

catena-Poly[[bis(μ -2-sulfonato- benzoato)bis[triaquagadolinium(III)]- μ -oxalato]

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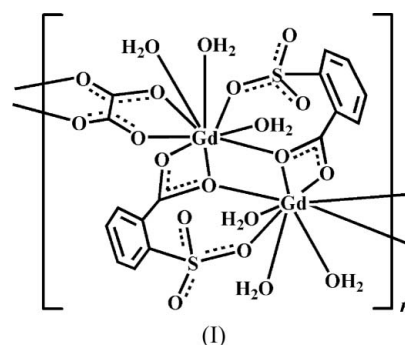
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The asymmetric unit of the title coordination polymer, $[\text{Gd}_2(\text{C}_7\text{H}_4\text{O}_5\text{S})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_6]_n$ or $[\text{Gd}(2\text{-SB})(\text{ox})_{0.5}(\text{H}_2\text{O})_3]_{2n}$ (2-SB is 2-sulfonatobenzoate and ox is oxalate), (I), consists of one Gd^{III} ion, one 2-SB anion, three coordinated water molecules and one half of an ox ligand. The ox ligand is located on a crystallographic inversion centre. The Gd^{III} centre shows a distorted tricapped trigonal–prismatic coordination formed by nine O atoms from two 2-SB anions, one ox ligand and three coordinated water molecules. The carboxylate and sulfonate groups of the 2-SB anions adopt $\mu_2\text{-}\eta^1\text{:}\eta^2$ and $\mu_1\text{-}\eta^0\text{:}\eta^0\text{:}\eta^1$ coordination modes to link two Gd^{III} ions, generating a centrosymmetric binuclear $[\text{Gd}_2(2\text{-SB})_2(\text{H}_2\text{O})_6]^{2-}$ subunit. The ox ligand acts as a bridge, linking the binuclear $[\text{Gd}_2(2\text{-SB})_2(\text{H}_2\text{O})_6]^{2-}$ subunits into a one-dimensional chain structure parallel to the *b* axis. Furthermore, extensive $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds connect the chains into a three-dimensional supramolecular architecture.

Comment

During the past decades, metal–organic coordination polymers (MOCs) containing lanthanide ions have attracted considerable attention, not only for their novel topologies but also for their potential in the areas of magnetic and fluorescence applications, molecular recognition and photovoltaic conversion (Kido & Okamoto, 2002; Tsukube & Shinoda, 2002; Li *et al.*, 2006; Manna *et al.*, 2006; Zhao *et al.*, 2008; Huang *et al.*, 2009). A key strategy in the construction of MOCs is to select suitable bi- or multidentate bridging ligands. 2-Sulfonatobenzoate (2-SB) is a prime example of such a ligand for the preparation of MOCs: its semi-rigidity allows the ligands to accommodate the coordination geometries of different metal centres, and its many O atoms can take part in hydrogen bonds leading to the formation of supramolecular structures. Many transition metal coordination

polymers with 2-SB have been prepared and characterized (Li & Yang, 2004; Su *et al.*, 2005; Xiao *et al.*, 2005; Chagas *et al.*, 2008). However, reports of lanthanide coordination compounds with 2-SB are relatively less common: only six lanthanide 2-SB complexes were reported by Li's group, namely, $\{[\text{Ln}_2(2\text{-SB})_3(\text{phen})_3(\text{H}_2\text{O})_2]\cdot n\text{H}_2\text{O}\}_2$ ($\text{Ln} = \text{Sm}$, $n = 3$; $\text{Ln} = \text{Eu}$, $n = 2$; $\text{Ln} = \text{Tb}$, $n = 2$; $\text{Ln} = \text{Dy}$, $n = 2.5$; $\text{Ln} = \text{Er}$, Y , $n = 4.5$; phen is 1,10-phenanthroline) (Li *et al.*, 2008; Wan *et al.*, 2009). In these compounds, 2-SB acts as a bridging and phen as a terminal ligand, and the structures consist of isolated tetranuclear complex molecules, which further assemble into three-dimensional supramolecular architectures through hydrogen bonding. During our research on coordination polymers containing 2-SB, the oxalate (ox) ligand was selected as a bridge to replace the terminal phen ligand, and the title one-dimensional coordination polymer, (I), was obtained under hydrothermal conditions. This is the first lanthanide metal coordination polymer with an 2-SB anion, according to the Cambridge Structural Database (CSD, Version 5.31 of August 2010; Allen, 2002).



