quality and therefore this data set was preferred. Since the earlier structure refinement converged to $R = 0.095$, as is common for studies carried out with visually estimated intensities, and the H atoms were not included in the refinement, it was considered appropriate to report the redetermination of the structure and to discuss the hydrogen-bonding pattern in this material.



(I)

It is worth noting that the cell volume reported by Vyas *et al.* (1978) differs by 100 Å^3 from our cell; they also reported a

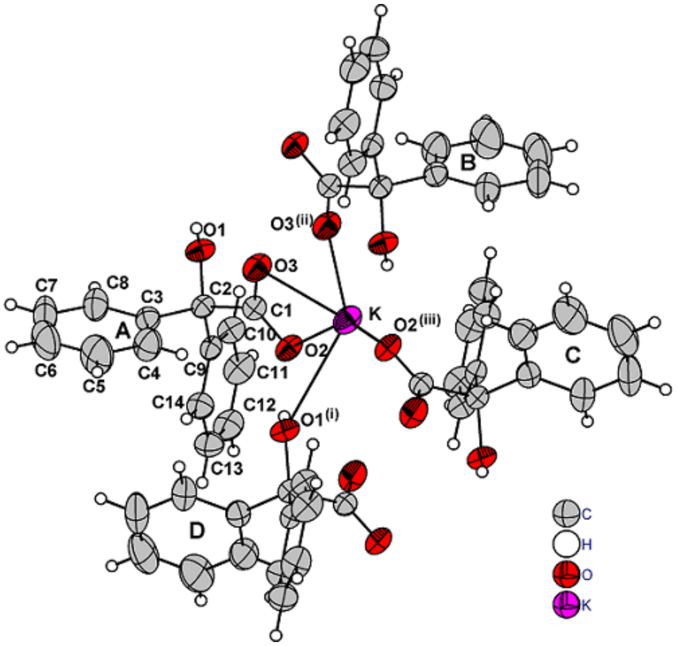


Figure 1
The coordination environment of K in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, -y, 2 - z$; (iii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$.]

very different calculated density (1.64 *versus* 1.428 Mg m^{-3}) and a measured density of 1.67 Mg m^{-3}. This calculated density, however, is recorded as a discrepancy in the Cambridge Structural Database (Allen, 2002; refcode KBZILT), and the high measured density is clearly also a mistake.

In (I), the K$^+$ ion is coordinated by five O atoms from four benzilate ligands. Fig. 1 shows the coordination sphere around the K$^+$ ion, with the labeling scheme for one crystallographically unique ligand. The K—O distances range from 2.6347 (14) to 3.0031 (14) Å. A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) for compounds with K coordinated by five O atoms resulted in K—O distances in the range 2.539–3.188 Å. The compounds with CSD refcodes MUBCIV (Park *et al.*, 2002), WIMCAW (van Oostenryck *et al.*, 1993), GOGBIN, GOGBOT, GOGBUZ (Murayama & Aoki, 1998) and ZUHYEG (Sellin *et al.*, 1996) are representative examples of these compounds. In tri-μ-aqua-μ-calix[6]arene-diaquadipotassium (GOGBUZ), for example, each K$^+$ ion is coordinated by five O atoms, one of them being an OH group joined to one of the phenyl rings. This K—O bond length is 2.943 (5) Å and the distances to the remaining O atoms are between 2.713 (3) and 2.845 (3) Å. The K—O distances obtained in the present study are, therefore, in the expected range. Looking at the distribution of differences between maximum and minimum K—O distances ($\Delta = d_{\rm max} - d_{\rm min}$) within the coordination sphere of five-coordinated K, the values are between 0.049 and 0.623 Å, with Δ = 0.368 Å in potassium benzilate.

