

Poly[hexaaquabis(μ_4 -4-carboxybenzenesulfonato)bis(μ_3 -4-carboxybenzenesulfonato)calcium(II)-dipotassium(I)]

G. Prochniak and V. Videnova-Adrabinska*

Department of Chemistry, Wrocław University of Technology, 27 Wybrzeże
Wyspiańskiego Street, 50-370 Wrocław, Poland
Correspondence e-mail: veneta.videnova-adrabinska@pwr.wroc.pl

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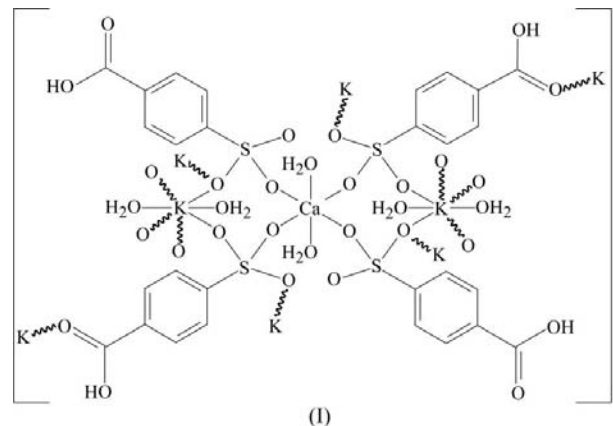
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This study presents the coordination modes and crystal organization of a calcium–potassium coordination polymer, poly[hexaaquabis(μ_4 -4-carboxybenzenesulfonato- $\kappa^4 O^1:O^{1'}:O^{1''}:O^4$)-bis(μ_3 -4-carboxybenzenesulfonato- $\kappa^2 O^1:O^{1'}$)calcium(II)-dipotassium(I)], $[\text{CaK}_2(\text{C}_7\text{H}_5\text{O}_5\text{S})_4(\text{H}_2\text{O})_6]_n$, displaying a novel two-dimensional framework. The potassium ion is seven-coordinated by four sulfonate and one carboxyl O atom located on five different acid ligands, two of which are unique, and by two symmetry-independent water O atoms. A pair of close potassium ions share two inversion-related sulfonate O-atom sites to form a dimeric K_2O_{12} unit, which is extended into a one-dimensional array along the a -axis direction. The six-coordinate Ca^{2+} ion occupies a special position ($\bar{1}$) at $(0, \frac{1}{2}, \frac{1}{2})$ and is surrounded by four sulfonate O atoms from two inversion-related pairs of unique acid monoanions and by two O atoms from aqua ligands. The compound displays a layered structure, with K_2O_{12} and CaO_6 polyhedra in the layers and aromatic linkers between the layers. The three-dimensional scaffold is open, with nano-sized channels along the c axis.

Comment

Hybrid inorganic–organic layered compounds, in particular organically functionalized metal phosphonates, are extensively studied for their potential applications in chemical separation, gas sorption, sensing and catalysis (Clearfield, 1998; Alberti & Constanino, 1996; Kong *et al.*, 2006; Sharma & Clearfield, 2000; Cabeza *et al.*, 2002). The metal organosulfonates, developed recently as analogous to the metal organophosphonates, are another class of novel materials with interesting functional properties, such as guest sorption and ion exchange (Cote & Shimizu, 2003). However, there is no direct structural relationship between arylsulfonates and arylphosphonates, since the metal binding preferences and, therefore, the coordination modes of the relatively soft-base

