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3,4-Dihydroxy-1,6-bis(4-methoxyphenyl)hexa-2,4-diene-1,6-dione, its 4-methylphenyl analogue, and a potassium salt of 2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid

Luke Nye,[a] Mark M. Turnbull[a]* and Jan L. Wikaira[b]

[a]Department of Chemistry, Clark University, 950 Main Street, Worcester, MA 01610, USA, and [b]Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand
Correspondence e-mail: mturnbull@clarku.edu

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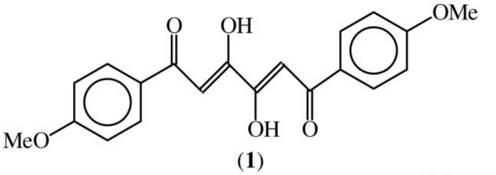
Reaction of 4-methoxyacetophenone with diethyl oxalate under basic conditions produced 3,4-dihydroxy-1,6-bis(4-methoxyphenyl)hexa-2,4-diene-1,6-dione, $C_{20}H_{18}O_6$, (1). The molecules lie across a crystallographic inversion centre and intramolecular hydrogen bonding, similar to acetylacetone, is observed, confirming that the molecule is in the di-enol-dione tautomeric form. Additional O—H⋯O hydrogen bonds link the molecules into chains parallel to the *b* axis. The structure is compared with that of redetermined 4-methylphenyl compound 3,4-dihydroxy-1,6-bis(4-methylphenyl)hexa-2,4-diene-1,6-dione, $C_{20}H_{18}O_4$, (2), which crystallizes in a similar fashion. The salt, *catena*-poly[[μ_2-2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoato-$\kappa^3O^1,O^2:O^4$][μ_2-2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid-$\kappa^2O^1:O^4$]potassium], $[K(C_{11}H_9O_5)(C_{11}H_{10}O_5)]_n$, (3), was isolated as a by-product of the synthesis of (1). The two organic species are linked by a strong hydrogen bond between the carboxylic acid and carboxylate groups. They are further stabilized and linked into a double-chain structure *via* the seven-coordinate potassium ion.

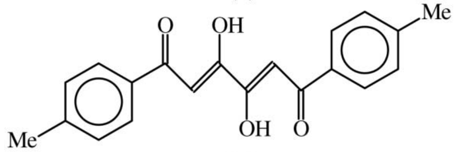
Keywords: crystal structure; 2,4-hexadiene-1,6-diones; potassium salt; di-enol-dione tautomers; metal-ion O_2-chelating sites.

1. Introduction

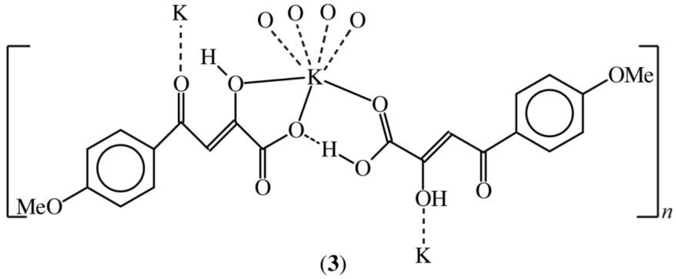
We have been examining organic compounds as templates for low-dimensional coordination polymers, and have been looking at polyones and pentane-2,4-dione (acac) derivatives in particular. The structure of the compound 3,4-dihydroxy-1,6-diphenylhexa-2,4-diene-1,6-dione (Kaitner *et al.*, 1992; Nawar, 1994) lends itself to such structures and in its deprotonated form possesses two equivalent O_2-chelating sites for metal ions. Multiple tautomers are possible for this compound, including the 1,3,4,6-tetrone form, but in the solid state the di-enol-dione form is observed. Substituted phenyl derivatives have also been reported, including the 4-methyl derivative, (2) [structure previously published from room-temperature data by Kaitner *et al.* (1992)] and the 4-chloro derivative (Chetkina, 1992), both of which also exhibit the di-enol-dione form, as does the parent molecule. We were interested in the effects of these substituents on the packing strucuture of the molecules and undertook the synthesis and structural analysis of the 4-methoxyphenyl derivative, (1). In the process, we serendipitously produced a potassium salt of the related 2-hydroxy-4-methoxyphenyl-4-oxobut-2-enoic acid complex, *i.e. catena*-poly[[μ_2-2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoato]-[μ_2-2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid]-potassium], (3). We report here the structures of 3,4-dihydroxy-1,6-bis(4-methoxyphenyl)hexa-2,4-diene-1,6-dione, (1), and (3), and the low-temperature redetermination of the structure of 3,4-dihydroxy-1,6-bis(4-methylphenyl)hexa-2,4-diene-1,6-dione, (2).



(1)



(2)



(3)

2. Experimental

2.1. Synthesis and crystallization

For the preparation of (1), ethyl oxalate (0.5898 g, 4.0 mmol) and 4-methoxyacetophenone (1.2614 g, 8.4 mmol) were dissolved in tetrahydrofuran (THF), and the resulting solution was added dropwise to a suspension of potassium *tert*-butoxide (1.371 g, 12.2 mmol) in THF. The resulting mixture was then refluxed for 21 h. The reaction mixture was cooled to room temperature, diluted with low-boiling petroleum ether (30 ml) and allowed to stand for 5 min. The mixture was filtered and the precipitate washed twice with 10 ml portions of petroleum ether, yielding a dark-orange powder and a dark-red filtrate. The orange powder was added to 85% acetic acid

Table 1
Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{20}H_{18}O_6$	$C_{20}H_{18}O_4$	$[K(C_{11}H_9O_5)(C_{11}H_{10}O_5)]$
M_r	354.34	322.34	482.47
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	116	116	116
a, b, c (Å)	15.4385 (6), 6.1475 (2), 8.7281 (3)	14.7710 (6), 6.1622 (2), 8.6184 (3)	15.3832 (4), 6.3481 (1), 21.1606 (5)
β (°)	105.029 (2)	91.896 (2)	90.582 (1)
V (Å^3)	800.03 (5)	784.03 (5)	2066.31 (8)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.10	0.32
Crystal size (mm)	0.55 × 0.33 × 0.12	0.62 × 0.46 × 0.06	0.57 × 0.55 × 0.39
Data collection			
Diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$, $T_{\max}$	0.943, 0.987	0.944, 0.994	0.840, 0.886
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16170, 2313, 2155	19282, 2288, 2150	52473, 6026, 5402
R_{int}	0.029	0.045	0.034
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.704	0.704	0.704
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.113, 1.12	0.067, 0.151, 1.25	0.032, 0.090, 1.06
No. of reflections	2313	2288	6026
No. of parameters	122	116	316
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.36, −0.32	0.41, −0.32	0.47, −0.42

Computer programs: *SHELXS97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL97* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip 2010).

(20 ml). The resulting mixture was stirred for 3 h, filtered and the solid obtained was washed with three 10 ml portions of cold water, yielding a pale-yellow–green powder isolated in 34.4% yield. IR (KBr pellet, ν, cm^{-1}): O—H 3436, C═C 1601, C═O 1571. The product was recrystallized from chloroform to yield pale-yellow prisms of (1) suitable for X-ray diffraction.

The potassium salt, (3), formed from the acidic filtrate after several days. The precipitate was recovered by filtration and washed with acetone to yield X-ray-quality orange crystals.

For the preparation of (2), ethyl oxalate (0.5828 g, 4.0 mmol) and 4-methylacetophenone (1.0861 g, 8.0 mmol) were dissolved in THF, and the resulting solution was added dropwise to a suspension of potassium *tert*-butoxide (1.329 g, 11.8 mmol, pink) in THF. During the addition, the reaction mixture changed color from pink to peach to orange to red. The reaction was then refluxed for 21 h, turning a dark cloudy red after 15 min and then dark orange after 45 min. After reflux, the reaction mixture was cooled to room temperature and diluted with low-boiling petroleum ether (30 ml), allowed to stand for 5 min and then filtered. The precipitate was washed twice with 10 ml portions of petroleum ether. The powder salt product was added to 85% acetic acid (20 ml) which had been previously used to wash the reaction flask. The salt mixture was stirred for 1.5 h, filtered, and the precipitate washed with three 10 ml portions of cold water, yielding a pale-yellow powder (yield 0.388 g, 30.3%). IR (KBr pellet, ν, cm^{-1}): O—H 3435, C—H 3112, C═C 1599, C═O 1571. The product was recrystallized from chloroform to yield pale-yellow prisms of (2) suitable for X-ray diffraction.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Except as indicated below, all H atoms bound to C atoms were refined using a riding model, with methyl C—H = 0.98 Å, and aromatic and vinylic C—H = 0.95 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bonded to O atoms, as well as the vinylic H atoms in (2) and (3), were located in a difference map and their positions refined using fixed U_{iso} values [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$].

