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ISSN 2414-3146

Bis{μ-ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate-κO}bis[aqua(4-{[4-(ethoxycarbonyl)phenyl]diazenyl}phenolato-κO){ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate-κO}potassium]

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Received 31 October 2017
Accepted 24 November 2017

Edited by M. Weil, Vienna University of Technology, Austria

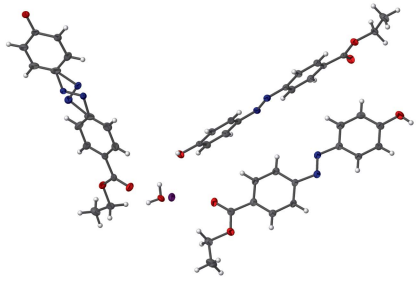
Keywords: crystal structure; supramolecular features; dinuclear structure; Hirshfeld surface.

CCDC reference: 1587513

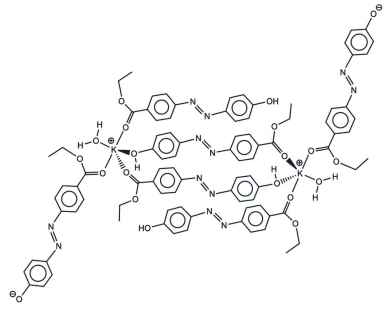
Structural data: full structural data are available from iucrdata.iucr.org

The two potassium cations in the dinuclear molecule of $[K_2\{OC(C_{14}H_{13}O\text{-}N_2)O\}_2\{OC(C_{14}H_{13}ON_2)OH\}_4(H_2O)_2]$ are connected through a double bridge involving two centrosymmetrically related ethyl-4-(phenylazophenol)benzoate ligands. Each cation is also bound to a further non-bridging ligand, one ethyl-4-(phenylazophenolate)benzoate anion and a water molecule, leading to a distorted fivefold coordination. The two uncharged ligands are almost planar, whereas in the anionic ligand the aromatic systems display a dihedral angle of 21.14 (11)°. A supramolecular network formed by hydrogen-bonding interactions between phenolate anions, phenol groups and water molecules connects the dimeric species along [001]. Hirshfeld surface calculations revealed the following contributions related to intermolecular interactions: C···H (24.4%), O···H (13.2%) and N···H (7.4%). The azo fragment is disordered over two sets of sites [occupancy ratio 0.824 (15):0.176 (5)].

3D view



Chemical scheme



Structure description

Azo dyes are a well known family of organic dyes including the azo group (—N=N—) bonded to aromatic ring systems (Zhang *et al.*, 2013). There are several compounds reported containing even more than one azo chromophore per molecule, also linked to heterocyclic systems (Patni & Patni, 2016). The compounds are commonly prepared through a coupling reaction between an arenediazonium salt and typically aromatic

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

D—H···A	D—H	H···A	D···A	D—H···A
C63—H63···O6^{i}	0.95	2.49	3.427 (3)	169
C8—H8B···O9^{ii}	0.99	2.64	3.476 (3)	142
C4—H4C···O9^{iii}	0.98	2.57	3.301 (3)	131
O1W—H1W···N4^{iv}	0.81 (3)	2.15 (3)	2.895 (3)	153 (3)
O1W—H1W···N31^{iv}	0.81 (3)	2.11 (4)	2.898 (13)	166 (3)
O9—H9···O1W^{ii}	0.98 (4)	1.74 (4)	2.709 (3)	171 (3)
O1W—H2W···O6^{v}	0.84 (3)	1.84 (3)	2.635 (2)	156 (3)
O3—H3···O6^{v}	0.88 (3)	1.63 (3)	2.490 (2)	163 (3)

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

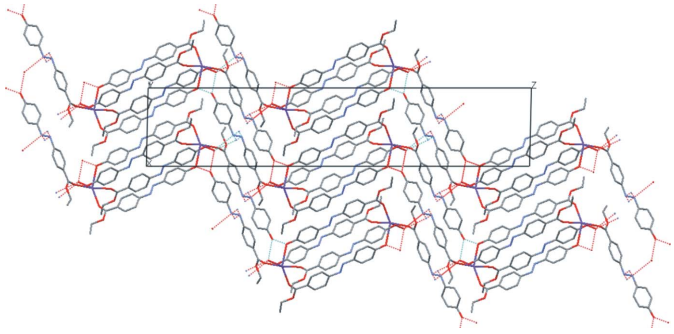


Figure 2
Crystal packing diagram of the title compound showing hydrogen-bonding interactions.

phenols or amines, although other substituents such as carboxylates or aldehydes can also be present (Purtas *et al.*, 2017). Besides the wide application of these compounds in both textile and paint industries, the molecular structures of the azo dyes can be modified and tuned to act as ligands in coordination chemistry. For instance, the choice of an appropriate metal ion can lead to new materials with remarkable properties, such as optical active media for lens production, recording of optical holograms or data storage (Davidenko *et al.*, 2008).