The asymmetric unit of the title complex contains one Gd^{III} ion, one 2-SB anion, three coordinated water molecules and one half of an ox ligand, located on an inversion centre. The Gd^{III} centre is coordinated by nine O atoms from two 2-SB

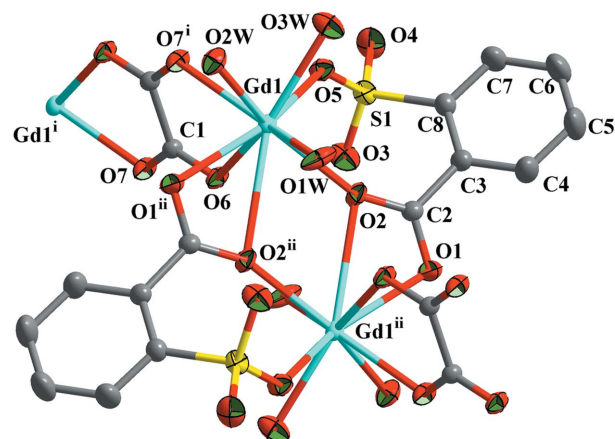
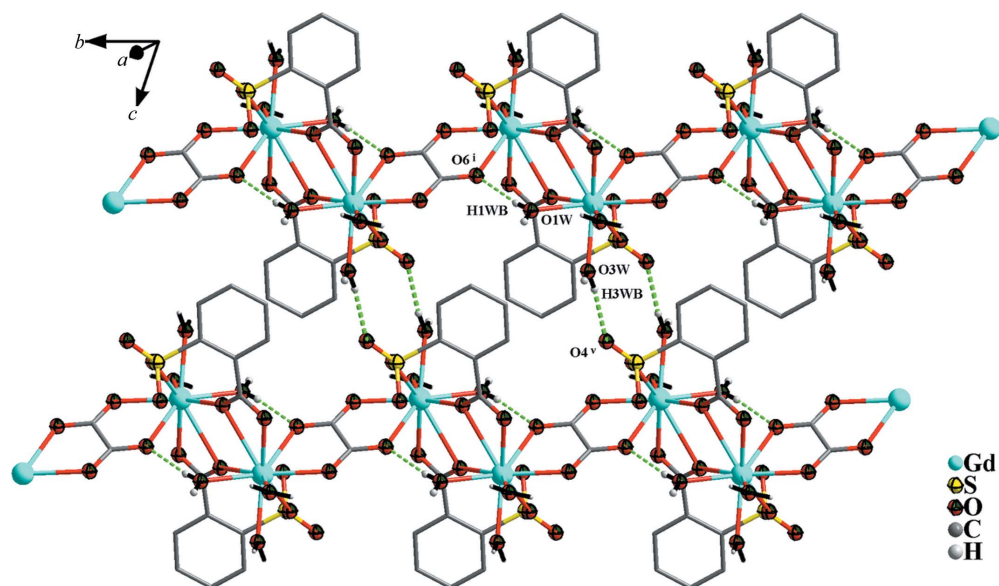
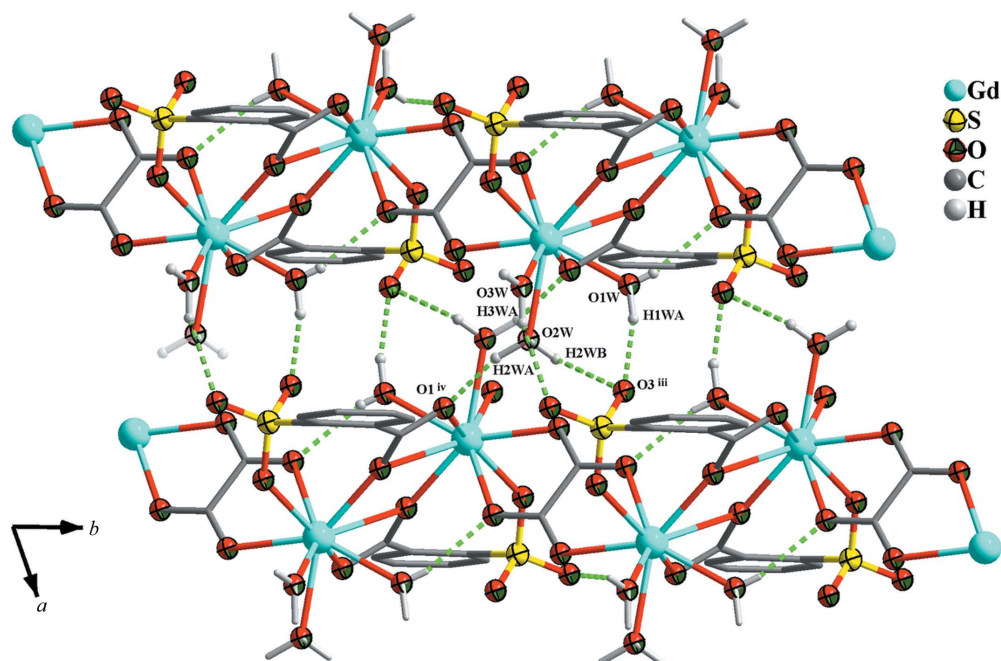


Figure 1
The coordination environment of the Gd^{III} ion in (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y + 1, -z$.]