3. Results and discussion

Compound (1) crystallizes as a centrosymmetric molecule in the di-enol-dione form with two intramolecular hydrogen bonds (Fig. 1). The H atoms on atoms O1 and C2 were located unambiguously in the difference Fourier map and the position of H1 was allowed to refine with a fixed isotropic displacement parameter. The intramolecular hydrogen bond (O1—H1···O2) and C—O bond lengths (see Table 2 and *Supplementary materials*) confirm the tautomer assignment. The atoms in the central chain are planar to within 0.006 (3) Å, while the benzene ring is canted by 18.33 (10)° relative to that

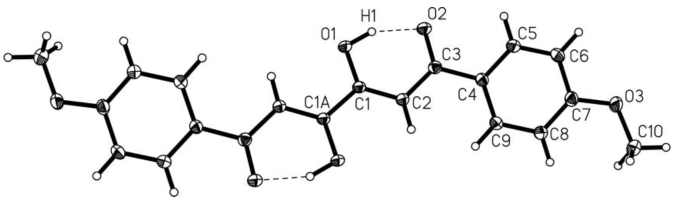


Figure 1
The molecular unit of (1), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The asymmetric unit is labelled, along with the hydrogen-bonding H atom (H1) and symmetry-equivalent atom C1A [symmetry code: (A) $-x$, $-y$, $-z + 1$]. Dashed lines represent hydrogen bonds.

Table 2
Hydrogen-bond geometry (Å, °) for (1).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.951 (15)	1.631 (15)	2.5224 (11)	154.4 (14)
O1—H1···O1^{i}	0.951 (15)	2.526 (15)	2.6760 (15)	88.5 (9)

Symmetry code: (i) $-x$, $-y + 1$, $-z + 2$.

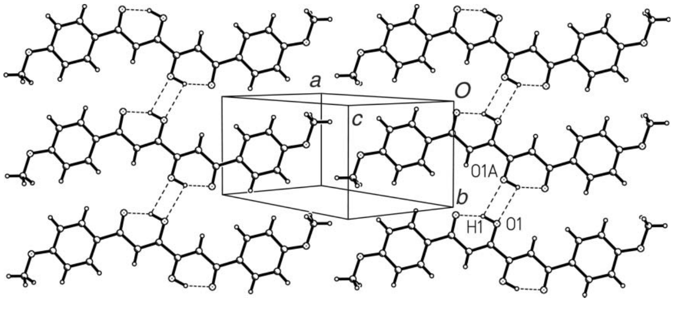


Figure 2
The packing of (1), viewed perpendicular to the chain mean plane. Dashed lines represent hydrogen bonds. The atoms labels are general and O1A is related to O1 by inversion; symmetry code: $-x + 1$, $-y + 1$, $-z + 3$.

plane. The C10—O3—C7—C8 torsion angle of −10.96 (17)° shows that the methoxy substituent is closer to coplanar with the central chain.

The molecules of (1) pack in sheets parallel to the *b* axis and the *ac*-face diagonal, and chains are formed within those sheets *via* bifurcated hydrogen bonds [O1—H1···O1A; Fig. 2; symmetry code: (A) $-x$, $-y + 1$, $-z + 2$]. Although the O—H···O angles are near 90° and the O···H distances somewhat long, the relative positions of the molecules is clearly not coincidental. The methoxy groups are oriented between the chains in such a way as to minimize the void space. No significant π-stacking is observed between layers.

The low-temperature structure for the 4-methylphenyl derivative, (2), was also obtained to allow direct comparison of the changes in packing between the methoxy- and methyl-substituted compounds, and to investigate the effects of temperature on the structure. The molecular unit is comparable in structure with (1), with the central chain atoms coplanar to within 0.0045 (19) Å and an equivalent hydrogen bond (see Table 3) (Fig. 3).

The same layer structure is observed in (2) as in (1), with intermolecular hydrogen bonds generating chains parallel to the *b* axis (Fig. 4). The smaller methyl groups (compared with methoxy) allow a closer approach of the benzene rings (intercentroid) parallel to the *ac*-face diagonal.

Table 3
Hydrogen-bond geometry (Å, °) for (2).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.92 (2)	1.68 (2)	2.5351 (17)	153 (2)
O1—H1···O1^{i}	0.92 (2)	2.54 (2)	2.698 (2)	89.7 (14)

Symmetry code: (i) $-x$, $-y + 1$, $-z + 1$.

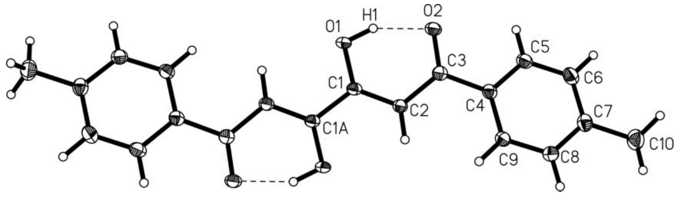


Figure 3
The molecular unit of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The asymmetric unit is labelled, along with the hydrogen-bonding H atom (H1) and symmetry-equivalent atom C1A [symmetry code: (A) $-x$, $-y$, $-z + 1$]. Dashed lines represent hydrogen bonds.

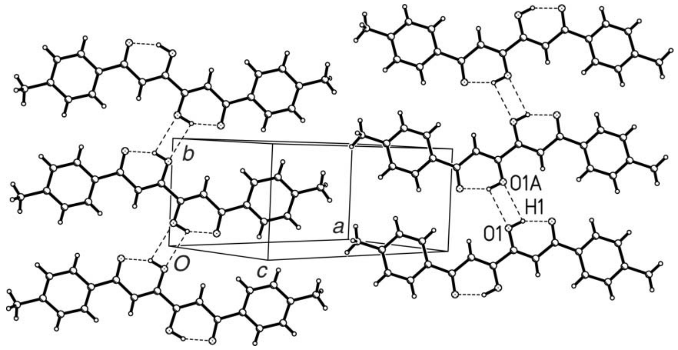


Figure 4
The packing of (2), viewed perpendicular to the chain mean plane. Dashed lines represent hydrogen bonds. The atoms labels are general and O1A is related to O1 by the symmetry code ($-x$, $-y + 1$, $-z - 1$).

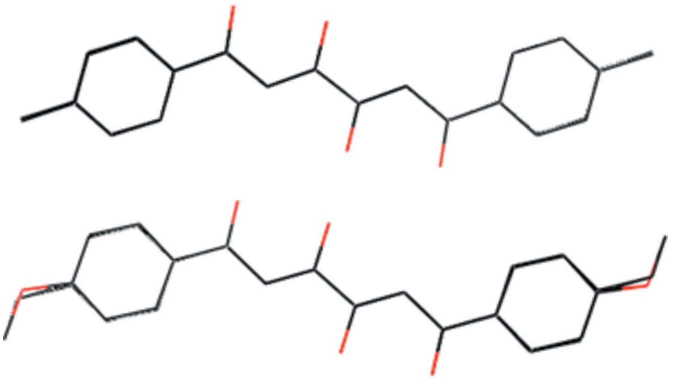


Figure 5
(Top) Superposition of the room-temperature and low-temperature structures of (2). (Bottom) Superposition of the low-temperature structures of (1) and (2).