The asymmetric unit of the title compound contains one potassium cation, one ethyl-4-(phenylazophenolate)benzoate anion $OC(C_{14}H_{13}ON_2)O^{-}$, two neutral ethyl-4-(phenylazophenol)benzoate ligands $OC(C_{14}H_{13}ON_2)OH$, and one water molecule (Fig. 1). The anion coordinates through the carbonyl oxygen atom, presenting a C44—$O6_{phenolic}$ distance of 1.309 (2) Å shorter than expected but compatible with a phenolate moiety due to resonance effects (Suter & Nonella, 1998). One of the neutral ethyl-4-(phenylazophenol)benzoate ligands is terminal and coordinates exclusively *via* the ester carbonyl group (C9—O8 = 1.127 (2) Å), whereas the second is bridging and coordinates through both phenol [C24—O3 = 1.325 (2) Å] and ester carbonyl [C3—O2 = 1.215 (2) Å] groups. A double bridge between two cations is formed by a third ethyl-4-(phenylazophenol)benzoate ligand generated by an inversion operation $(2-x, 1-y, 1-z)$, leading to dimeric species (Fig. 2). The fivefold coordination environment of the cation was computed by the method of Addison *et al.* (1984). The resulting τ_5 index was found to be 0.56, indicating a coordination sphere between a trigonal bipyramid ($\tau_5 = 1$) and a square pyramid ($\tau_5 = 0$).

The two uncharged ethyl-4-(phenylazophenol)benzoate ligands are almost planar, with r.m.s. deviations of 0.0236 Å (monodentate ligand) and 0.0591 Å (bridging ligand) for all non-hydrogen atoms. The dihedral angles between the phenyl rings are 2.53 (9)° (C51 ring and C61 ring) and 2.49 (9)° (C11 ring and C21 ring). The azo fragment N3/N4 of the ethyl-4-(phenylazophenolate)benzoate anion is disordered over two sets of sites, and the whole anion is not planar (r.m.s. deviation of 0.1696). Notably, the dihedral angle between the phenyl rings (C31 and C41 rings) is 21.14 (11)°.

The dimers follow a zigzag arrangement along [001] (Fig. 2). The dinuclear entities are connected through classical hydrogen bonding interactions involving phenolate anions, phenol groups and coordinating water molecules. Likewise, weak C—H···O interactions are also present (Table 1). In order to analyse the hydrogen-bonding contribution quantitatively, a Hirshfeld surface calculation was performed. The contribution of C···H is 24.4% for non-classic interactions,

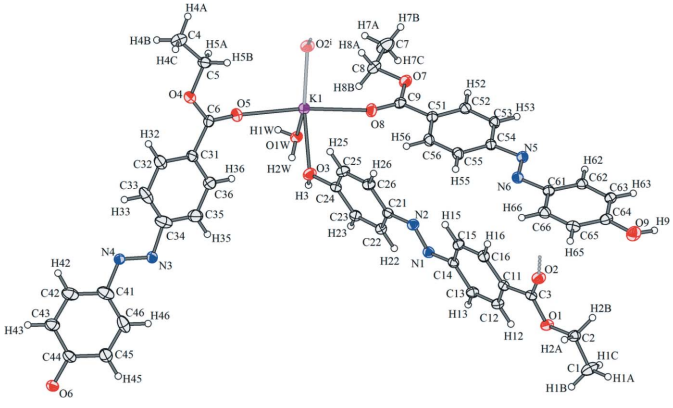


Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

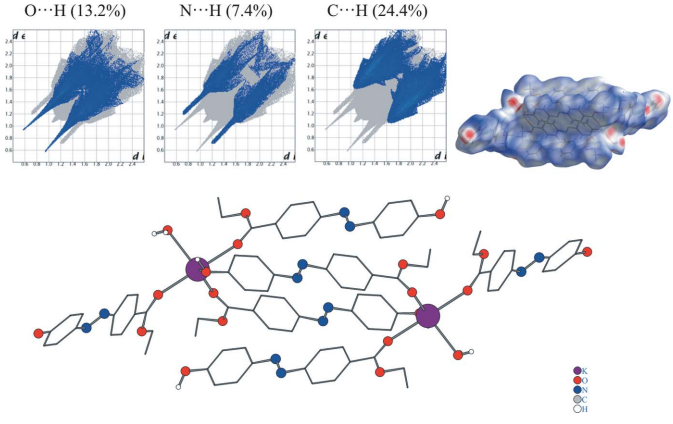


Figure 3
The dimeric structure of the title compound comprising double bridging ethyl 4-(phenylazophenol)benzoate units. The inset shows the calculated Hirshfeld surface and two-dimensional fingerprint plots.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[K_2(C_{15}H_{14}N_2O_3)_4(C_{15}H_{13}N_2O_3)_2(H_2O)_2]$
M_r	1733.91
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.241 (2), 10.241 (2), 45.261 (9)
β (°)	91.31 (3)
V (Å^3)	4282.2 (15)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.19
Crystal size (mm)	0.30 × 0.26 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.701, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	89218, 13099, 9788
R_{int}	0.050
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.158, 1.05
No. of reflections	13099
No. of parameters	594
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, −0.69

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2006), *Mercury* (Macrae *et al.*, 2006), *CrystalExplorer17* (Turner *et al.*, 2017) and *publCIF* (Westrip, 2010).

whereas classic bonding related to O···H and N···H correspond to 13.2% and 7.4%, respectively (Fig. 3).

Synthesis and crystallization

To 1.5 g (3.33 mmol) of ethyl-4-(phenylazophenol)benzoate dissolved in 10.0 ml of methanol were added 0.560 g (9.99 mmol) of KOH dissolved in 5.0 m of methanol. The reaction mixture was kept under constant stirring at room temperature for two h. The solvent was then partially evaporated under reduced pressure, affording orange block-like single crystals of the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The azo fragment comprising atoms N3 and N4 was found to be disordered over two sets of sites [occupancy ratio 0.824 (15):0.176 (5)]. The disorder was treated by using PART instruction in *SHELXL* (Sheldrick, 2015*b*).