**Figure 2**

Hydrogen bonds in (I) connecting neighbouring chains into a two-dimensional layer, projected on the $(\bar{7}14)$ plane. Inter-chain hydrogen bonds are denoted by thick and intra-chain hydrogen bonds by thin dashed lines. H atoms not bonded to water have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y, -z$; (v) $-x + 1, -y, -z + 1$.]

**Figure 3**

Hydrogen bonds connecting the two-dimensional layer into a three-dimensional supramolecular network in (I), viewed along the c axis. Hydrogen bonds are denoted by dashed lines. H atoms not bonded to water have been omitted for clarity. [Symmetry codes: (iii) $x + 1, y, z$; (iv) $x + 1, y - 1, z$.]

anions, one ox ligand and three coordinated water molecules in a tricapped distorted trigonal–prismatic geometry (Fig. 1). The carboxylate and sulfonate groups of the 2-SB anion adopt $\mu_2\text{-}\eta^1:\eta^2$ and $\mu_1\text{-}\eta^0:\eta^0:\eta^1$ modes to link two Gd^{III} ions, generating a centrosymmetric binuclear $[\text{Gd}_2(2\text{-SB})_2(\text{H}_2\text{O})_6]^{2-}$ subunit. The ox ligand forms a bis- $\mu_1\text{-}\eta^1:\eta^1$ chelating bridge so that the binuclear $[\text{Gd}_2(2\text{-SB})_2(\text{H}_2\text{O})_6]^{2-}$ subunits form chains parallel to the b axis (Fig. 2). In the structure of the previously reported six lanthanide 2-SB complexes (Li *et al.*, 2008; Wan *et al.*, 2009), the carboxylate and sulfonate groups of the 2-SB anions adopt $\mu_2\text{-}\eta^1:\eta^1$ and $\mu_1\text{-}\eta^0:\eta^0:\eta^1$ modes or $\mu_1\text{-}\eta^0:\eta^1$ and

$\mu_1\text{-}\eta^0:\eta^0:\eta^1$ modes. In (I), atoms atoms O2/O5/O6 and O1W/O2W/O1ⁱⁱⁱ [symmetry code: (ii) $-x + 1, -y + 1, -z$] define the upper and lower triangular faces of the trigonal prism: the dihedral angle between these two faces is $33.7(1)^\circ$, indicating a major distortion from ideal trigonal prismatic coordination geometry around the Gd^{III} centre. Atoms O2ⁱⁱ, O7ⁱ and O3W [symmetry code: (i) $-x + 1, -y, -z$] are situated on the capping positions of three quadrilateral faces. The Gd–O bond lengths are in the range 2.368 (3)–2.820 (3) Å, which are similar to values reported for the Gd complex with 5-sulfoisophthalic acid (Song *et al.*, 2004). The S–O bond lengths

vary from 1.454 (3) to 1.467 (3) Å, and fall within the typical range of S—O bond distances in the sulfonate anion according to the CSD (Allen, 2002). The similarity in the three S—O bond lengths indicates that the strong delocalization in the sulfonate group is predominant in the structure of the title polymer. In the chain, Gd^{III} ions adopt a zigzag arrangement, in which the Gd···Gd···Gd angles are 104.202 (8)°. The shortest Gd···Gd distance is 4.389 (2) Å, which is shorter than in the previously reported six lanthanide 2-SB complexes (Li *et al.*, 2008; Wan *et al.*, 2009), namely Ln···Ln = 5.454 (3) Å. The short distance between metal centres can improve the magnetic coupling. The variance in Ln···Ln distance may be due to the fact that the bulky phen co-ligand has larger steric hindrance than ox. In the structure of (I), the Gd···Gd distance separated by the ox ligand is 6.282 (2) Å.