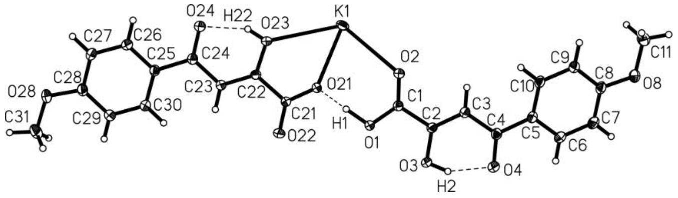


Figure 6
The asymmetric unit of (3), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent hydrogen bonds.

Table 4
Hydrogen-bond geometry (Å, °) for (3).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O21	1.071 (15)	1.361 (15)	2.4322 (10)	178.2 (15)
O3—H2$\cdots$O4	0.875 (16)	1.731 (16)	2.5326 (11)	151.1 (15)
O23—H22$\cdots$O24	0.836 (16)	1.800 (16)	2.5599 (11)	150.4 (15)

The effects of temperature and the nature of the benzene-ring substituents on the molecular structure can most easily be seen from an overlay of the respective structures. The structure of (2) has previously been reported at room temperature (Kaitner *et al.*, 1992). The expected decrease in cell volume with decreasing temperature is observed [806.7 (2) Å^3 at 295 K *versus* 784.03 (5) Å^3 at 116 K, a decrease of approximately 3%], but the structure and conformation of the molecule itself are virtually unchanged, as shown in Fig. 5, indicating that the thermal contraction is absorbed by changes in intermolecular contacts. In spite of the difference in the size of the substituents in the 4-positions, the conformations of the molecular units of (1) and (2) are remarkably similar (Fig. 5), indicating the degree to which the conjugation and intramolecular hydrogen bonding dictate the structure.

Salt (3) crystallized as a by-product of the synthesis of (1) and is best described as a 1:1 complex of 2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid and its mono-potassium salt (Fig. 6). The organic entities are linked *via* a very strong hydrogen bond between the carboxylic acid and carboxylate groups (see Table 4). These groups can be assigned unambiguously *via* the differences in the C—O bond lengths (see *Supplementary materials*). The central hydrogen-bond-bridged chain structure is nearly planar (the mean deviation from the plane for the non-H atoms from C5 to C25 is 0.0345 Å). The two benzene rings are canted out of that plane [the C5 ring by 19.4 (2)° and the C25 ring by 11.5 (2)°].

The hydrogen-bond-bridged carboxylate/carboxylic acid structure is also observed in a variety of structures. In some, such as the structures of the potassium salts of 4-fluorobenzoic acid (Longo & Richardson, 1982) and 4-hydroxybenzoic acid (Manojlović, 1968), or the sodium salt of malic acid (Moore *et al.*, 1980), the central H atom lies on a crystallographic inversion centre and, as a result, the O—H bonds are constrained to be identical. However, there are numerous examples where the H atom does not lie on a symmetry centre and its position has been allowed to refine, resulting in unequal O—H bond lengths, as observed in the present compound. These include salts of hexanedioic acid (Meng *et al.*, 2009), butanedioic acid (Hsu & Schlemper, 1978), 3,5-dinitrobenzoic acid (Madej & Oleksyn, 1986), phthalic acid (Kuppers *et al.*, 1985), a subsituted imidazoledicarboxylic acid (Gao & Gu, 2011), pyrazine-2,3-dicarboxylic acid (Smith *et al.*, 1995), 4,4′-bi(benzene-1,2-carboxylic acid) (Wang *et al.*, 2006) and maleic acid (Madsen & Larsen, 1998). The difference in the O—H bond lengths for these compounds ranges from 0.018 (Madsen & Larsen, 1998) to 0.225 Å (Smith *et al.*, 1995).

The carboxylate/carboxylic acid pairs are further linked *via* the K$^+$ cation, which also bridges them to form a dimeric structure (Fig. 7). The seven-coordinate K$^+$ cation lies somewhat above [0.6600 (8) Å] the plane generated by five O atoms [O2, O1B, O3B, O21 and O23; the deviation from the mean plane is 0.07 (2) Å; symmetry code: (B) $x, y + 1, z$] and is then further linked to two additional O atoms [O22C and O24A; symmetry codes: (A) $-x, -y + 1, -z$; (C) $-x, -y, -z$] at distances of 3.0350 (12) and 3.1779 (13) Å, respectively, above the plane. This generates potassium-bridged chains parallel to the *b* axis.

A copper complex of the anion of 2-hydroxy-4-oxo-4-phenylbut-2-enoic acid has been reported (Landry *et al.*, 2007) and exhibits a distinctly different coordination mode. Here, the enol has been deprotonated to generate an acac-like structure which chelates the Cu$^{\rm II}$ cation, while the carboxylic acid function remains protonated (ancillary ligands prevent the formation of a Cu-bridged chain structure). This suggests, not unexpectedly, varying coordination modes for these ligands as a function of the metal ion. The similarity of the current structures to the parent phenyl compound, and the robust nature of the molecular conformation at varying

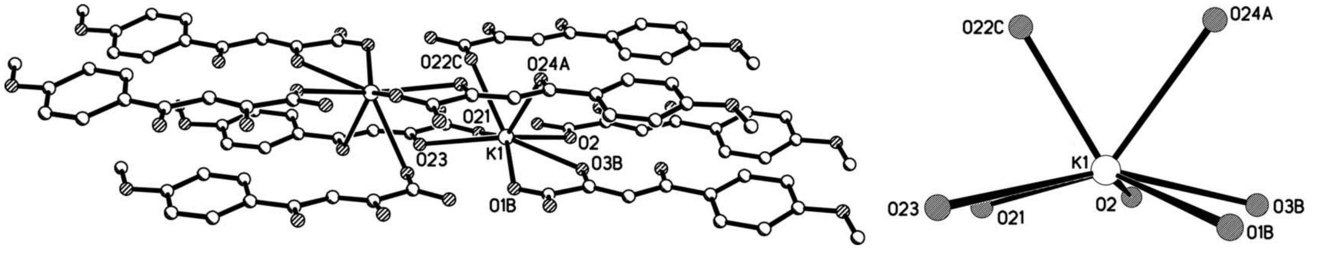


Figure 7
(Left) The potassium-bridged dimer structure of (3) and (right) the K$^+$ cation coordination environment. Symmetry codes A, B, C are as defined in §3.

temperatures, should allow for the preparation of families of coordination complexes and such work is in progress.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3105). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2013). C**69**, 1317-1321   [doi:10.1107/S0108270113025973]

3,4-Dihydroxy-1,6-bis(4-methoxyphenyl)hexa-2,4-diene-1,6-dione, its 4-methylphenyl analogue, and a potassium salt of 2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid

Luke Nye, Mark M. Turnbull and Jan L. Wikaira

Computing details

For all compounds, data collection: *SHELXTL* (Sheldrick, 2008); cell refinement: *SHELXTL* (Sheldrick, 2008); data reduction: *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008). Software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip 2010) for compound1, compound3; *SHELXL97* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010) for compound2.

(compound1) 3,4-Dihydroxy-1,6-bis(4-methoxyphenyl)hexa-2,4-diene-1,6-dione

Crystal data

$C_{20}H_{18}O_6$	$F(000) = 372$
$M_r = 354.34$	$D_x = 1.471$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6419 reflections
$a = 15.4385$ (6) Å	$\theta = 2.7$–$30.4°$
$b = 6.1475$ (2) Å	$\mu = 0.11$ mm^{-1}
$c = 8.7281$ (3) Å	$T = 116$ K
$\beta = 105.029$ (2)°	Plate, yellow
$V = 800.03$ (5) Å^3	0.55 × 0.33 × 0.12 mm
$Z = 2$	