Funding information

The authors acknowledge CT–Infra (FINEP) and FIPE JUNIOR CCNE/UFSM-2017 for support.

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full crystallographic data

IUCrData (2017). **2**, x171695 [https://doi.org/10.1107/S2414314617016959]

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Crystal data

$[K_2(C_{15}H_{14}N_2O_3)_4(C_{15}H_{13}N_2O_3)_2(H_2O)_2]$
M_r = 1733.91
Monoclinic, $P2_1/c$
a = 9.241 (2) Å
b = 10.241 (2) Å
c = 45.261 (9) Å
β = 91.31 (3)°
V = 4282.2 (15) Å^3
Z = 2
$F(000)$ = 1816
D_x = 1.345 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9137 reflections
θ = 2.3–30.6°
μ = 0.19 mm^{-1}
T = 100 K
Block, orange
0.30 × 0.26 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2014)
T_{min} = 0.701, T_{max} = 0.746
89218 measured reflections
13099 independent reflections
9788 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 30.6°, θ_{min} = 2.2°
h = −13→13
k = −14→14
l = −64→64

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.158
S = 1.05
13099 reflections
594 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 6.316P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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. Hydrogen atoms of the water molecule and the phenol OH groups were located from a difference Fourier map, while all other hydrogen atoms were calculated at idealized positions.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
K1	1.27684 (5)	0.37517 (5)	0.36022 (2)	0.02488 (11)	
O1W	1.20241 (17)	0.16449 (16)	0.32369 (3)	0.0244 (3)	
O1	0.31758 (15)	0.34718 (14)	0.60941 (3)	0.0209 (3)	
O4	1.27370 (15)	0.70828 (14)	0.29247 (3)	0.0228 (3)	
O8	1.28617 (16)	0.23893 (14)	0.40874 (3)	0.0230 (3)	
O3	0.99472 (16)	0.38866 (16)	0.37042 (3)	0.0249 (3)	
O7	1.43811 (16)	0.07337 (15)	0.41841 (3)	0.0242 (3)	
O2	0.48657 (16)	0.49718 (16)	0.62057 (3)	0.0255 (3)	
O6	0.07140 (15)	0.71962 (16)	0.16708 (3)	0.0249 (3)	
O9	0.74694 (18)	0.07815 (17)	0.65459 (4)	0.0310 (4)	
O5	1.23235 (17)	0.51173 (17)	0.31213 (4)	0.0328 (4)	
N2	0.75278 (17)	0.42064 (16)	0.48120 (4)	0.0190 (3)	
N6	0.99329 (18)	0.14434 (16)	0.54520 (4)	0.0198 (3)	
N1	0.64857 (17)	0.34744 (16)	0.48747 (4)	0.0186 (3)	
N5	1.09568 (18)	0.06925 (16)	0.53849 (4)	0.0197 (3)	
N4	0.6031 (5)	0.6895 (2)	0.22523 (8)	0.0190 (8)	0.824 (15)
N41	0.553 (3)	0.6257 (12)	0.2396 (3)	0.022 (4)	0.176 (15)
N3	0.6216 (5)	0.6131 (2)	0.24702 (8)	0.0206 (9)	0.824 (15)
N31	0.665 (3)	0.6882 (13)	0.2334 (4)	0.026 (4)	0.176 (15)
C11	0.4813 (2)	0.40352 (18)	0.57239 (4)	0.0169 (4)	
C24	0.9343 (2)	0.38920 (19)	0.39736 (4)	0.0186 (4)	
C14	0.5950 (2)	0.37235 (18)	0.51635 (4)	0.0170 (3)	
C21	0.8101 (2)	0.40234 (18)	0.45282 (4)	0.0172 (4)	
C51	1.2699 (2)	0.12855 (18)	0.45474 (4)	0.0183 (4)	
C23	0.8278 (2)	0.29877 (19)	0.40525 (4)	0.0198 (4)	
H23	0.798274	0.232722	0.391666	0.024*	
C3	0.4304 (2)	0.42201 (19)	0.60299 (4)	0.0177 (4)	
C9	1.3302 (2)	0.15315 (18)	0.42524 (4)	0.0194 (4)	
C61	0.9366 (2)	0.12062 (19)	0.57348 (4)	0.0188 (4)	
C54	1.1494 (2)	0.09357 (18)	0.50966 (4)	0.0183 (4)	
C6	1.1915 (2)	0.6053 (2)	0.29772 (4)	0.0215 (4)	
C22	0.7657 (2)	0.30535 (19)	0.43269 (4)	0.0197 (4)	
H22	0.693083	0.244393	0.437910	0.024*	
C15	0.6489 (2)	0.47054 (19)	0.53493 (4)	0.0193 (4)	