sulfonate group are different (Cote & Shimizu, 2003; Videnova-Adrabinska, 2007). A Cambridge Structural Database (Version 5.30; Allen, 2002) review revealed 1514 total hits of sulfonate structures containing metal ions, of which 995 contain transition metal ions and 340 contain group IA or IIA metal ions (both transition and IA or IIA metal ions are found in 54 structures). The remaining structures contain rare earth metal ions (159) or such main group metals as Pb (42), Sb (26), Sn (30), Tl (2), Bi (18), Al (1) and Ga (3). Direct coordination of the metal ion to the sulfonate group is observed in only 638 compounds (426 *d* and *f* metal ion complexes, and 143 group IA and IIA complexes). The organic ligand in most of the retrieved structures is endowed with one or more additional functional groups ($-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$, $-\text{CH}_3$ or $-\text{NH}_2$). In particular, the sulfoisophthalic, sulfosalicylic and disulfonic acids have been used as versatile ligands. Surprisingly, the sulfobenzoic acids are significantly less well studied (20 hits for 3-sulfobenzoic and 32 hits for 4-sulfobenzoic acid). Up to now only four potassium and/or rubidium, two barium, and one strontium 4-sulfonobenzoate (4sb) structures have been published (Gunderman & Squattrito, 1994; Kariuki & Jones, 1995; Wagner & Merzweiler, 2008; Prochniak & Videnova-Adrabinska, 2009). They all demonstrate layered inorganic regions, linked *via* the arene rings. So far, mixed IA–IIA compounds of sulfobenzoic acids are not known and we report here the crystal structure of the first such example, (I).



The asymmetric unit of (I) contains half a calcium ion, one potassium ion, two unique 4-carboxybenzenesulfonate monoanions and three different water molecules (Fig. 1). The two crystallographically nonequivalent 4sb ligands are designated as *A* and *B*. The calcium ion is six-coordinate with an elongated octahedral geometry and lies on an inversion center at $(0, \frac{1}{2}, \frac{1}{2})$. The coordination environment of Ca^{2+} consists of four 4sb ligands, one of which is symmetry unique, and two water molecules. The sulfonate O atoms [O42A, O42Aⁱ, O43B and O43Bⁱ; symmetry codes: (i) $-x, -y + 1, -z + 1$] act as equatorial ligands and form two pairs of similar bonds (Ca–O42A and Ca–O43B), while the axial aqua ligands (OW1 and OW1ⁱ) form a slightly longer bond (Table 1). The coordination environment of K^+ includes five 4sb ligands (two *A* and three *B*) and two independent water molecules. The potassium ion is

seven-coordinated *via* four sulfonate atoms (O41A, O42Bⁱⁱ, O41A^{iv} and O41B), one carboxyl O atom (O11Bⁱⁱⁱ) and two water O atoms (O2W and O3W) [symmetry codes: (ii) $-x, -y + 2, -z + 1$; (iii) $x, y, z - 1$; (iv) $-x + 1, -y + 2, -z + 1$; Table 1]. The coordination geometry of K⁺ can be described as a distorted monocapped triangular prism, where atoms O41B, O41A, O11Bⁱⁱⁱ and O42Bⁱⁱ form the rectangular face capped by atom O3W (Fig. 1). The dihedral angles between the best fitted planes forming the polyhedron faces are 73.3 (1) and 85.7 (1)° between the capped rectangular face and the triangular faces, and 64.0 (1), 51.8 (1) and 64.2 (1)° between the rectangular faces (Brandenburg, 2008). The nearest neighboring potassium ions [the K···K distance is 3.8382 (6) Å] share two of their O-atom sites (O41A and O41A^{iv}) in order to form a dimeric K₂O₂ unit. Thus, neighboring inversion-related trigonal prisms become paired to develop the K₂O₁₂ polyhedron.

The compound is lamellar and built of alternating organic and inorganic layers that are connected in an extended three-dimensional structure. The inorganic part consists of K₂O₁₂ polyhedra, CaO₆ octahedra and CSO₃ tetrahedra (*A* and *B*). The K₂O₁₂ polyhedra are extended into coordination rods along the crystallographic *a*-axis direction by sharing two pairs of opposite corners with four *B* tetrahedra. The CaO₆ octahedra are located symmetrically between the K₂O₁₂ rods and serve to link them *via* shared corners with both *A* and *B* tetrahedra (Fig. 2). Three different windows (one large and two smaller) are generated between the K₂O₁₂ polyhedra, CaO₆ octahedra and CSO₃ tetrahedra. The inorganic layers are arranged one over the other in order to form channels along the *c* axis, where the arene rings and the water molecules reside.