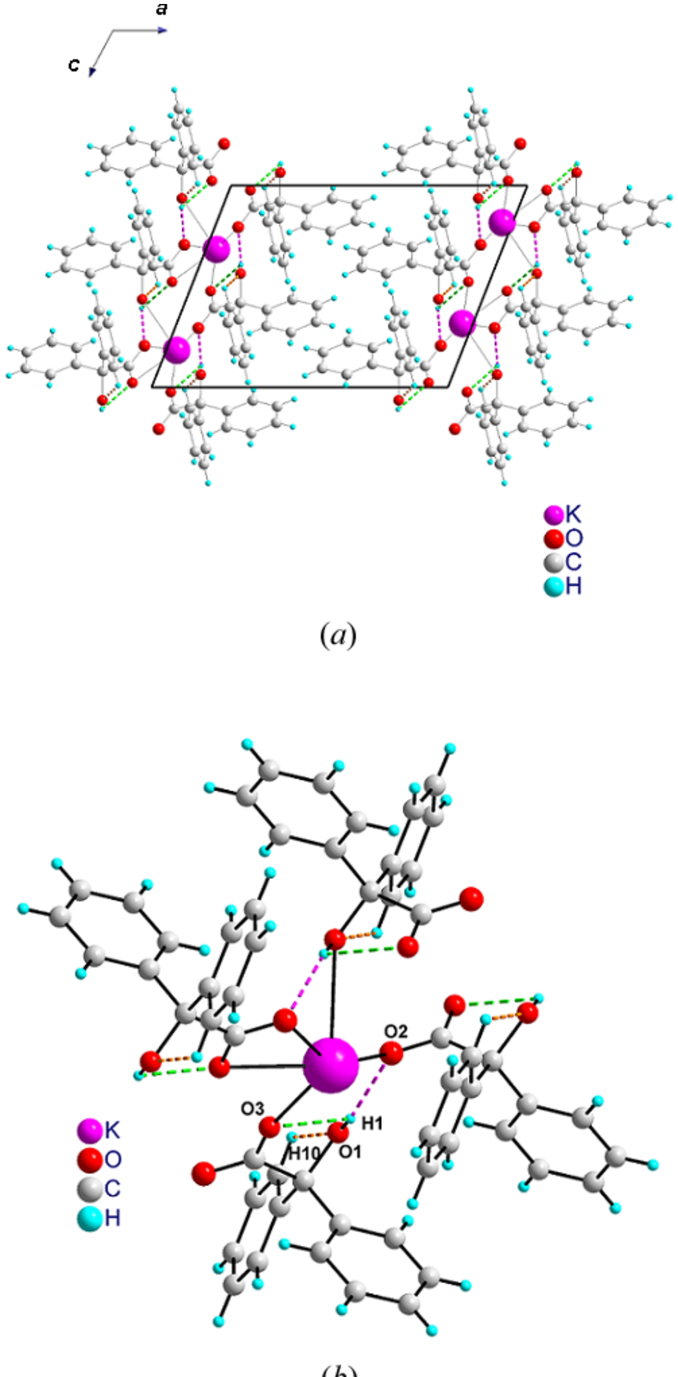


Figure 2
(*a*) Packing arrangement and hydrogen-bond assembly viewed down the *b* axis. (*b*) Detailed view of the intra- and intermolecular hydrogen bonds.

As in most of the five-coordinated K compounds, the polyhedron formed by the O atoms around the K$^+$ ion is a distorted, flattened square-based pyramid (Fig. 2). The base of this pyramid is composed of atom O3 from the ligand in the original asymmetric unit (labeled *A* in Fig. 1), another O3 related by $(-x, -y, 2 - z)$ (ligand *B*), O2 from a ligand at $(-x, y - \frac{1}{2}, \frac{3}{2} - z)$ (ligand *C*), and O1 at $(x, \frac{1}{2} - y, z - \frac{1}{2})$ (ligand *D*). The atom O2 of ligand *A* is the apex of the pyramid. The K atom is displaced 0.9132 (4) Å from the basal mean plane.