H15	0.723888	0.526643	0.528574	0.023*
C64	0.8110 (2)	0.0899 (2)	0.62814 (5)	0.0224 (4)
C12	0.4253 (2)	0.30763 (19)	0.55331 (4)	0.0197 (4)
H12	0.348799	0.252746	0.559466	0.024*
C44	0.1954 (2)	0.7087 (2)	0.18141 (4)	0.0224 (4)
C31	1.0441 (2)	0.6151 (2)	0.28387 (4)	0.0221 (4)
C52	1.3218 (2)	0.02940 (19)	0.47333 (4)	0.0200 (4)
H52	1.398285	−0.025634	0.467245	0.024*
C62	0.9815 (2)	0.01903 (19)	0.59217 (4)	0.0195 (4)
H62	1.054992	−0.039486	0.586150	0.023*
C13	0.4819 (2)	0.29296 (19)	0.52538 (4)	0.0200 (4)
H13	0.443280	0.228425	0.512349	0.024*
C26	0.9178 (2)	0.49068 (19)	0.44501 (5)	0.0211 (4)
H26	0.949080	0.555584	0.458731	0.025*
C16	0.5917 (2)	0.48523 (19)	0.56273 (4)	0.0198 (4)
H16	0.628111	0.551937	0.575453	0.024*
C55	1.0957 (2)	0.19174 (19)	0.49087 (4)	0.0207 (4)
H55	1.018788	0.246402	0.496915	0.025*
C56	1.1556 (2)	0.20817 (19)	0.46357 (4)	0.0205 (4)
H56	1.119061	0.273976	0.450619	0.025*
C63	0.9193 (2)	0.0038 (2)	0.61932 (4)	0.0209 (4)
H63	0.949862	−0.065184	0.632044	0.025*
C25	0.9794 (2)	0.4845 (2)	0.41753 (5)	0.0225 (4)
H25	1.052359	0.545151	0.412380	0.027*
C53	1.2606 (2)	0.01194 (19)	0.50075 (4)	0.0204 (4)
H53	1.294605	−0.055795	0.513458	0.025*
C65	0.7645 (2)	0.1902 (2)	0.60946 (5)	0.0241 (4)
H65	0.690645	0.248421	0.615448	0.029*
C66	0.8266 (2)	0.2047 (2)	0.58212 (5)	0.0225 (4)
H66	0.794070	0.272076	0.569165	0.027*
C2	0.2632 (2)	0.3610 (2)	0.63923 (4)	0.0225 (4)
H2A	0.229633	0.451580	0.642460	0.027*
H2B	0.341026	0.341377	0.653963	0.027*
C32	1.0009 (2)	0.7238 (2)	0.26758 (5)	0.0274 (4)
H32	1.065267	0.794999	0.265069	0.033*
C43	0.3165 (2)	0.7844 (2)	0.17357 (5)	0.0288 (5)
H43	0.308413	0.842533	0.157251	0.035*
C5	1.4195 (2)	0.7053 (2)	0.30541 (5)	0.0253 (4)
H5A	1.473364	0.628960	0.297964	0.030*
H5B	1.415562	0.699049	0.327202	0.030*
C36	0.9485 (2)	0.5108 (3)	0.28754 (5)	0.0305 (5)
H36	0.978309	0.436777	0.298758	0.037*
C45	0.2121 (2)	0.6226 (2)	0.20566 (5)	0.0279 (5)
H45	0.132559	0.570430	0.211465	0.033*
C8	1.4990 (2)	0.0952 (2)	0.38945 (5)	0.0262 (4)
H8A	1.544284	0.182640	0.388577	0.031*
H8B	1.422180	0.089838	0.373881	0.031*
C42	0.4458 (2)	0.7755 (3)	0.18914 (6)	0.0330 (5)