Data collection

Bruker APEXII CCD area-detector diffractometer	16170 measured reflections
Radiation source: fine-focus sealed tube	2313 independent reflections
Graphite monochromator	2155 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.029$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 30.0°$, $\theta_{min} = 2.7°$
	$h = -20 \rightarrow 21$
	$k = -8 \rightarrow 8$
$T_{min} = 0.943$, $T_{max} = 0.987$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$S = 1.12$
Least-squares matrix: full	2313 reflections
$R[F^2 > 2\sigma(F^2)] = 0.043$	122 parameters
$wR(F^2) = 0.113$	0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.2726P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.00663 (6)	0.71487 (12)	0.97532 (10)	0.02027 (19)
H1	−0.0476 (10)	0.642 (2)	0.8907 (18)	0.024*
O2	−0.12517 (5)	0.63048 (12)	0.72353 (9)	0.01960 (18)
O3	−0.41635 (6)	1.05028 (14)	0.16040 (10)	0.0264 (2)
C1	−0.02613 (7)	0.92265 (16)	0.94117 (12)	0.0153 (2)
C2	−0.08909 (7)	0.98991 (17)	0.80906 (12)	0.0168 (2)
H2	−0.1000	1.1407	0.7894	0.020*
C3	−0.13895 (7)	0.83071 (17)	0.69928 (12)	0.0162 (2)
C4	−0.20934 (7)	0.90088 (17)	0.55747 (12)	0.0166 (2)
C5	−0.27195 (8)	0.74536 (17)	0.48004 (13)	0.0195 (2)
H5	−0.2677	0.6003	0.5188	0.023*
C6	−0.33969 (8)	0.80018 (18)	0.34814 (13)	0.0221 (2)
H6	−0.3820	0.6936	0.2974	0.026*
C7	−0.34583 (8)	1.01304 (18)	0.28942 (13)	0.0196 (2)
C8	−0.28320 (7)	1.16862 (17)	0.36206 (12)	0.0192 (2)
H8	−0.2863	1.3120	0.3205	0.023*
C9	−0.21571 (7)	1.11223 (17)	0.49676 (12)	0.0182 (2)
H9	−0.1736	1.2191	0.5478	0.022*
C10	−0.43629 (8)	1.27080 (19)	0.11246 (15)	0.0256 (3)
H10A	−0.4505	1.3524	0.1993	0.031*
H10B	−0.4879	1.2747	0.0192	0.031*
H10C	−0.3842	1.3366	0.0859	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0253 (4)	0.0111 (3)	0.0207 (4)	0.0012 (3)	−0.0008 (3)	−0.0001 (3)
O2	0.0235 (4)	0.0139 (3)	0.0202 (4)	0.0000 (3)	0.0037 (3)	0.0001 (3)
O3	0.0272 (5)	0.0211 (4)	0.0235 (4)	0.0017 (3)	−0.0069 (3)	−0.0026 (3)
C1	0.0176 (5)	0.0125 (4)	0.0156 (4)	0.0001 (3)	0.0038 (4)	0.0000 (4)

C2	0.0197 (5)	0.0137 (4)	0.0158 (4)	0.0002 (3)	0.0022 (4)	0.0003 (4)
C3	0.0175 (5)	0.0160 (4)	0.0155 (4)	0.0001 (3)	0.0047 (3)	0.0004 (4)
C4	0.0174 (5)	0.0168 (4)	0.0149 (4)	−0.0005 (4)	0.0029 (4)	−0.0016 (4)
C5	0.0223 (5)	0.0149 (4)	0.0198 (5)	−0.0011 (4)	0.0026 (4)	−0.0011 (4)
C6	0.0231 (6)	0.0178 (5)	0.0218 (5)	−0.0025 (4)	−0.0003 (4)	−0.0048 (4)
C7	0.0200 (5)	0.0202 (5)	0.0165 (5)	0.0013 (4)	0.0011 (4)	−0.0030 (4)
C8	0.0211 (5)	0.0171 (5)	0.0181 (5)	−0.0008 (4)	0.0025 (4)	0.0004 (4)
C9	0.0186 (5)	0.0172 (5)	0.0177 (5)	−0.0024 (4)	0.0024 (4)	−0.0007 (4)
C10	0.0250 (6)	0.0243 (5)	0.0240 (5)	0.0025 (4)	0.0002 (4)	0.0032 (4)

Geometric parameters (Å, º)

O1—C1	1.3284 (12)	C5—C6	1.3813 (15)
O1—H1	0.951 (15)	C5—H5	0.9500
O2—C3	1.2577 (12)	C6—C7	1.3996 (15)
O3—C7	1.3675 (13)	C6—H6	0.9500
O3—C10	1.4285 (14)	C7—C8	1.3906 (15)
C1—C2	1.3653 (14)	C8—C9	1.3974 (14)
C1—C1^{i}	1.476 (2)	C8—H8	0.9500
C2—C3	1.4443 (14)	C9—H9	0.9500
C2—H2	0.9500	C10—H10A	0.9800
C3—C4	1.4837 (14)	C10—H10B	0.9800
C4—C9	1.3970 (15)	C10—H10C	0.9800
C4—C5	1.4023 (14)		

C1—O1—H1	102.2 (9)	C5—C6—H6	120.1
C7—O3—C10	117.72 (9)	C7—C6—H6	120.1
O1—C1—C2	123.44 (9)	O3—C7—C8	124.84 (10)
O1—C1—C1^{i}	114.34 (11)	O3—C7—C6	114.96 (10)
C2—C1—C1^{i}	122.23 (11)	C8—C7—C6	120.20 (10)
C1—C2—C3	119.69 (9)	C7—C8—C9	119.44 (10)
C1—C2—H2	120.2	C7—C8—H8	120.3
C3—C2—H2	120.2	C9—C8—H8	120.3
O2—C3—C2	120.91 (9)	C4—C9—C8	120.91 (10)
O2—C3—C4	118.70 (9)	C4—C9—H9	119.5
C2—C3—C4	120.37 (9)	C8—C9—H9	119.5
C9—C4—C5	118.65 (10)	O3—C10—H10A	109.5
C9—C4—C3	123.44 (9)	O3—C10—H10B	109.5
C5—C4—C3	117.91 (9)	H10A—C10—H10B	109.5
C6—C5—C4	120.90 (10)	O3—C10—H10C	109.5
C6—C5—H5	119.5	H10A—C10—H10C	109.5
C4—C5—H5	119.5	H10B—C10—H10C	109.5
C5—C6—C7	119.87 (10)		

O1—C1—C2—C3	0.73 (16)	C4—C5—C6—C7	0.61 (18)
C1^{i}—C1—C2—C3	−179.17 (12)	C10—O3—C7—C8	−10.96 (17)
C1—C2—C3—O2	−0.05 (16)	C10—O3—C7—C6	168.78 (10)
C1—C2—C3—C4	178.32 (10)	C5—C6—C7—O3	−178.81 (10)
O2—C3—C4—C9	−163.46 (10)	C5—C6—C7—C8	0.94 (18)
C2—C3—C4—C9	18.13 (16)	O3—C7—C8—C9	177.88 (10)

O2—C3—C4—C5	15.87 (15)	C6—C7—C8—C9	−1.84 (17)
C2—C3—C4—C5	−162.54 (10)	C5—C4—C9—C8	0.27 (16)
C9—C4—C5—C6	−1.20 (17)	C3—C4—C9—C8	179.59 (10)
C3—C4—C5—C6	179.44 (10)	C7—C8—C9—C4	1.24 (16)

Symmetry code: (i) −*x*, −*y*+2, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.951 (15)	1.631 (15)	2.5224 (11)	154.4 (14)
O1—H1···O1^{ii}	0.951 (15)	2.526 (15)	2.6760 (15)	88.5 (9)

Symmetry code: (ii) −*x*, −*y*+1, −*z*+2.