Hydrogen-bonding and π - π stacking interactions play an important role in the structure of (I). The hydrogen-bond geometry is given in Table 2. Within the one-dimensional chain, a carboxylate O atom of ox, acting as hydrogen-bond acceptor, is involved in an intra-chain hydrogen bond *via* atom H1WB of one coordinated water molecule with graph set C(6) (Bernstein *et al.*, 1995). The sulfonate group coordinates to the Gd^{III} ion only through one O atom, and the uncoordinated sulfonate O atoms form four types of inter-chain hydrogen bonds with coordinated water molecules (*via* H1WA, H2WB, H3WA and H3WB). Within these hydrogen bonds, one type (*via* H3WB) connects the neighbouring chains into a two-dimensional layer (Fig. 2), with an $R_2^2(12)$ ring. Furthermore, a carboxylate O atom of 2-SB forms one type of inter-chain hydrogen bond *via* atom H2WA of one coordinated water molecule with a C(6) chain; this connects the two-dimensional hydrogen-bond-supported layers into a three-dimensional supramolecular architecture (Fig. 3). In addition, three types of hydrogen bond (*via* H1WA, H3WA and H2WB) exist between the two-dimensional layers, forming hydrogen-bonded $R_2^2(8)$ and $R_1^2(6)$ rings to promote the stability of the structure. There also exist weak inter-chain π - π stacking interactions, with a $Cg\cdots Cg(-x+1, -y+1, -z+1)$ separation of 3.982 (8) Å, between the benzene rings of 2-SB anions.

Experimental

A mixture of 2-sulfobenzoic acid (30.6 mg, 0.16 mmol), Gd(NO₃)₃·6H₂O (72.5 mg, 0.16 mmol), oxalic acid (7.3 mg, 0.08 mmol) and KOH aqueous solution (0.6 ml, 1 M) was added to H₂O (10 ml). After stirring, the reaction mixture was sealed in a 23 ml Teflon-lined stainless steel reactor and heated at 393 K for 72 h, then cooled slowly to room temperature. Yellow block-shaped crystals of the title coordination polymer were obtained in 32% yield (based on Gd).

Crystal data

[Gd ₂ (C ₇ H ₄ O ₅ S) ₂ (C ₂ O ₄)(H ₂ O) ₆]	$\gamma = 70.32 (3)^\circ$
$M_r = 910.94$	$V = 622.7 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.7597 (16) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.4998 (17) \text{ \AA}$	$\mu = 5.54 \text{ mm}^{-1}$
$c = 10.641 (2) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 70.98 (3)^\circ$	$0.26 \times 0.15 \times 0.09 \text{ mm}$
$\beta = 87.90 (3)^\circ$	

Data collection

Rigaku Saturn 724 CCD area-detector diffractometer	4598 measured reflections
Absorption correction: numerical (RAPID-AUTO; Rigaku, 1998)	2308 independent reflections
$T_{\min} = 0.20, T_{\max} = 0.47$	2290 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.050$	$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$
2308 reflections	
199 parameters	
9 restraints	

Three reflections [(110), (111) and $(\bar{1}66)$] were omitted from the refinement due to high values of $\Delta F^2/\text{s.u.}$ (16.90, 13.35 and 18.32, respectively): since $F_o^2 \ll F_c^2$, for the first two (low-angle) reflections this may be due to the use of an inappropriate beam stop mask file for data reduction. These reflections were omitted in the refinement. H atoms bonded to C atoms were refined in idealized positions using the riding-model approximation, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the coordinated water molecules were located in difference maps and refined with an O—H distance

Table 1
Selected geometric parameters (Å, °).