The topological consideration of the crystal organization is most appropriate for uncovering the connectivity patterns inside the layers, and for revealing the symmetry relationships

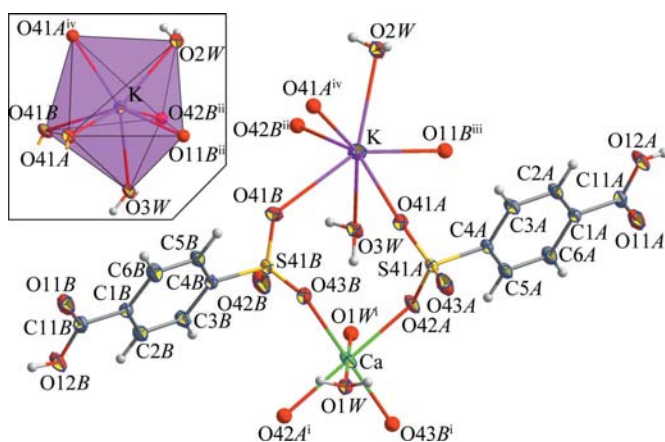


Figure 1

The asymmetric unit of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. The coordination polyhedron of the potassium ion is shown in the inset. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x, -y + 2, -z + 1$; (iii) $x, y, z - 1$; (iv) $-x + 1, -y + 2, -z + 1$.]

of the framework. In fact, each sulfonate tetrahedron (*A* and *B*) associates one calcium ion with two potassium ions, but the *A* tetrahedron shares only two O-atom corners, while the *B* tetrahedron shares three O-atom corners (Fig. 2*a*). This means that each of the sulfonate groups (*A* and *B*) bridges the metal ions in a different coordination manner ($\eta^2\mu_3$ and $\eta^3\mu_3$). The *A* group uses a single O-atom site (μ_2 -O41A) to interlock close potassium ions *via* an R2,2(4) coordination motif in