H42	0.525225	0.828567	0.183676	0.040*
C41	0.4612 (2)	0.6903 (2)	0.21262 (5)	0.0310 (5)
C46	0.3432 (3)	0.6133 (2)	0.22108 (5)	0.0317 (5)
H46	0.353157	0.554977	0.237325	0.038*
C4	1.4926 (3)	0.8298 (2)	0.29658 (5)	0.0314 (5)
H4A	1.591417	0.831422	0.304902	0.047*
H4B	1.495816	0.834680	0.274979	0.047*
H4C	1.438273	0.904456	0.304086	0.047*
C33	0.8616 (3)	0.7271 (3)	0.25492 (5)	0.0333 (5)
H33	0.830543	0.801323	0.243896	0.040*
C34	0.7678 (2)	0.6214 (3)	0.25847 (5)	0.0321 (5)
C1	0.1402 (3)	0.2674 (2)	0.64255 (5)	0.0319 (5)
H1A	0.101783	0.274963	0.662482	0.048*
H1B	0.063604	0.287864	0.627939	0.048*
H1C	0.174590	0.178063	0.639400	0.048*
C35	0.8103 (3)	0.5148 (3)	0.27491 (5)	0.0344 (5)
H35	0.745429	0.444049	0.277624	0.041*
C7	1.6105 (3)	−0.0094 (3)	0.38500 (6)	0.0403 (6)
H7A	1.654181	0.001927	0.365643	0.060*
H7B	1.685725	−0.002989	0.400539	0.060*
H7C	1.564175	−0.095371	0.385910	0.060*
H2W	1.113 (4)	0.176 (3)	0.3215 (7)	0.049 (9)*
H1W	1.232 (3)	0.183 (3)	0.3076 (7)	0.043 (8)*
H9	0.775 (4)	−0.006 (4)	0.6632 (7)	0.059 (10)*
H3	0.962 (3)	0.321 (3)	0.3600 (7)	0.047 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0214 (2)	0.0310 (2)	0.0220 (2)	−0.00758 (18)	−0.00356 (16)	0.00664 (18)
O1W	0.0173 (7)	0.0361 (8)	0.0199 (7)	0.0005 (6)	0.0055 (6)	0.0033 (6)
O1	0.0178 (6)	0.0241 (7)	0.0209 (7)	−0.0035 (5)	0.0028 (5)	−0.0042 (5)
O4	0.0204 (7)	0.0252 (7)	0.0227 (7)	−0.0005 (6)	−0.0035 (6)	0.0031 (6)
O8	0.0284 (8)	0.0199 (7)	0.0205 (7)	−0.0033 (6)	−0.0012 (6)	0.0041 (5)
O3	0.0211 (7)	0.0316 (8)	0.0222 (7)	−0.0040 (6)	0.0043 (6)	−0.0011 (6)
O7	0.0230 (7)	0.0248 (7)	0.0250 (7)	−0.0017 (6)	0.0041 (6)	0.0031 (6)
O2	0.0236 (7)	0.0332 (8)	0.0198 (7)	−0.0089 (6)	−0.0003 (6)	−0.0053 (6)
O6	0.0173 (7)	0.0350 (8)	0.0223 (7)	0.0013 (6)	−0.0003 (5)	0.0027 (6)
O9	0.0302 (8)	0.0347 (9)	0.0284 (8)	0.0035 (7)	0.0091 (7)	−0.0014 (7)
O5	0.0256 (8)	0.0374 (9)	0.0352 (9)	−0.0012 (7)	−0.0051 (7)	0.0185 (7)
N2	0.0174 (8)	0.0186 (8)	0.0210 (8)	0.0007 (6)	0.0017 (6)	−0.0002 (6)
N6	0.0208 (8)	0.0185 (8)	0.0199 (8)	−0.0035 (6)	−0.0029 (6)	0.0005 (6)
N1	0.0178 (8)	0.0178 (7)	0.0201 (8)	0.0004 (6)	−0.0002 (6)	0.0000 (6)
N5	0.0207 (8)	0.0186 (8)	0.0197 (8)	−0.0040 (6)	−0.0022 (6)	0.0006 (6)
N4	0.0153 (16)	0.0230 (11)	0.0187 (15)	0.0028 (10)	0.0029 (12)	0.0030 (9)
N41	0.027 (10)	0.028 (5)	0.011 (5)	0.009 (5)	−0.003 (6)	−0.006 (4)
N3	0.0190 (19)	0.0254 (12)	0.0175 (13)	0.0021 (10)	0.0015 (12)	0.0028 (9)
N31	0.022 (9)	0.033 (6)	0.023 (7)	−0.002 (5)	−0.003 (6)	0.001 (5)