(compound2) 3,4-Dihydroxy-1,6-bis(4-methylphenyl)hexa-2,4-diene-1,6-dione

Crystal data

$C_{20}H_{18}O_4$	$F(000) = 340$
$M_r = 322.34$	$D_x = 1.365$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5544 reflections
$a = 14.7710$ (6) Å	$\theta = 2.8$–30.7°
$b = 6.1622$ (2) Å	$\mu = 0.10$ mm^{-1}
$c = 8.6184$ (3) Å	$T = 116$ K
$\beta = 91.896$ (2)°	Plate, yellow
$V = 784.03$ (5) Å^3	0.62 × 0.46 × 0.06 mm
$Z = 2$	

Data collection

Bruker APEXII CCD area-detector diffractometer	19282 measured reflections
Radiation source: fine-focus sealed tube	2288 independent reflections
Graphite monochromator	2150 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.045$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 30.0°$, $\theta_{min} = 2.8°$
$T_{min} = 0.944$, $T_{max} = 0.994$	$h = -20 \rightarrow 20$
	$k = -8 \rightarrow 8$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.067$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.151$	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.5796P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.25$	$(\Delta/\sigma)_{max} < 0.001$
2288 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
116 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.00746 (9)	0.28418 (18)	0.52331 (14)	0.0208 (3)
H1	0.0479 (15)	0.356 (4)	0.589 (3)	0.025*
O2	0.12923 (8)	0.36429 (19)	0.72956 (13)	0.0203 (3)
C1	0.02699 (11)	0.0771 (2)	0.54860 (17)	0.0159 (3)
C2	0.09117 (11)	0.0077 (2)	0.65506 (18)	0.0175 (3)
H2	0.0990 (14)	−0.144 (3)	0.670 (2)	0.021*
C3	0.14247 (11)	0.1644 (3)	0.74647 (17)	0.0169 (3)
C4	0.21345 (11)	0.0898 (3)	0.86024 (17)	0.0174 (3)
C5	0.27745 (12)	0.2403 (3)	0.91639 (19)	0.0213 (3)
H5	0.2746	0.3861	0.8807	0.026*
C6	0.34485 (12)	0.1800 (3)	1.0230 (2)	0.0240 (4)
H6	0.3880	0.2843	1.0589	0.029*
C7	0.34998 (11)	−0.0329 (3)	1.07841 (19)	0.0217 (3)
C8	0.28543 (12)	−0.1814 (3)	1.02491 (19)	0.0216 (3)
H8	0.2871	−0.3257	1.0638	0.026*
C9	0.21839 (12)	−0.1234 (3)	0.91558 (19)	0.0199 (3)
H9	0.1759	−0.2286	0.8785	0.024*
C10	0.42402 (13)	−0.1005 (3)	1.1934 (2)	0.0306 (4)
H10A	0.4808	−0.1191	1.1394	0.037*
H10B	0.4074	−0.2379	1.2422	0.037*
H10C	0.4319	0.0117	1.2734	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0289 (6)	0.0104 (5)	0.0227 (6)	0.0004 (4)	−0.0055 (5)	−0.0011 (4)
O2	0.0276 (6)	0.0138 (5)	0.0196 (5)	−0.0009 (4)	−0.0003 (5)	−0.0004 (4)
C1	0.0207 (7)	0.0126 (6)	0.0146 (6)	0.0004 (5)	0.0020 (5)	−0.0007 (5)
C2	0.0235 (8)	0.0138 (7)	0.0152 (7)	−0.0006 (6)	−0.0007 (6)	−0.0001 (5)
C3	0.0204 (7)	0.0168 (7)	0.0137 (6)	−0.0005 (6)	0.0028 (5)	0.0003 (5)
C4	0.0212 (7)	0.0177 (7)	0.0133 (6)	−0.0005 (6)	0.0019 (5)	−0.0016 (5)
C5	0.0263 (8)	0.0172 (7)	0.0204 (7)	−0.0032 (6)	0.0002 (6)	−0.0008 (6)
C6	0.0239 (8)	0.0245 (8)	0.0235 (8)	−0.0051 (6)	−0.0022 (6)	−0.0029 (6)
C7	0.0207 (8)	0.0258 (8)	0.0186 (7)	0.0012 (6)	−0.0001 (6)	−0.0024 (6)
C8	0.0261 (8)	0.0178 (7)	0.0206 (7)	0.0008 (6)	−0.0012 (6)	−0.0001 (6)
C9	0.0246 (8)	0.0171 (7)	0.0180 (7)	−0.0023 (6)	−0.0010 (6)	−0.0003 (6)
C10	0.0250 (9)	0.0353 (10)	0.0310 (9)	0.0028 (7)	−0.0057 (7)	−0.0024 (8)

Geometric parameters (Å, º)

O1—C1	1.3248 (18)	C5—H5	0.9500
O1—H1	0.92 (2)	C6—C7	1.397 (2)
O2—C3	1.2552 (19)	C6—H6	0.9500
C1—C2	1.366 (2)	C7—C8	1.390 (2)
C1—C1$^{\rm i}$	1.482 (3)	C7—C10	1.510 (2)
C2—C3	1.445 (2)	C8—C9	1.391 (2)
C2—H2	0.95 (2)	C8—H8	0.9500
C3—C4	1.485 (2)	C9—H9	0.9500
C4—C9	1.399 (2)	C10—H10A	0.9800
C4—C5	1.399 (2)	C10—H10B	0.9800
C5—C6	1.383 (2)	C10—H10C	0.9800

C1—O1—H1	103.3 (14)	C5—C6—H6	119.7
O1—C1—C2	123.67 (14)	C7—C6—H6	119.7
O1—C1—C1$^{\rm i}$	114.48 (17)	C8—C7—C6	118.44 (16)
C2—C1—C1$^{\rm i}$	121.85 (17)	C8—C7—C10	120.67 (16)
C1—C2—C3	119.81 (14)	C6—C7—C10	120.88 (16)
C1—C2—H2	118.6 (13)	C7—C8—C9	121.39 (16)
C3—C2—H2	121.5 (13)	C7—C8—H8	119.3
O2—C3—C2	121.04 (15)	C9—C8—H8	119.3
O2—C3—C4	118.97 (14)	C8—C9—C4	120.02 (15)
C2—C3—C4	119.98 (14)	C8—C9—H9	120.0
C9—C4—C5	118.53 (15)	C4—C9—H9	120.0
C9—C4—C3	122.93 (14)	C7—C10—H10A	109.5
C5—C4—C3	118.53 (14)	C7—C10—H10B	109.5
C6—C5—C4	121.01 (16)	H10A—C10—H10B	109.5
C6—C5—H5	119.5	C7—C10—H10C	109.5
C4—C5—H5	119.5	H10A—C10—H10C	109.5
C5—C6—C7	120.59 (16)	H10B—C10—H10C	109.5

O1—C1—C2—C3	−0.5 (2)	C3—C4—C5—C6	179.73 (15)
C1$^{\rm i}$—C1—C2—C3	179.62 (17)	C4—C5—C6—C7	−0.7 (3)
C1—C2—C3—O2	−0.2 (2)	C5—C6—C7—C8	−0.5 (3)
C1—C2—C3—C4	−178.88 (14)	C5—C6—C7—C10	179.30 (17)
O2—C3—C4—C9	163.58 (15)	C6—C7—C8—C9	1.7 (3)
C2—C3—C4—C9	−17.7 (2)	C10—C7—C8—C9	−178.10 (16)
O2—C3—C4—C5	−15.4 (2)	C7—C8—C9—C4	−1.7 (3)
C2—C3—C4—C5	163.33 (15)	C5—C4—C9—C8	0.5 (2)
C9—C4—C5—C6	0.7 (2)	C3—C4—C9—C8	−178.51 (15)

Symmetry code: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.92 (2)	1.68 (2)	2.5351 (17)	153 (2)
O1—H1···O1$^{\rm ii}$	0.92 (2)	2.54 (2)	2.698 (2)	89.7 (14)

Symmetry code: (ii) −*x*, −*y*+1, −*z*+1.