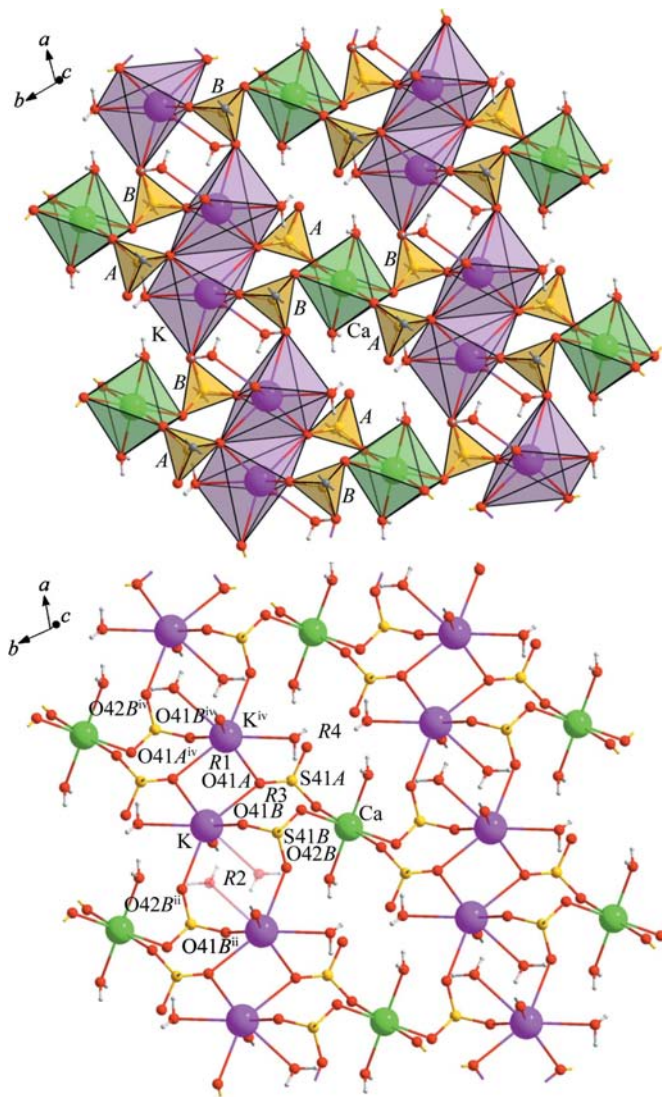


Figure 2

Two alternative presentations of the inorganic monolayer: (*a*) as a two-dimensional arrangement of corner-sharing K₂O₁₂, CaO₆ and CSO₃ polyhedra, and (*b*) as a two-dimensional coordination framework formed from K ribbons, which are interweaved at the Ca ions. R1 and R2 are the centrosymmetric ring motifs R2,2(4) and R2,4(8) interlinking the potassium ions inside the ribbon; R3 is the noncentrosymmetric R2,4(8) motif interlinking the calcium and potassium metal centers; and R4 is the nano-sized R4,8(16) window generated in the framework. The R4 windows are stacked one over the other in order to form nano-sized channels along the *c* axis. For the sake of clarity, the arene rings and the terminal carboxyl groups (except for the coordinating O11B atom) have been omitted. [Symmetry codes: (ii) $-x, -y + 2, -z + 1$; (iv) $-x + 1, -y + 2, -z + 1$.]

order to form the centrosymmetric K_2O_2 dimer unit, and another site (O42A) to link the K_2O_2 dimer with the calcium center in a monodentate manner. The *B* group uses two O-atom sites (O41B and O42B) to bridge the K_2O_2 dimers along the *a* axis, and the third site (O43B) to connect the K_2O_2 dimer with the Ca center. The K ribbons are generated *via* two different centrosymmetric ring motifs, alternating along the *a* axis, namely the interlocking $R2,2(4)$ motif, formed *via* K—O41A and K—O41A^{iv} bonds, and the bridging $R2,4(8)$ motif, formed by K—O41B and K—O42Bⁱⁱ bonds. The two K···K distances [3.8382 (6) and 5.828 (1) Å] observed in the crystal structure correspond to the metal center interdistances in these rings. The two-dimensional framework of the inorganic monolayer can be considered as a result of an antiparallel arrangement of potassium ribbons, interweaved at the Ca ions. The interweaving $R_2^4(8)$ motif, closed between the K and Ca ions, is formed *via* K—O41A, Ca—O42A, Ca—O43B and K—O41B bonds. The motif itself is noncentrosymmetric, but is symmetrically arranged, incorporating both the Ca centers and the geometrical centers of the K_2O_2 dimers. The resulting two-dimensional network is 4,4-connected and displays large $R4,8(16)$ nano-sized windows, arranged one over the other along the *c* axis. The arene rings of the *A* ligands and two of the water molecules are found here. The third water molecule projects into the centrosymmetric $R2,4(8)$ motif (Fig. 2b). Numerous intralayer hydrogen bonds, established between the water molecules and the sulfonate O-atom sites, serve to stabilize the two-dimensional coordination network. The O2W—H4W···O43B^{iv} and O3W—H5W···O41Bⁱⁱ hydrogen bonds are extended along the potassium ribbons, whereas the O1W—H2W···O43A^{vi}, O2W—H3W···O43A^{vii} and O3W—H6W···O1Wⁱ interactions crosslink neighboring ribbons