C11	0.0161 (8)	0.0165 (8)	0.0180 (9)	0.0014 (7)	−0.0011 (7)	−0.0009 (7)
C24	0.0135 (8)	0.0219 (9)	0.0205 (9)	0.0023 (7)	0.0005 (7)	0.0025 (7)
C14	0.0160 (8)	0.0160 (8)	0.0190 (9)	0.0016 (7)	−0.0012 (7)	0.0007 (7)
C21	0.0151 (8)	0.0183 (9)	0.0182 (9)	0.0014 (7)	−0.0006 (7)	0.0003 (7)
C51	0.0208 (9)	0.0158 (8)	0.0183 (9)	−0.0057 (7)	−0.0028 (7)	−0.0007 (7)
C23	0.0183 (9)	0.0205 (9)	0.0204 (9)	−0.0014 (7)	−0.0014 (7)	−0.0015 (7)
C3	0.0140 (8)	0.0192 (9)	0.0200 (9)	0.0023 (7)	−0.0014 (7)	0.0002 (7)
C9	0.0201 (9)	0.0157 (8)	0.0222 (9)	−0.0065 (7)	−0.0011 (7)	−0.0010 (7)
C61	0.0191 (9)	0.0176 (8)	0.0197 (9)	−0.0047 (7)	−0.0029 (7)	−0.0006 (7)
C54	0.0203 (9)	0.0163 (8)	0.0181 (9)	−0.0052 (7)	−0.0038 (7)	0.0008 (7)
C6	0.0210 (9)	0.0271 (10)	0.0165 (9)	0.0005 (8)	0.0017 (7)	0.0036 (7)
C22	0.0185 (9)	0.0202 (9)	0.0204 (9)	−0.0020 (7)	0.0000 (7)	0.0018 (7)
C15	0.0202 (9)	0.0164 (8)	0.0212 (9)	−0.0038 (7)	−0.0003 (7)	0.0008 (7)
C64	0.0190 (9)	0.0245 (10)	0.0239 (10)	−0.0047 (7)	0.0021 (8)	−0.0018 (8)
C12	0.0170 (9)	0.0206 (9)	0.0214 (9)	−0.0027 (7)	0.0012 (7)	−0.0021 (7)
C44	0.0182 (9)	0.0294 (10)	0.0197 (9)	0.0091 (8)	0.0009 (7)	−0.0046 (8)
C31	0.0186 (9)	0.0331 (11)	0.0145 (9)	0.0025 (8)	0.0009 (7)	0.0001 (8)
C52	0.0196 (9)	0.0178 (9)	0.0225 (10)	−0.0024 (7)	−0.0021 (7)	0.0001 (7)
C62	0.0176 (9)	0.0191 (9)	0.0216 (9)	−0.0024 (7)	−0.0013 (7)	−0.0001 (7)
C13	0.0190 (9)	0.0200 (9)	0.0210 (9)	−0.0032 (7)	−0.0007 (7)	−0.0039 (7)
C26	0.0198 (9)	0.0188 (9)	0.0248 (10)	−0.0020 (7)	0.0006 (7)	−0.0030 (7)
C16	0.0221 (9)	0.0169 (9)	0.0202 (9)	−0.0021 (7)	−0.0028 (7)	−0.0003 (7)
C55	0.0228 (9)	0.0177 (9)	0.0214 (9)	−0.0002 (7)	−0.0023 (7)	0.0010 (7)
C56	0.0237 (9)	0.0164 (8)	0.0211 (9)	−0.0007 (7)	−0.0032 (8)	0.0031 (7)
C63	0.0198 (9)	0.0200 (9)	0.0228 (10)	−0.0034 (7)	−0.0010 (7)	0.0019 (7)
C25	0.0189 (9)	0.0209 (9)	0.0278 (10)	−0.0043 (7)	0.0024 (8)	−0.0009 (8)
C53	0.0222 (9)	0.0169 (9)	0.0220 (9)	−0.0027 (7)	−0.0036 (7)	0.0046 (7)
C65	0.0193 (9)	0.0241 (10)	0.0287 (11)	0.0011 (8)	−0.0008 (8)	−0.0029 (8)
C66	0.0209 (9)	0.0193 (9)	0.0271 (10)	−0.0017 (7)	−0.0040 (8)	0.0009 (8)
C2	0.0196 (9)	0.0289 (10)	0.0190 (9)	−0.0026 (8)	0.0016 (7)	−0.0024 (8)
C32	0.0271 (11)	0.0328 (11)	0.0223 (10)	0.0068 (9)	−0.0020 (8)	0.0006 (9)
C43	0.0200 (10)	0.0344 (12)	0.0321 (12)	0.0049 (9)	0.0020 (8)	−0.0021 (9)
C5	0.0173 (9)	0.0330 (11)	0.0257 (10)	−0.0013 (8)	−0.0009 (8)	0.0001 (9)
C36	0.0241 (10)	0.0438 (13)	0.0237 (11)	−0.0050 (10)	−0.0014 (8)	0.0053 (9)
C45	0.0254 (10)	0.0354 (12)	0.0231 (10)	0.0082 (9)	0.0036 (8)	0.0002 (9)
C8	0.0249 (10)	0.0271 (10)	0.0270 (11)	−0.0052 (8)	0.0063 (8)	0.0002 (8)
C42	0.0203 (10)	0.0412 (13)	0.0375 (13)	0.0073 (9)	0.0011 (9)	−0.0058 (10)
C41	0.0219 (10)	0.0399 (13)	0.0311 (12)	0.0105 (9)	−0.0018 (9)	−0.0125 (10)
C46	0.0383 (13)	0.0377 (12)	0.0189 (10)	0.0168 (10)	−0.0029 (9)	−0.0020 (9)
C4	0.0261 (11)	0.0327 (12)	0.0355 (12)	−0.0048 (9)	0.0066 (9)	−0.0038 (10)
C33	0.0368 (13)	0.0385 (13)	0.0242 (11)	0.0185 (10)	−0.0073 (9)	−0.0025 (9)
C34	0.0202 (10)	0.0500 (14)	0.0260 (11)	0.0052 (10)	−0.0006 (8)	−0.0154 (10)
C1	0.0280 (11)	0.0352 (12)	0.0330 (12)	−0.0098 (9)	0.0121 (9)	−0.0082 (10)
C35	0.0240 (11)	0.0500 (15)	0.0291 (12)	−0.0063 (10)	−0.0005 (9)	0.0000 (10)
C7	0.0334 (13)	0.0367 (13)	0.0514 (16)	0.0020 (11)	0.0182 (12)	0.0014 (12)

Geometric parameters (Å, º)

K1—O8	2.6016 (16)	C64—C63	1.399 (3)
K1—O5	2.6121 (18)	C12—C13	1.387 (3)
K1—O3	2.6614 (16)	C12—H12	0.9500
K1—O2^{i}	2.6754 (17)	C44—C43	1.413 (3)
K1—O1W	2.7947 (19)	C44—C45	1.414 (3)
K1—H2W	3.07 (3)	C31—C32	1.388 (3)
K1—H3	2.96 (3)	C31—C36	1.398 (3)
O1W—H2W	0.84 (3)	C52—C53	1.387 (3)
O1W—H1W	0.81 (3)	C52—H52	0.9500
O1—C3	1.331 (2)	C62—C63	1.378 (3)
O1—C2	1.458 (2)	C62—H62	0.9500
O4—C6	1.325 (3)	C13—H13	0.9500
O4—C5	1.457 (2)	C26—C25	1.381 (3)
O8—C9	1.217 (2)	C26—H26	0.9500
O3—C24	1.353 (2)	C16—H16	0.9500
O3—H3	0.88 (3)	C55—C56	1.376 (3)
O7—C9	1.331 (2)	C55—H55	0.9500
O7—C8	1.455 (2)	C56—H56	0.9500
O2—C3	1.215 (2)	C63—H63	0.9500
O6—C44	1.309 (2)	C25—H25	0.9500
O9—C64	1.352 (3)	C53—H53	0.9500
O9—H9	0.98 (4)	C65—C66	1.384 (3)
O5—C6	1.214 (3)	C65—H65	0.9500
N2—N1	1.258 (2)	C66—H66	0.9500
N2—C21	1.413 (2)	C2—C1	1.498 (3)
N6—N5	1.262 (2)	C2—H2A	0.9900
N6—C61	1.415 (3)	C2—H2B	0.9900
N1—C14	1.431 (2)	C32—C33	1.397 (3)
N5—C54	1.429 (3)	C32—H32	0.9500
N4—N3	1.267 (7)	C43—C42	1.377 (3)
N4—C41	1.418 (6)	C43—H43	0.9500
N41—N31	1.25 (3)	C5—C4	1.501 (3)
N41—C41	1.61 (2)	C5—H5A	0.9900
N3—C34	1.439 (5)	C5—H5B	0.9900
N31—C34	1.62 (2)	C36—C35	1.387 (3)
C11—C16	1.397 (3)	C36—H36	0.9500
C11—C12	1.399 (3)	C45—C46	1.387 (3)
C11—C3	1.485 (3)	C45—H45	0.9500
C24—C25	1.394 (3)	C8—C7	1.503 (3)
C24—C23	1.404 (3)	C8—H8A	0.9900
C14—C13	1.393 (3)	C8—H8B	0.9900
C14—C15	1.395 (3)	C42—C41	1.380 (4)
C21—C26	1.397 (3)	C42—H42	0.9500
C21—C22	1.403 (3)	C41—C46	1.406 (4)
C51—C52	1.396 (3)	C46—H46	0.9500
C51—C56	1.400 (3)	C4—H4A	0.9800