Gd1—O1W	2.368 (3)	Gd1—O3W	2.451 (3)
Gd1—O2	2.370 (3)	Gd1—O2W	2.471 (3)
Gd1—O5	2.415 (3)	Gd1—O2 ⁱⁱ	2.820 (3)
Gd1—O7 ⁱ	2.418 (2)	S1—O4	1.454 (3)
Gd1—O6	2.429 (2)	S1—O3	1.454 (3)
Gd1—O1 ⁱⁱ	2.433 (3)	S1—O5	1.467 (3)
O1W—Gd1—O2	72.97 (9)	O7 ⁱ —Gd1—O3W	93.85 (10)
O1W—Gd1—O5	125.62 (10)	O6—Gd1—O3W	143.70 (9)
O2—Gd1—O5	74.39 (9)	O1 ⁱⁱ —Gd1—O3W	134.03 (10)
O1W—Gd1—O7 ⁱ	145.33 (9)	O1W—Gd1—O2W	73.36 (10)
O2—Gd1—O7 ⁱ	141.66 (9)	O2—Gd1—O2W	145.70 (9)
O5—Gd1—O7 ⁱ	78.34 (9)	O5—Gd1—O2W	122.03 (10)
O1W—Gd1—O6	136.48 (9)	O7 ⁱ —Gd1—O2W	72.37 (9)
O2—Gd1—O6	81.26 (9)	O6—Gd1—O2W	129.33 (9)
O5—Gd1—O6	77.70 (9)	O1 ⁱⁱ —Gd1—O2W	69.29 (10)
O7 ⁱ —Gd1—O6	66.86 (9)	O3W—Gd1—O2W	65.35 (10)
O1W—Gd1—O1 ⁱⁱ	84.13 (11)	O1W—Gd1—O2 ⁱⁱ	69.10 (9)
O2—Gd1—O1 ⁱⁱ	113.26 (9)	O2—Gd1—O2 ⁱⁱ	64.83 (10)
O5—Gd1—O1 ⁱⁱ	149.37 (10)	O5—Gd1—O2 ⁱⁱ	129.63 (8)
O7 ⁱ —Gd1—O1 ⁱⁱ	79.11 (9)	O7 ⁱ —Gd1—O2 ⁱⁱ	117.65 (8)
O6—Gd1—O1 ⁱⁱ	74.51 (10)	O6—Gd1—O2 ⁱⁱ	68.33 (8)
O1W—Gd1—O3W	76.45 (10)	O1 ⁱⁱ —Gd1—O2 ⁱⁱ	48.45 (8)
O2—Gd1—O3W	100.30 (11)	O3W—Gd1—O2 ⁱⁱ	145.11 (9)
O5—Gd1—O3W	68.12 (9)	O2W—Gd1—O2 ⁱⁱ	108.28 (9)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA···O3 ⁱⁱⁱ	0.84 (2)	1.82 (2)	2.636 (4)	165 (4)
O1W—H1WB···O6 ⁱⁱ	0.83 (2)	1.94 (2)	2.750 (4)	163 (4)
O2W—H2WA···O1 ^{iv}	0.86 (2)	1.94 (2)	2.779 (4)	168 (4)
O2W—H2WB···O3 ⁱⁱⁱ	0.84 (2)	2.47 (4)	2.983 (4)	120 (4)
O3W—H3WA···O4 ⁱⁱⁱ	0.85 (2)	2.27 (3)	3.080 (4)	160 (5)
O3W—H3WB···O4 ^v	0.85 (2)	1.96 (2)	2.787 (4)	164 (4)

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

restraint of 0.85 (2) Å and an H···H distance restraint of 1.34 (2) Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXL97* and *pubCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3047). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brandenburg, K. (2004). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Chagas, L. H., Janczak, J., Gomes, F. S., Fernandes, N. G., de Oliveira, L. F. C. & Diniz, R. (2008). *J. Mol. Struct.* **892**, 305–310.
- Huang, W., Wu, D., Zhou, P., Yan, W., Guo, D., Duan, C. & Meng, Q. (2009). *Cryst. Growth Des.* **9**, 1361–1369.
- Kido, J. & Okamoto, Y. (2002). *Chem. Rev.* **102**, 2357–2368.
- Li, X., Wang, C.-Y. & Hu, H.-M. (2008). *Inorg. Chem. Commun.* **11**, 345–348.
- Li, X.-H. & Yang, S.-Z. (2004). *Acta Cryst.* **C60**, m423–m425.
- Li, Y., Zheng, F.-K., Liu, X., Zou, W.-Q., Guo, G.-C., Lu, C.-Z. & Huang, J.-S. (2006). *Inorg. Chem.* **45**, 6308–6316.
- Manna, S. C., Zangrando, E., Bencini, A., Benelli, C. & Chaudhuri, N. R. (2006). *Inorg. Chem.* **45**, 9114–9122.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2002). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Song, J.-L., Lei, C. & Mao, J.-G. (2004). *Inorg. Chem.* **43**, 5630–5634.
- Su, W., Bi, W.-H., Li, X. & Cao, R. (2005). *Acta Cryst.* **C61**, m16–m18.
- Tsukube, H. & Shinoda, S. (2002). *Chem. Rev.* **102**, 2389–2404.
- Wan, C.-Q., Li, X., Wang, C.-Y. & Qiu, X. (2009). *J. Mol. Struct.* **930**, 32–36.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Xiao, H.-P., Li, X.-H. & Hu, M.-L. (2005). *Acta Cryst.* **E61**, m506–m508.
- Zhao, X., Zhu, G., Fang, Q., Wang, Y., Sun, F. & Qiu, S. (2008). *Cryst. Growth Des.* **9**, 737–742.