(compound3) *catena*-poly[[μ_2-2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoato-κ^2O^1,O^2][μ_2-2-hydroxy-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid-κO^1]potassium]

Crystal data

$[K(C_{11}H_9O_5)(C_{11}H_{10}O_5)]$
$M_r = 482.47$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 15.3832$ (4) Å
$b = 6.3481$ (1) Å
$c = 21.1606$ (5) Å
$\beta = 90.582$ (1)°
$V = 2066.31$ (8) Å^3
$Z = 4$

$F(000) = 1000$
$D_x = 1.551$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9844 reflections
$\theta = 2.7$–33.6°
$\mu = 0.32$ mm^{-1}
$T = 116$ K
Block, orange
0.57 × 0.55 × 0.39 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.840$, $T_{max} = 0.886$

52473 measured reflections
6026 independent reflections
5402 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.7°$
$h = -21 \rightarrow 21$
$k = -8 \rightarrow 8$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.090$
$S = 1.06$
6026 reflections
316 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.7703P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0018 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
K1	0.094861 (16)	0.35025 (4)	0.081718 (11)	0.02174 (7)
O1	0.10832 (5)	−0.25622 (12)	0.12862 (4)	0.02025 (16)

H1	0.0616 (10)	−0.146 (2)	0.1106 (7)	0.024*
O2	0.19157 (5)	0.02958 (12)	0.14601 (4)	0.01979 (16)
O3	0.23039 (5)	−0.51295 (12)	0.16089 (4)	0.02209 (17)
H2	0.2761 (10)	−0.580 (3)	0.1754 (7)	0.027*
O4	0.37824 (5)	−0.58187 (12)	0.21043 (4)	0.02280 (17)
O8	0.71085 (5)	−0.13407 (13)	0.32273 (5)	0.02622 (18)
C1	0.17878 (7)	−0.15990 (15)	0.14749 (5)	0.01563 (18)
C2	0.24789 (7)	−0.31033 (16)	0.17157 (5)	0.01602 (18)
C3	0.32152 (7)	−0.23950 (16)	0.20031 (5)	0.01704 (19)
H3	0.3295 (9)	−0.094 (2)	0.2060 (7)	0.020*
C4	0.38838 (7)	−0.38792 (16)	0.21960 (5)	0.01727 (19)
C5	0.47061 (7)	−0.31106 (16)	0.24838 (5)	0.01718 (19)
C6	0.54056 (7)	−0.45201 (17)	0.25357 (6)	0.0221 (2)
H6	0.5335	−0.5935	0.2399	0.027*
C7	0.61938 (7)	−0.38761 (18)	0.27830 (6)	0.0244 (2)
H7	0.6666	−0.4839	0.2806	0.029*
C8	0.63018 (7)	−0.18150 (17)	0.29998 (5)	0.0195 (2)
C9	0.56060 (7)	−0.04037 (17)	0.29702 (5)	0.0196 (2)
H9	0.5669	0.0987	0.3130	0.024*
C10	0.48194 (7)	−0.10559 (17)	0.27046 (5)	0.0186 (2)
H10	0.4351	−0.0085	0.2673	0.022*
C11	0.72737 (8)	0.07866 (19)	0.34241 (6)	0.0270 (2)
H11A	0.7198	0.1736	0.3063	0.032*
H11B	0.7870	0.0899	0.3587	0.032*
H11C	0.6865	0.1177	0.3757	0.032*
O21	0.00426 (5)	−0.00255 (12)	0.08664 (4)	0.02243 (17)
O22	−0.08478 (5)	−0.24898 (12)	0.04660 (4)	0.02125 (16)
O23	−0.09110 (5)	0.30340 (12)	0.04625 (4)	0.01976 (16)
H22	−0.1306 (10)	0.386 (2)	0.0348 (7)	0.024*
O24	−0.23541 (5)	0.43226 (12)	−0.00102 (4)	0.02236 (17)
O28	−0.59212 (5)	0.11734 (14)	−0.11483 (5)	0.02695 (19)
C21	−0.06453 (6)	−0.06570 (15)	0.05847 (5)	0.01456 (18)
C22	−0.12488 (7)	0.11186 (15)	0.03830 (5)	0.01493 (18)
C23	−0.20529 (7)	0.07281 (16)	0.01429 (5)	0.01698 (19)
H23	−0.2255 (9)	−0.066 (2)	0.0116 (7)	0.020*
C24	−0.26057 (7)	0.24507 (16)	−0.00662 (5)	0.01689 (19)
C25	−0.34704 (6)	0.20051 (16)	−0.03497 (5)	0.01650 (19)
C26	−0.40475 (7)	0.36872 (16)	−0.04486 (5)	0.0202 (2)
H26	−0.3879	0.5072	−0.0330	0.024*
C27	−0.48552 (7)	0.33529 (18)	−0.07160 (6)	0.0228 (2)
H27	−0.5242	0.4503	−0.0776	0.027*
C28	−0.51075 (7)	0.13258 (17)	−0.09002 (5)	0.0196 (2)
C29	−0.45353 (7)	−0.03595 (17)	−0.08203 (6)	0.0212 (2)
H29	−0.4697	−0.1734	−0.0954	0.025*
C30	−0.37267 (7)	−0.00053 (17)	−0.05422 (5)	0.0201 (2)
H30	−0.3340	−0.1156	−0.0482	0.024*
C31	−0.62155 (8)	−0.0852 (2)	−0.13503 (6)	0.0278 (2)
H31A	−0.5838	−0.1373	−0.1686	0.033*
H31B	−0.6813	−0.0741	−0.1511	0.033*

H31C	−0.6197	−0.1831	−0.0992	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.02692 (13)	0.01534 (11)	0.02285 (12)	−0.00585 (8)	−0.00509 (9)	−0.00186 (8)
O1	0.0181 (4)	0.0139 (3)	0.0286 (4)	−0.0009 (3)	−0.0086 (3)	0.0010 (3)
O2	0.0204 (4)	0.0137 (3)	0.0252 (4)	−0.0008 (3)	−0.0055 (3)	0.0001 (3)
O3	0.0232 (4)	0.0131 (3)	0.0298 (4)	0.0011 (3)	−0.0099 (3)	0.0011 (3)
O4	0.0246 (4)	0.0166 (3)	0.0271 (4)	0.0022 (3)	−0.0061 (3)	−0.0004 (3)
O8	0.0151 (4)	0.0239 (4)	0.0396 (5)	0.0013 (3)	−0.0071 (3)	0.0008 (3)
C1	0.0165 (4)	0.0151 (4)	0.0153 (4)	0.0005 (3)	−0.0020 (3)	−0.0002 (3)
C2	0.0185 (5)	0.0139 (4)	0.0157 (4)	0.0004 (3)	−0.0020 (4)	0.0010 (3)
C3	0.0180 (5)	0.0155 (4)	0.0175 (5)	0.0013 (3)	−0.0029 (4)	−0.0002 (3)
C4	0.0182 (5)	0.0186 (4)	0.0150 (4)	0.0012 (4)	−0.0014 (4)	0.0002 (3)
C5	0.0163 (4)	0.0184 (4)	0.0169 (5)	0.0026 (4)	−0.0015 (4)	0.0008 (3)
C6	0.0208 (5)	0.0172 (5)	0.0284 (6)	0.0042 (4)	−0.0036 (4)	0.0002 (4)
C7	0.0183 (5)	0.0208 (5)	0.0339 (6)	0.0063 (4)	−0.0035 (4)	0.0017 (4)
C8	0.0144 (4)	0.0220 (5)	0.0220 (5)	0.0020 (4)	−0.0019 (4)	0.0037 (4)
C9	0.0172 (5)	0.0187 (5)	0.0229 (5)	0.0025 (4)	−0.0031 (4)	−0.0012 (4)
C10	0.0164 (5)	0.0193 (5)	0.0202 (5)	0.0048 (4)	−0.0022 (4)	−0.0012 (4)
C11	0.0197 (5)	0.0265 (6)	0.0348 (6)	−0.0025 (4)	−0.0026 (5)	−0.0007 (5)
O21	0.0185 (4)	0.0140 (3)	0.0346 (4)	−0.0009 (3)	−0.0112 (3)	0.0001 (3)
O22	0.0229 (4)	0.0131 (3)	0.0277 (4)	−0.0023 (3)	−0.0056 (3)	−0.0009 (3)
O23	0.0196 (4)	0.0115 (3)	0.0280 (4)	−0.0002 (3)	−0.0056 (3)	−0.0003 (3)
O24	0.0213 (4)	0.0159 (3)	0.0297 (4)	−0.0002 (3)	−0.0068 (3)	−0.0005 (3)
O28	0.0174 (4)	0.0265 (4)	0.0368 (5)	−0.0006 (3)	−0.0097 (3)	−0.0003 (3)
C21	0.0144 (4)	0.0134 (4)	0.0159 (4)	−0.0001 (3)	−0.0008 (3)	0.0008 (3)
C22	0.0163 (4)	0.0131 (4)	0.0153 (4)	0.0000 (3)	−0.0002 (3)	0.0000 (3)
C23	0.0160 (4)	0.0144 (4)	0.0204 (5)	−0.0003 (3)	−0.0024 (4)	0.0012 (3)
C24	0.0162 (4)	0.0176 (4)	0.0168 (4)	0.0006 (3)	−0.0015 (3)	0.0004 (3)
C25	0.0149 (4)	0.0177 (4)	0.0169 (5)	0.0008 (3)	−0.0016 (3)	0.0007 (3)
C26	0.0194 (5)	0.0162 (4)	0.0249 (5)	0.0017 (4)	−0.0033 (4)	−0.0016 (4)
C27	0.0185 (5)	0.0197 (5)	0.0300 (6)	0.0043 (4)	−0.0051 (4)	−0.0008 (4)
C28	0.0156 (5)	0.0227 (5)	0.0206 (5)	−0.0005 (4)	−0.0023 (4)	0.0014 (4)
C29	0.0189 (5)	0.0178 (5)	0.0268 (5)	−0.0014 (4)	−0.0037 (4)	−0.0001 (4)
C30	0.0173 (5)	0.0173 (5)	0.0256 (5)	0.0011 (4)	−0.0032 (4)	0.0012 (4)
C31	0.0230 (5)	0.0320 (6)	0.0284 (6)	−0.0072 (5)	−0.0056 (4)	−0.0017 (5)