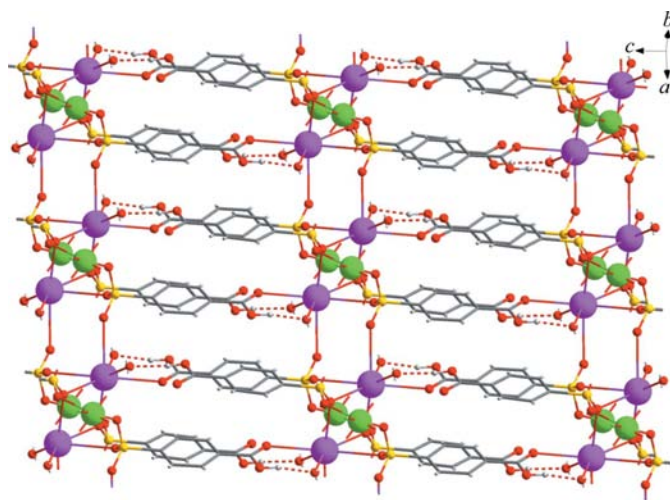


Figure 3

A view along the [110] direction demonstrating the open three-dimensional scaffold. The *A* and *B* rings alternate along the [110] direction and link neighboring inorganic monolayers *via* coordination bonds (*B* rings) and hydrogen bonds (*A* rings). For the sake of clarity, O1W and the noncoordinating O43A atoms, as well as all H atoms, except those of the carboxyl groups participating in the interlayer hydrogen bonds, have been omitted.

inside the monolayer (see Table 2 for symmetry codes). The organic portions of the ligands are arranged outward from both sides of the coordination monolayer and the rings are organized into *A* and *B* columns alternating along the *b* axis. The carboxyl group of the *B* monoanion is used to connect the monolayers in a bridging fashion *via* the K—O11Bⁱⁱⁱ bond. Thus, the *B*-ring columns act as pillars between the layers, whereas the *A* rings fit the corridors generated between the pillars (Fig. 3). Three different hydrogen bonds (O12B—H12B···O3W^v, O12A—H12A···O2W^{viii} and O1W—H1W···O11A^v), formed from or toward the carboxyl groups of both *A* and *B* ligands, additionally bring together the inorganic monolayers. The arene rings formally belonging to adjacent coordination monolayers are intermingled along the [110] direction, with an interlayer $CgA\cdots CgB$ distance (where *Cg* denotes the ring centroid) of 4.655 (1) Å. The closest $CgA\cdots CgA$ and $CgB\cdots CgB$ distances are 4.838 (1) and 4.542 (1) Å, respectively, with a slippage of 3.371 Å between adjacent *A* rings and 3.009 Å between *B* rings. *Y*—*X*···*Cg* interactions are established between the carbonyl group of the *A* ligand and the π -electronic system of the adjacent *A* and *B* rings [$C11A—O11A\cdots CgA = 3.960$ (2) Å and $C11A—O11A\cdots CgB = 3.663$ (2) Å; Spek, 2009].

The structure of this new mixed dipotassium calcium 4-sulfobenzoic acid compound may be compared with those of the potassium, dipotassium (Gunderman & Squattrito, 1994; Kariuki & Jones, 1995), barium (Wagner & Merzweiler, 2008) and strontium (Prochniak & Videnova-Adrabinska, 2009) compounds of the same ligand. All reported structures display separate organic and inorganic regions, with metal—SO₃ units forming the inorganic layers. However, both the connectivity patterns inside the inorganic monolayers and the arrangement of the arene rings in the organic regions differ from one structure to another. While the potassium ion is six-coordinate in $K(HO_2CC_6H_4SO_3)\cdot H_2O$, six- and seven-coordinate in $K_2(O_2CC_6H_4SO_3)$, and eight-coordinate in $K(HO_2CC_6H_4SO_3)\cdot H_2O$, the strontium ion is eight-coordinate in $[Sr(4sb)_2(H_2O)_3]$, and the barium ion is nine-coordinate in both $Ba(O_3SC_6H_4COO)_2\cdot 3H_2O$ and $Ba(O_3SC_6H_4COO)_2\cdot 2H_2O$. [Note that the chemical formula units of the potassium and barium compounds given in the original papers do not distinguish the crystalline water molecule(s) from the aqua ligand(s) in the crystal structure.] It is obvious that the lack of *d* electrons and therefore the lack of crystal field stabilization energy make the geometrical preferences of the metal ion less dominant, which allows for variable coordination environments and different coordination modes. On the other hand, the presence of two different ions (K^+ and Ca^{2+}) dramatically changes the symmetry relations and the connectivity patterns both inside the inorganic monolayers and between them. The irregular coordination geometry of the potassium ion is compensated by the formation of a centrosymmetric dimeric K_2O_{12} unit in order to adapt the symmetry requirements of the frameworks forced by the octahedral geometry of the calcium ion. The effect of this compromise is the formation of an open three-dimensional scaffold consisting of a grids of inorganic monolayers, with organic pillars between them.