C51—C9	1.480 (3)	C4—H4B	0.9800
C23—C22	1.382 (3)	C4—H4C	0.9800
C23—H23	0.9500	C33—C34	1.398 (4)
C61—C66	1.395 (3)	C33—H33	0.9500
C61—C62	1.398 (3)	C34—C35	1.374 (4)
C54—C53	1.391 (3)	C1—H1A	0.9800
C54—C55	1.400 (3)	C1—H1B	0.9800
C6—C31	1.490 (3)	C1—H1C	0.9800
C22—H22	0.9500	C35—H35	0.9500
C15—C16	1.384 (3)	C7—H7A	0.9800
C15—H15	0.9500	C7—H7B	0.9800
C64—C65	1.393 (3)	C7—H7C	0.9800

O8—K1—O5	172.84 (5)	C12—C13—H13	119.8
O8—K1—O3	83.98 (6)	C14—C13—H13	119.8
O5—K1—O3	88.89 (6)	C25—C26—C21	120.57 (19)
O8—K1—O2^{i}	88.66 (6)	C25—C26—H26	119.7
O5—K1—O2^{i}	96.95 (6)	C21—C26—H26	119.7
O3—K1—O2^{i}	135.62 (5)	C15—C16—C11	121.05 (18)
O8—K1—O1W	95.07 (5)	C15—C16—H16	119.5
O5—K1—O1W	83.59 (6)	C11—C16—H16	119.5
O3—K1—O1W	85.06 (6)	C56—C55—C54	119.29 (19)
O2^{i}—K1—O1W	139.27 (5)	C56—C55—H55	120.4
O8—K1—H2W	97.6 (6)	C54—C55—H55	120.4
O5—K1—H2W	79.2 (6)	C55—C56—C51	120.44 (18)
O3—K1—H2W	70.1 (6)	C55—C56—H56	119.8
O2^{i}—K1—H2W	154.2 (6)	C51—C56—H56	119.8
O1W—K1—H2W	15.6 (6)	C62—C63—C64	119.94 (19)
O8—K1—H3	85.2 (6)	C62—C63—H63	120.0
O5—K1—H3	87.7 (6)	C64—C63—H63	120.0
O3—K1—H3	17.0 (6)	C26—C25—C24	119.96 (18)
O2^{i}—K1—H3	152.6 (6)	C26—C25—H25	120.0
O1W—K1—H3	68.0 (6)	C24—C25—H25	120.0
H2W—K1—H3	53.2 (9)	C52—C53—C54	120.03 (18)
K1—O1W—H2W	101 (2)	C52—C53—H53	120.0
K1—O1W—H1W	106 (2)	C54—C53—H53	120.0
H2W—O1W—H1W	102 (3)	C66—C65—C64	119.56 (19)
C3—O1—C2	115.74 (15)	C66—C65—H65	120.2
C6—O4—C5	116.11 (16)	C64—C65—H65	120.2
C9—O8—K1	155.41 (14)	C65—C66—C61	120.30 (19)
C24—O3—K1	125.63 (12)	C65—C66—H66	119.9
C24—O3—H3	110 (2)	C61—C66—H66	119.9
K1—O3—H3	101 (2)	O1—C2—C1	108.01 (17)
C9—O7—C8	114.94 (16)	O1—C2—H2A	110.1
C3—O2—K1^{i}	148.90 (13)	C1—C2—H2A	110.1
C64—O9—H9	108 (2)	O1—C2—H2B	110.1
C6—O5—K1	155.65 (16)	C1—C2—H2B	110.1
N1—N2—C21	115.52 (17)	H2A—C2—H2B	108.4