Geometric parameters (Å, º)

K1—O21	2.6404 (8)	C10—K1^{vi}	3.3665 (11)
K1—O1^{i}	2.6953 (8)	C10—H10	0.9500
K1—O22^{ii}	2.7931 (9)	C11—H11A	0.9800
K1—O3^{i}	2.7994 (8)	C11—H11B	0.9800
K1—O2	2.8578 (8)	C11—H11C	0.9800
K1—O23	2.9651 (8)	O21—C21	1.2740 (12)
K1—O24^{iii}	3.0939 (9)	O21—H1	1.361 (15)
K1—C10^{iv}	3.3665 (11)	O22—C21	1.2297 (12)
K1—C21^{ii}	3.5003 (10)	O22—K1^{ii}	2.7931 (9)

K1—K1^{iii}	4.8876 (5)	O23—C22	1.3323 (12)
O1—C1	1.3037 (12)	O23—H22	0.836 (16)
O1—K1^{v}	2.6953 (8)	O24—C24	1.2549 (13)
O1—H1	1.071 (15)	O24—K1^{iii}	3.0939 (9)
O2—C1	1.2193 (12)	O28—C28	1.3559 (13)
O3—C2	1.3329 (12)	O28—C31	1.4270 (15)
O3—K1^{v}	2.7994 (8)	C21—C22	1.5188 (14)
O3—H2	0.875 (16)	C21—K1^{ii}	3.5003 (10)
O4—C4	1.2559 (13)	C22—C23	1.3554 (14)
O8—C8	1.3603 (13)	C23—C24	1.4516 (14)
O8—C11	1.4351 (15)	C23—H23	0.938 (15)
C1—C2	1.5135 (14)	C24—C25	1.4810 (14)
C2—C3	1.3569 (14)	C25—C30	1.3952 (14)
C3—C4	1.4503 (14)	C25—C26	1.4029 (14)
C3—H3	0.939 (15)	C26—C27	1.3765 (15)
C4—C5	1.4810 (14)	C26—H26	0.9500
C5—C10	1.3959 (14)	C27—C28	1.3984 (15)
C5—C6	1.4030 (14)	C27—H27	0.9500
C6—C7	1.3778 (16)	C28—C29	1.3946 (15)
C6—H6	0.9500	C29—C30	1.3890 (14)
C7—C8	1.3959 (16)	C29—H29	0.9500
C7—H7	0.9500	C30—H30	0.9500
C8—C9	1.3967 (14)	C31—H31A	0.9800
C9—C10	1.3919 (14)	C31—H31B	0.9800
C9—H9	0.9500	C31—H31C	0.9800

O21—K1—O1^{i}	144.12 (3)	C5—C6—H6	119.6
O21—K1—O22^{ii}	79.57 (3)	C6—C7—C8	120.28 (10)
O1^{i}—K1—O22^{ii}	125.07 (2)	C6—C7—H7	119.9
O21—K1—O3^{i}	129.03 (3)	C8—C7—H7	119.9
O1^{i}—K1—O3^{i}	55.82 (2)	O8—C8—C7	115.39 (9)
O22^{ii}—K1—O3^{i}	133.38 (3)	O8—C8—C9	124.74 (10)
O21—K1—O2	69.48 (2)	C7—C8—C9	119.86 (10)
O1^{i}—K1—O2	116.57 (2)	C10—C9—C8	119.34 (10)
O22^{ii}—K1—O2	108.81 (2)	C10—C9—H9	120.3
O3^{i}—K1—O2	63.58 (2)	C8—C9—H9	120.3
O21—K1—O23	54.31 (2)	C9—C10—C5	121.21 (9)
O1^{i}—K1—O23	104.86 (2)	C9—C10—K1^{vi}	87.79 (7)
O22^{ii}—K1—O23	71.76 (2)	C5—C10—K1^{vi}	100.92 (7)
O3^{i}—K1—O23	153.30 (3)	C9—C10—H10	119.4
O2—K1—O23	123.05 (2)	C5—C10—H10	119.4
O21—K1—O24^{iii}	140.57 (3)	K1^{vi}—C10—H10	81.2
O1^{i}—K1—O24^{iii}	74.82 (2)	O8—C11—H11A	109.5
O22^{ii}—K1—O24^{iii}	66.32 (2)	O8—C11—H11B	109.5
O3^{i}—K1—O24^{iii}	70.82 (2)	H11A—C11—H11B	109.5
O2—K1—O24^{iii}	102.55 (2)	O8—C11—H11C	109.5
O23—K1—O24^{iii}	125.66 (2)	H11A—C11—H11C	109.5
O21—K1—C10^{iv}	81.00 (3)	H11B—C11—H11C	109.5
O1^{i}—K1—C10^{iv}	66.86 (3)	C21—O21—K1	133.21 (7)