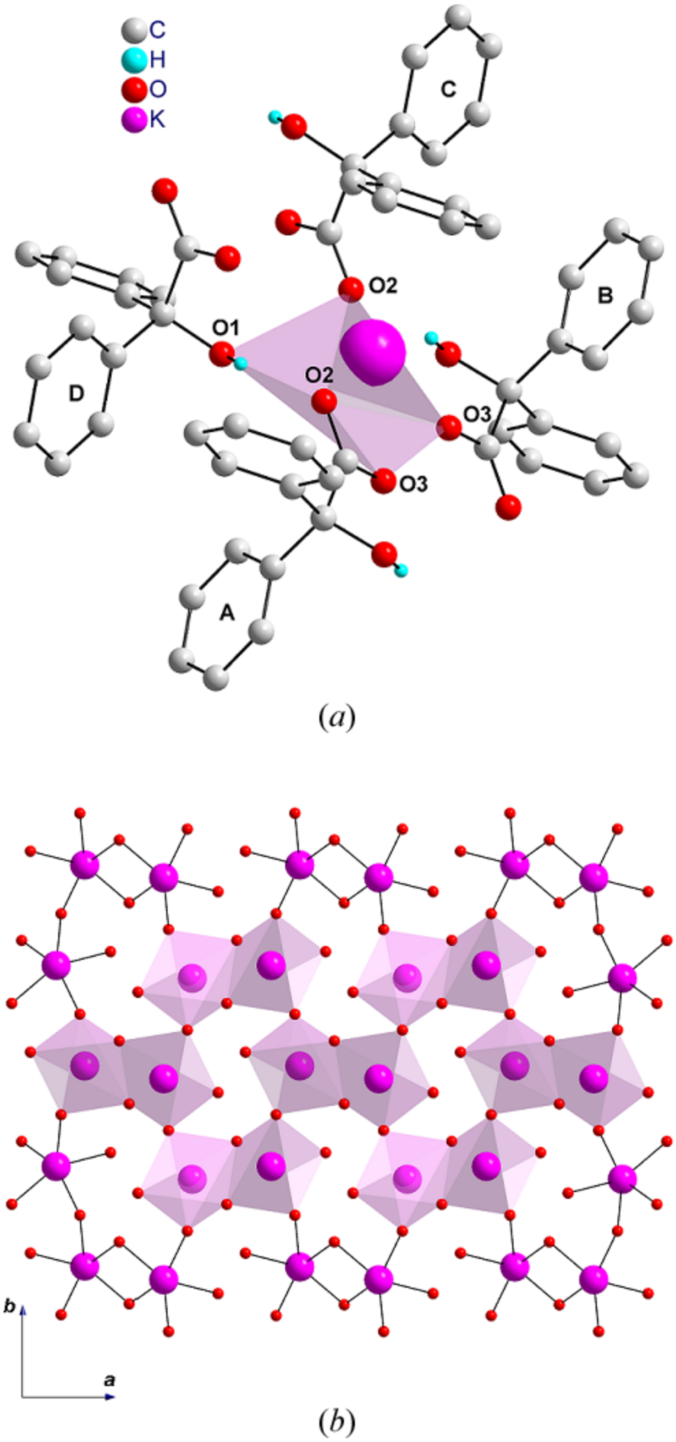


Figure 3
(*a*) Coordination polyhedron for K in (I). For clarity, only the hydroxyl H atoms are shown. (*b*) View in the *bc* plane of the arrangement of K_2O_8 units. The aromatic rings have been omitted.

In the carboxylate group, the C1—O2 and C1—O3 distances are equal within standard uncertainty [1.249 (2) and 1.247 (2) Å, respectively], indicating a delocalized carboxylate group. This group coordinates to a K^+ ion, and each O atom coordinates additionally to a K^+ ion related by symmetry codes [$(-x, \frac{1}{2}+y, \frac{3}{2}-z)$ for O2 and $(-x, -y, 2-z)$ for O3], resulting in a combination of symmetrical chelate and *syn–anti* bidentate bridging modes. The dihedral angle between the phenyl rings within one ligand is 86.65 (12)°.