N5—N6—C61	114.10 (17)	C31—C32—C33	119.2 (2)
N2—N1—C14	112.48 (16)	C31—C32—H32	120.4
N6—N5—C54	113.08 (16)	C33—C32—H32	120.4
N3—N4—C41	115.1 (4)	C42—C43—C44	121.2 (2)
N31—N41—C41	92.4 (16)	C42—C43—H43	119.4
N4—N3—C34	110.7 (4)	C44—C43—H43	119.4
N41—N31—C34	96.0 (16)	O4—C5—C4	107.02 (18)
C16—C11—C12	119.33 (18)	O4—C5—H5A	110.3
C16—C11—C3	117.68 (17)	C4—C5—H5A	110.3
C12—C11—C3	122.99 (17)	O4—C5—H5B	110.3
O3—C24—C25	118.05 (18)	C4—C5—H5B	110.3
O3—C24—C23	122.22 (18)	H5A—C5—H5B	108.6
C25—C24—C23	119.73 (18)	C35—C36—C31	120.4 (2)
C13—C14—C15	120.21 (18)	C35—C36—H36	119.8
C13—C14—N1	116.21 (17)	C31—C36—H36	119.8
C15—C14—N1	123.58 (17)	C46—C45—C44	120.8 (2)
C26—C21—C22	119.61 (18)	C46—C45—H45	119.6
C26—C21—N2	115.35 (17)	C44—C45—H45	119.6
C22—C21—N2	125.04 (17)	O7—C8—C7	106.95 (19)
C52—C51—C56	120.15 (18)	O7—C8—H8A	110.3
C52—C51—C9	122.44 (18)	C7—C8—H8A	110.3
C56—C51—C9	117.40 (18)	O7—C8—H8B	110.3
C22—C23—C24	120.33 (19)	C7—C8—H8B	110.3
C22—C23—H23	119.8	H8A—C8—H8B	108.6
C24—C23—H23	119.8	C43—C42—C41	120.6 (2)
O2—C3—O1	123.15 (18)	C43—C42—H42	119.7
O2—C3—C11	123.48 (18)	C41—C42—H42	119.7
O1—C3—C11	113.37 (17)	C42—C41—C46	119.8 (2)
O8—C9—O7	122.85 (18)	C42—C41—N4	113.1 (2)
O8—C9—C51	123.31 (19)	C46—C41—N4	127.1 (2)
O7—C9—C51	113.84 (17)	C42—C41—N41	152.5 (7)
C66—C61—C62	119.86 (18)	C46—C41—N41	87.7 (6)
C66—C61—N6	115.76 (18)	C45—C46—C41	119.9 (2)
C62—C61—N6	124.36 (18)	C45—C46—H46	120.1
C53—C54—C55	120.62 (18)	C41—C46—H46	120.1
C53—C54—N5	115.73 (17)	C5—C4—H4A	109.5
C55—C54—N5	123.65 (18)	C5—C4—H4B	109.5
O5—C6—O4	123.49 (19)	H4A—C4—H4B	109.5
O5—C6—C31	123.3 (2)	C5—C4—H4C	109.5
O4—C6—C31	113.17 (18)	H4A—C4—H4C	109.5
C23—C22—C21	119.78 (18)	H4B—C4—H4C	109.5
C23—C22—H22	120.1	C34—C33—C32	120.1 (2)
C21—C22—H22	120.1	C34—C33—H33	120.0
C16—C15—C14	119.22 (18)	C32—C33—H33	120.0
C16—C15—H15	120.4	C35—C34—C33	120.5 (2)
C14—C15—H15	120.4	C35—C34—N3	113.8 (2)
O9—C64—C65	117.89 (19)	C33—C34—N3	125.7 (2)
O9—C64—C63	121.79 (19)	C35—C34—N31	150.8 (6)

C65—C64—C63	120.31 (19)	C33—C34—N31	87.1 (6)
C13—C12—C11	119.78 (18)	C2—C1—H1A	109.5
C13—C12—H12	120.1	C2—C1—H1B	109.5
C11—C12—H12	120.1	H1A—C1—H1B	109.5
O6—C44—C43	121.2 (2)	C2—C1—H1C	109.5
O6—C44—C45	121.1 (2)	H1A—C1—H1C	109.5
C43—C44—C45	117.7 (2)	H1B—C1—H1C	109.5
C32—C31—C36	120.0 (2)	C34—C35—C36	119.7 (2)
C32—C31—C6	121.8 (2)	C34—C35—H35	120.2
C36—C31—C6	118.19 (19)	C36—C35—H35	120.2
C53—C52—C51	119.45 (19)	C8—C7—H7A	109.5
C53—C52—H52	120.3	C8—C7—H7B	109.5
C51—C52—H52	120.3	H7A—C7—H7B	109.5
C63—C62—C61	120.00 (19)	C8—C7—H7C	109.5
C63—C62—H62	120.0	H7A—C7—H7C	109.5
C61—C62—H62	120.0	H7B—C7—H7C	109.5
C12—C13—C14	120.35 (18)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C63—H63···O6^{ii}	0.95	2.49	3.427 (3)	169
C8—H8*B*···O9^{iii}	0.99	2.64	3.476 (3)	142
C4—H4*C*···O9^{i}	0.98	2.57	3.301 (3)	131
O1*W*—H1*W*···N4^{iv}	0.81 (3)	2.15 (3)	2.895 (3)	153 (3)
O1*W*—H1*W*···N31^{iv}	0.81 (3)	2.11 (4)	2.898 (13)	166 (3)
O9—H9···O1*W*^{iii}	0.98 (4)	1.74 (4)	2.709 (3)	171 (3)
O1*W*—H2*W*···O6^{v}	0.84 (3)	1.84 (3)	2.635 (2)	156 (3)
O3—H3···O6^{v}	0.88 (3)	1.63 (3)	2.490 (2)	163 (3)

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