O22^{ii}—K1—C10^{iv}	154.94 (3)	C21—O21—H1	119.7 (6)
O3^{i}—K1—C10^{iv}	71.60 (3)	K1—O21—H1	104.0 (6)
O2—K1—C10^{iv}	78.63 (3)	C21—O22—K1^{ii}	115.33 (7)
O23—K1—C10^{iv}	84.07 (2)	C22—O23—K1	119.84 (6)
O24^{iii}—K1—C10^{iv}	136.84 (2)	C22—O23—H22	104.7 (10)
O21—K1—C21^{ii}	61.96 (3)	K1—O23—H22	135.0 (10)
O1^{i}—K1—C21^{ii}	143.08 (2)	C24—O24—K1^{iii}	125.95 (7)
O22^{ii}—K1—C21^{ii}	18.52 (2)	C28—O28—C31	117.98 (9)
O3^{i}—K1—C21^{ii}	139.40 (3)	O22—C21—O21	126.93 (9)
O2—K1—C21^{ii}	95.75 (2)	O22—C21—C22	119.46 (9)
O23—K1—C21^{ii}	67.28 (2)	O21—C21—C22	113.60 (8)
O24^{iii}—K1—C21^{ii}	81.40 (2)	O22—C21—K1^{ii}	46.16 (5)
C10^{iv}—K1—C21^{ii}	141.75 (2)	O21—C21—K1^{ii}	131.45 (7)
O21—K1—K1^{iii}	92.650 (18)	C22—C21—K1^{ii}	93.95 (6)
O1^{i}—K1—K1^{iii}	86.737 (17)	O23—C22—C23	124.58 (9)
O22^{ii}—K1—K1^{iii}	51.303 (17)	O23—C22—C21	113.91 (9)
O3^{i}—K1—K1^{iii}	137.606 (18)	C23—C22—C21	121.50 (9)
O2—K1—K1^{iii}	156.663 (18)	C22—C23—C24	120.40 (9)
O23—K1—K1^{iii}	44.949 (16)	C22—C23—H23	119.7 (9)
O24^{iii}—K1—K1^{iii}	81.459 (16)	C24—C23—H23	119.9 (9)
C10^{iv}—K1—K1^{iii}	114.35 (2)	O24—C24—C23	120.36 (9)
C21^{ii}—K1—K1^{iii}	61.807 (17)	O24—C24—C25	119.60 (9)
C1—O1—K1^{v}	127.44 (6)	C23—C24—C25	120.04 (9)
C1—O1—H1	110.8 (8)	C30—C25—C26	118.44 (9)
K1^{v}—O1—H1	115.2 (8)	C30—C25—C24	122.89 (9)
C1—O2—K1	129.17 (7)	C26—C25—C24	118.64 (9)
C2—O3—K1^{v}	123.28 (6)	C27—C26—C25	120.74 (10)
C2—O3—H2	104.5 (10)	C27—C26—H26	119.6
K1^{v}—O3—H2	130.5 (10)	C25—C26—H26	119.6
C8—O8—C11	117.98 (9)	C26—C27—C28	120.22 (10)
O2—C1—O1	126.06 (10)	C26—C27—H27	119.9
O2—C1—C2	121.21 (9)	C28—C27—H27	119.9
O1—C1—C2	112.72 (8)	O28—C28—C29	124.84 (10)
O3—C2—C3	124.19 (9)	O28—C28—C27	115.22 (10)
O3—C2—C1	114.32 (9)	C29—C28—C27	119.94 (10)
C3—C2—C1	121.47 (9)	C30—C29—C28	119.25 (10)
C2—C3—C4	119.81 (9)	C30—C29—H29	120.4
C2—C3—H3	119.4 (9)	C28—C29—H29	120.4
C4—C3—H3	120.7 (9)	C29—C30—C25	121.39 (10)
O4—C4—C3	120.45 (10)	C29—C30—H30	119.3
O4—C4—C5	119.39 (9)	C25—C30—H30	119.3
C3—C4—C5	120.13 (9)	O28—C31—H31A	109.5
C10—C5—C6	118.46 (10)	O28—C31—H31B	109.5
C10—C5—C4	123.28 (9)	H31A—C31—H31B	109.5
C6—C5—C4	118.25 (10)	O28—C31—H31C	109.5
C7—C6—C5	120.79 (10)	H31A—C31—H31C	109.5
C7—C6—H6	119.6	H31B—C31—H31C	109.5

O21—K1—O2—C1	14.89 (9)	C10^{iv}—K1—O21—C21	112.06 (10)

O1^{i}—K1—O2—C1	156.16 (9)
O22^{ii}—K1—O2—C1	−55.74 (10)
O3^{i}—K1—O2—C1	174.39 (10)
O23—K1—O2—C1	24.30 (10)
O24^{iii}—K1—O2—C1	−124.71 (9)
C10^{iv}—K1—O2—C1	99.44 (9)
C21^{ii}—K1—O2—C1	−42.27 (9)
K1^{iii}—K1—O2—C1	−27.13 (12)
K1—O2—C1—O1	−12.97 (16)
K1—O2—C1—C2	165.83 (7)
K1^{v}—O1—C1—O2	150.54 (9)
K1^{v}—O1—C1—C2	−28.34 (12)
K1^{v}—O3—C2—C3	−167.82 (8)
K1^{v}—O3—C2—C1	10.92 (12)
O2—C1—C2—O3	−169.60 (10)
O1—C1—C2—O3	9.35 (13)
O2—C1—C2—C3	9.18 (16)
O1—C1—C2—C3	−171.88 (10)
O3—C2—C3—C4	2.06 (16)
C1—C2—C3—C4	−176.58 (9)
C2—C3—C4—O4	−0.69 (16)
C2—C3—C4—C5	177.25 (10)
O4—C4—C5—C10	−168.35 (10)
C3—C4—C5—C10	13.69 (16)
O4—C4—C5—C6	11.75 (15)
C3—C4—C5—C6	−166.21 (10)
C10—C5—C6—C7	−1.75 (17)
C4—C5—C6—C7	178.16 (11)
C5—C6—C7—C8	1.48 (19)
C11—O8—C8—C7	176.55 (11)
C11—O8—C8—C9	−3.15 (17)
C6—C7—C8—O8	−179.24 (11)
C6—C7—C8—C9	0.48 (18)
O8—C8—C9—C10	177.59 (10)
C7—C8—C9—C10	−2.10 (17)
C8—C9—C10—C5	1.82 (17)
C8—C9—C10—K1^{vi}	103.26 (10)
C6—C5—C10—C9	0.09 (16)
C4—C5—C10—C9	−179.81 (10)
C6—C5—C10—K1^{vi}	−93.99 (10)
C4—C5—C10—K1^{vi}	86.11 (10)
O1^{i}—K1—O21—C21	85.91 (11)
O22^{ii}—K1—O21—C21	−52.02 (10)
O3^{i}—K1—O21—C21	169.40 (9)
O2—K1—O21—C21	−166.79 (10)
O23—K1—O21—C21	22.92 (9)
O24^{iii}—K1—O21—C21	−81.94 (10)
C21^{ii}—K1—O21—C21	−58.09 (10)
K1^{iii}—K1—O21—C21	−2.18 (10)
O21—K1—O23—C22	−13.80 (7)
O1^{i}—K1—O23—C22	−161.10 (7)
O22^{ii}—K1—O23—C22	76.32 (7)
O3^{i}—K1—O23—C22	−121.11 (8)
O2—K1—O23—C22	−24.66 (8)
O24^{iii}—K1—O23—C22	117.13 (7)
C10^{iv}—K1—O23—C22	−96.97 (7)
C21^{ii}—K1—O23—C22	57.12 (7)
K1^{iii}—K1—O23—C22	129.34 (8)
K1^{ii}—O22—C21—O21	−115.23 (10)
K1^{ii}—O22—C21—C22	64.36 (11)
K1—O21—C21—O22	152.29 (8)
K1—O21—C21—C22	−27.32 (14)
K1—O21—C21—K1^{ii}	91.77 (10)
K1—O23—C22—C23	−170.99 (8)
K1—O23—C22—C21	8.72 (11)
O22—C21—C22—O23	−171.70 (9)
O21—C21—C22—O23	7.94 (13)
K1^{ii}—C21—C22—O23	−131.02 (8)
O22—C21—C22—C23	8.02 (15)
O21—C21—C22—C23	−172.34 (10)
K1^{ii}—C21—C22—C23	48.70 (10)
O23—C22—C23—C24	1.78 (16)
C21—C22—C23—C24	−177.91 (9)
K1^{iii}—O24—C24—C23	73.12 (12)
K1^{iii}—O24—C24—C25	−106.63 (10)
C22—C23—C24—O24	−2.02 (16)
C22—C23—C24—C25	177.73 (10)
O24—C24—C25—C30	166.98 (10)
C23—C24—C25—C30	−12.77 (16)
O24—C24—C25—C26	−10.87 (15)
C23—C24—C25—C26	169.37 (10)
C30—C25—C26—C27	1.46 (17)
C24—C25—C26—C27	179.41 (10)
C25—C26—C27—C28	−0.77 (18)
C31—O28—C28—C29	−0.75 (17)
C31—O28—C28—C27	179.51 (10)
C26—C27—C28—O28	178.95 (11)
C26—C27—C28—C29	−0.81 (18)
O28—C28—C29—C30	−178.08 (11)
C27—C28—C29—C30	1.65 (17)
C28—C29—C30—C25	−0.94 (17)
C26—C25—C30—C29	−0.60 (17)
C24—C25—C30—C29	−178.45 (10)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*, −*y*, −*z*; (iii) −*x*, −*y*+1, −*z*; (iv) −*x*+1/2, *y*+1/2, −*z*+1/2; (v) *x*, *y*−1, *z*; (vi) −*x*+1/2, *y*−1/2, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O21	1.071 (15)	1.361 (15)	2.4322 (10)	178.2 (15)
O3—H2···O4	0.875 (16)	1.731 (16)	2.5326 (11)	151.1 (15)
O23—H22···O24	0.836 (16)	1.800 (16)	2.5599 (11)	150.4 (15)