Experimental

The title compound was synthesized by dissolving 4-sulfobenzoic acid potassium salt (Aldrich; 2.50 mmol) and calcium nitrate tetrahydrate (POCh; 1.25 mmol) in distilled water (3.5 ml). The mixture was sealed in a glass vial and heated at 348 K for 4 h, and then cooled slowly at a rate of 1.0 K h⁻¹ to room temperature. Plate-shaped and slightly opaque crystals suitable for X-ray measurements were obtained after the cooling process.

Crystal data

[CaK ₂ (C ₇ H ₅ O ₅ S) ₄ (H ₂ O) ₆]	$\gamma = 105.491 (2)^\circ$
$M_r = 1031.10$	$V = 969.63 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.1321 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.0250 (2) \text{ \AA}$	$\mu = 0.69 \text{ mm}^{-1}$
$c = 12.6802 (3) \text{ \AA}$	$T = 183 \text{ K}$
$\alpha = 98.474 (2)^\circ$	$0.19 \times 0.15 \times 0.06 \text{ mm}$
$\beta = 97.472 (2)^\circ$	

Data collection

Oxford Diffraction Xcalibur diffractometer	30945 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	5921 independent reflections
$T_{\min} = 0.880$, $T_{\max} = 0.960$	4670 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	1 restraint
$wR(F^2) = 0.095$	Only H-atom coordinates refined
$S = 1.05$	$\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$
5921 reflections	$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$
301 parameters	

Table 1

Selected bond lengths (Å).

Ca—O42A	2.3300 (11)	K—O42B ⁱⁱ	2.8031 (15)
Ca—O42A ⁱ	2.3300 (11)	K—O11B ⁱⁱⁱ	2.8078 (13)
Ca—O43B	2.3415 (13)	K—O3W	2.8128 (14)
Ca—O43B ⁱ	2.3415 (13)	K—O41A ^{iv}	2.8446 (13)
Ca—O1W ⁱ	2.3554 (13)	K—O2W	2.8623 (13)
Ca—O1W	2.3554 (13)	K—O41B	2.9807 (13)
K—O41A	2.7256 (12)		

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

The H atoms of the carboxyl groups and the water molecules were observed in difference Fourier maps and their positional parameters refined. One restraint was used for the O2W—H3W distance. The H atoms of the aromatic rings were placed at calculated positions, with C—H = 0.95 Å. All H atoms were assigned fixed isotropic displacement parameters, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduc-

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W ⁱ ...O11A ^v	0.80 (2)	1.93 (2)	2.7248 (18)	175 (2)
O1W—H2W ⁱ ...O43A ^{vi}	0.80 (2)	1.97 (2)	2.7425 (18)	161 (2)
O2W—H3W ⁱ ...O43A ^{vii}	0.770 (16)	2.236 (18)	2.9374 (19)	152 (2)
O2W—H4W ⁱ ...O43B ^{iv}	0.79 (2)	2.06 (2)	2.846 (2)	175 (2)
O3W—H5W ⁱ ...O41B ⁱⁱ	0.84 (2)	2.06 (2)	2.880 (2)	163 (2)
O3W—H6W ⁱ ...O1W ⁱ	0.85 (2)	1.99 (2)	2.8281 (17)	171 (2)
O12A—H12A ⁱ ...O2W ^{viii}	0.83 (2)	1.83 (3)	2.6531 (18)	168 (2)
O12B—H12B ⁱ ...O3W ^v	0.87 (2)	1.75 (3)	2.6104 (18)	168 (2)

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

tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3195). Services for accessing these data are described at the back of the journal.

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