It is also worth pointing out the cation–π interaction present in potassium benzilate, as well as in other alkali metal–arene complexes (Gokel *et al.*, 2000). The K^+ ion is located 3.1001 (11) Å ($D1$) from the centroid of ring C9–C14 and at a perpendicular distance of 3.0899 (4) Å ($D2$) with respect to this ring plane. The displacement of the metal ion from the ring centroid is referred to as the 'slippage' (s) and is given by the offset of the perpendicular projection of the heavy atom on the ring least-squares plane from the ring centroid. For a significant interaction, $D1$ should be less than 3.5 Å, and $D2$ must be greater than 1.5 Å to produce a value of s less than 2.0 Å. For potassium benzilate the value of s calculated by *PLATON* is 0.252 Å. In similar compounds, for example GOGBIN and GOGBUZ, Murayama & Aoki (1998) report $D1$ distances in the range 3.168 (6)–3.582 (6) Å.

In potassium benzilate, two intramolecular and one intermolecular hydrogen bonds are observed. The hydroxyl group participates in an intramolecular hydrogen bond with O3 of the carboxylate group (Table 2). The other intramolecular contact occurs between C10—H10 of phenyl ring C9–C14 and the hydroxyl O atom. This contact, along with the K–π interaction described above, is believed to account for the lower spread of displacement parameter values in the C9–C14 phenyl ring (max/min $U_{\rm eq}$ = 1.60, compared with a value of 2.16 for the C3–C8 ring). Both intramolecular hydrogen bonds have a first-order graph set motif $S(5)$ (Bernstein *et al.*, 1995) and their combination has a second-order graph-set motif $S_2^2(8)$. The intermolecular hydrogen bond occurs between the hydroxyl group and atom O2 of the carboxylate group of a neighboring molecule (Table 2). The hydroxyl group thus participates in a bifurcated hydrogen bond, which forms chains along the c axis and has a graph-set motif $C_1^2(4)$.

In the structure of potassium benzilate, pairs of edge-sharing polyhedra are connected by four of their six other vertices, to form corrugated layers parallel to the *ab* plane, with benzilate ligands above and below the plane (Fig. 3*a*). As shown in Fig. 3*b*, these layers stack in an interlocking fashion along the *a* axis and are held together by van der Waals interactions.

It should be pointed out that an orthorhombic pseudo-*C*-centered cell with dimensions 26.297 (3), 9.0238 (9), 10.3650 (11) Å (cell II) was obtained in the indexing procedure with *SMART* (Bruker, 1998) after data collection. Further analysis converted this cell to the monoclinic cell used in the final refinement. However, in order to explore the possibility of the existence of a *C*-centered orthorhombic cell and/or a sub-superstructure relationship, the data were reduced with *SAINT* (Bruker, 1998) in the larger orthorhombic cell. The structure solution was attempted in space group $P1$ and, after locating the K and O atoms, the cell was transformed by *PLATON* (Spek, 1990) to monoclinic $P2_1/c$ with cell dimensions *ca* 26 × 9 × 10 Å, and β very close to 90°. The two independent K atoms obtained (K1 at 0.01752, 0.46824, 0.20147, and K2 at 0.51781, 0.03174, 0.20139) are, indeed, related by pseudo-*C*-centering and the refinement of K, O and C positions and anisotropic displacement parameters converged to $R = 0.066$ for the 2249 observed reflections, $wR = 0.279$, and $S = 0.93$. Further refinement with H atoms included did not improve the fit. This cell II is related to the true monoclinic cell I by the transformation $a_{\rm II} = [0,0,1/0,1,0/-\frac{1}{2},0,-\frac{1}{2}]a_{\rm I}$.

The strontium salt of benzilic acid has also been prepared and will be reported soon.

Experimental

Potassium benzilate was prepared by slow evaporation of an aqueous solution containing benzilic acid and K_2CO_3 in a 1:1 molar ratio. Colorless plates grew in the solution over a period of two months. The IR spectra were recorded from KBr discs, using a PE-1600 FT–IR Spectrometer with IRDM software. IR (cm^{-1}): ν(O—H) 3358; ν(C—H sp^2) 3050; ν(CO_2 asymmetric) 1602–1591; ν(CO_2 symmetric) 1387; ν(O—H) 1170; ν(C—O) 1171–1048. Thermogravimetric analysis (TG and DTG) and differential scanning calorimetry measurements (DSC) were performed in a Perkin–Elmer TGA7 thermal analyser and a Perkin–Elmer DSC7 cell, under a dynamic dry nitrogen atmosphere at a heating rate of 10 K min^{-1}. TGA (temperature range 298–773 K): weight loss to only step 1: 73.67% to 563–603 K; DSC (temperature range 298–873 K): step 1: 565–573 K *endo*; step 2: 613–710 K *endo*.

Crystal data

$K^+\cdot C_{14}H_{11}O_3^-$
$M_r = 266.33$
Monoclinic, $P2_1/c$
$a = 14.1283$ (15) Å
$b = 9.0230$ (10) Å
$c = 10.3639$ (11) Å
$\beta = 111.474$ (1)°
$V = 1229.5$ (2) Å^3
$Z = 4$
$D_x = 1.439$ Mg m^{-3}
$D_m = 1.428$ Mg m^{-3}
D_m measured by neutral buoyancy in $CHCl_3/C_4H_{10}O$
Mo $K\alpha$ radiation
Cell parameters from 3427 reflections
$\theta = 1.6$–28.5°
$\mu = 0.43$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.50 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.757$, $T_{\rm max} = 0.880$
15415 measured reflections
2864 independent reflections
2213 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 28.5°$
$h = -16 \rightarrow 18$
$k = -8 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.120$
$S = 1.07$
2864 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.0399P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K—O2	2.7937 (13)	C3—C8	1.388 (3)
K—O3	2.8525 (13)	C4—C5	1.384 (3)
K—O1$^{\rm i}$	3.0031 (14)	C5—C6	1.366 (4)
K—O3$^{\rm ii}$	2.6347 (13)	C6—C7	1.365 (4)
K—O2$^{\rm iii}$	2.6414 (13)	C7—C8	1.393 (3)
O1—C2	1.432 (2)	C9—C10	1.385 (2)
O2—C1	1.249 (2)	C9—C14	1.394 (2)
O3—C1	1.247 (2)	C10—C11	1.387 (3)
C1—C2	1.559 (2)	C11—C12	1.373 (3)
C2—C9	1.530 (2)	C12—C13	1.382 (3)
C2—C3	1.531 (2)	C13—C14	1.388 (3)
C3—C4	1.382 (3)	O1—H1	0.77 (2)

O2—K—O3	46.18 (4)	C3—C4—C5	120.6 (2)
O3—C1—O2	125.11 (16)	C6—C5—C4	120.6 (3)
O3—C1—C2	115.85 (14)	C7—C6—C5	119.8 (2)
O2—C1—C2	119.05 (14)	C6—C7—C8	120.2 (2)
O1—C2—C9	107.22 (13)	C3—C8—C7	120.4 (2)
O1—C2—C9	107.22 (13)	C10—C9—C14	118.48 (16)
O1—C2—C3	109.74 (13)	C10—C9—C2	121.22 (15)
C9—C2—C3	110.83 (13)	C14—C9—C2	120.26 (15)
O1—C2—C1	107.70 (13)	C9—C10—C11	120.63 (17)
C9—C2—C1	111.55 (13)	C12—C11—C10	120.66 (18)
C3—C2—C1	109.71 (13)	C11—C12—C13	119.43 (18)
C4—C3—C8	118.35 (18)	C12—C13—C14	120.31 (18)
C4—C3—C2	122.24 (16)	C13—C14—C9	120.48 (18)
C8—C3—C2	119.41 (17)	K$^{\rm iv}$—O1—H1	75.1 (18)

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $-x, -y, 2-z$; (iii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2$^{\rm iv}$	0.77 (2)	2.09 (2)	2.7986 (18)	154 (2)
O1—H1···O3	0.77 (2)	2.47 (3)	2.7454 (18)	103 (2)
C10—H10···O1	0.93	2.37	2.712 (2)	101

Symmetry code: (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The hydroxyl H atom was located in a difference Fourier map and its coordinates and isotropic displacement parameter were refined. The rest of the H atoms were included in geometrically calculated positions, with C—H = 0.93 Å, and refined using a riding model. Their isotropic displacement parameters were set to 1.2 times $U_{\rm eq}$ of their parent C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990).

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