Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Was Bijvoet right? Sodium rubidium (+)-tartrate tetrahydrate revisited

Martin Lutz* and Antoine M. M. Schreurs

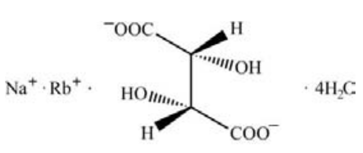
Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
Correspondence e-mail: m.lutz@uu.nl

Received 16 July 2008
Accepted 17 July 2008
Online 26 July 2008

The first determination of the absolute configuration of an organic compound was published in 1951 on sodium rubidium (+)-tartrate tetrahydrate, $Na^+ \cdot Rb^+ \cdot C_4H_4O_6^{2-} \cdot 4H_2O$, but the atomic coordinates are not available in the public literature. This structure has therefore been redetermined using current equipment. The most up-to-date techniques for the determination of the absolute configuration have been applied and the question posed in the title can be answered with an unequivocal 'yes'.

Comment

In their seminal experiment on sodium rubidium tartrate, (I), the group of Bijvoet (Peerdeman *et al.*, 1951; Bijvoet *et al.*, 1951) performed the first determination of the absolute configuration of an organic compound. This experiment changed the history of organic chemistry, because the stereochemistry could now be determined by experiment. It also started a new era in X-ray crystallography, because molecular properties could now be related to the absolute configuration.



(I)

The Bijvoet experiment to determine the absolute configuration of the organic tartrate molecule made use of the resonant scattering effect, which had been discovered a few years before with the inorganic compound ZnS (Coster *et al.*, 1930). By choosing a wavelength close to the *K*-absorption edge, the equivalence of reflection intensities due to Friedel's law is broken and a difference of intensities occurs. Nowadays, these differences are often called 'Bijvoet differences'. By comparing 15 of these differences from the diffraction experiment with the differences calculated from the structural model, Bijvoet *et al.* (1951) could confirm that the arbitrary Fischer nomenclature and absolute structure assignment for the organic stereochemistry were actually correct.

The experimental X-ray data used by Bijvoet *et al.* (1951) were measured with monochromated Zr radiation and obtained from a first layer (001) Weissenberg diagram. The structural model and atomic coordinates were taken from a Cu experiment by Beevers & Hughes (1941). These atomic coordinates, which are also given in the PhD thesis of Peerdeman (1955), are not available in the Cambridge Structural Database (Allen, 2002). Interestingly, newer X-ray crystal structure determinations of (I) are also absent from this database. We therefore decided to redetermine the crystal structure with modern equipment and experimental conditions, and to apply current methods and algorithms for the absolute structure determination.

The crystal structure of (I) is isomorphous with the corresponding sodium potassium tartrate (Rochelle salt or Seignette's salt) and sodium ammonium tartrate (ammonium Rochelle salt). The crystal structures of these salts have been described before (Brożek & Stadnicka, 1994; Brożek *et al.*, 1994; Suzuki, Muta *et al.*, 1996; Suzuki, Kabasawa *et al.*, 1996; Solans *et al.*, 1997). The rubidium ions are located on two independent special positions on twofold rotation axes (Wyckoff positions *a* and *b*) and the sodium ions are on general positions. Therefore, the overall composition in the asymmetric unit is one tartrate anion, one sodium ion, two half rubidium ions and four water molecules (Fig. 1).

The crystal structure consists of alternating layers of metal coordination polyhedra and hydrogen-bonded tartrate–water networks, which are both parallel to the crystallographic *ac* plane (Fig. 2). Atom Rb1 has a very large variation in Rb—O distances. It is thus difficult to define its first coordination sphere. We assume for atom Rb1 a sixfold coordination with a severely distorted octahedral geometry, but it should be noted that the Rb—O distances of 3.4088 (18) and 3.5925 (15) Å, which we consider to be in the second coordination sphere, are also quite short. For atom Rb2, the range of Rb—O distances is more narrow and we consider this ion as eight-coordinated

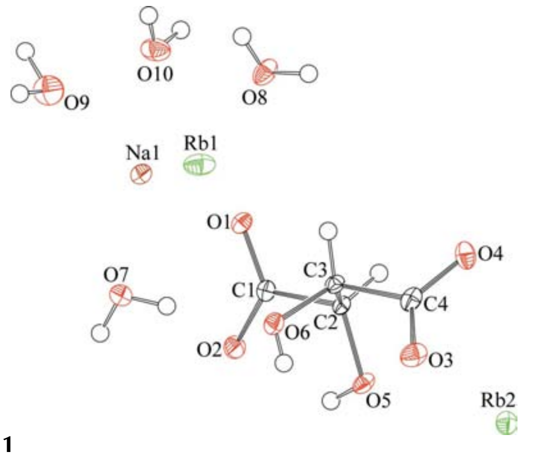


Figure 1
A displacement ellipsoid plot of (I), showing the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres with arbitrary radii.

doi:10.1107/S0108270108022415

with a bicapped trigonal prismatic geometry. Atom Na1 has a distorted octahedral geometry.

The tartrate molecule has no molecular symmetry. The O1—C1—C2—C3 and O4—C4—C3—C2 torsion angles, which should be equal in the case of twofold symmetry, differ by 10.4 (2)°. Both carboxylate groups are deprotonated, while the hydroxy groups are still protonated. Atoms O2 of a carboxylate group and O6 of a hydroxy group are not directly coordinated to an alkali metal ion, but there is no difference in C—O distances compared with the corresponding coordinated atoms. The uncoordinated O6 atom is an acceptor of two hydrogen bonds, in contrast to the coordinated O5 atom, which does not accept hydrogen bonds. The hydrogen bonds between the tartrate ions and the water molecules, with the exception of water molecule O8, form a complicated two-dimensional network, which is located between the layers of coordination polyhedra. The coordination polyhedra are linked in the *b* direction *via* the hydrogen-bonded network, and *vice versa*. Water molecule O8 is an exception, because it does not belong to the two-dimensional hydrogen-bonded network but is coordinated to three alkali metal ions and is a linker between the water–tartrate layers. Atom O8 does not accept hydrogen bonds but is a donor of two. The geometry of the hydrogen bonds (Table 2) corresponds well with the published data (Solans *et al.*, 1997). Atoms C2 and C3 both have the *R* configuration, which is established from the enantiopure starting material and by the absolute structure determination in the X-ray diffraction experiment (see below).

In the original Bijvoet experiment, Zr radiation with a wavelength of 0.788 Å was used because it is close to the *K*-absorption limit of rubidium (0.814 Å; Peerdeman, 1955). This led to values of −3.1 and 3.2 for f' and f'', respectively. With the software *SCATFAC* (Laugier & Bochu, 2002), using the method of Waasmaier & Kirfel (1995), newer values for f' and f'' are calculated as −2.523 and 3.535, respectively, and the latest edition of the *International Tables for Crystallography* (Deslattes *et al.*, 2004) gives a theoretical value of 0.815270 (12) Å for the *K*-absorption edge of Rb. In the present diffraction experiment of (I), we used Mo radiation with a wavelength of 0.71073 Å, which is more readily available but is slightly further away from the rubidium *K*-absorption edge. Therefore, the magnitudes of f' and f'' are somewhat smaller, at −0.953 and 2.928, respectively.

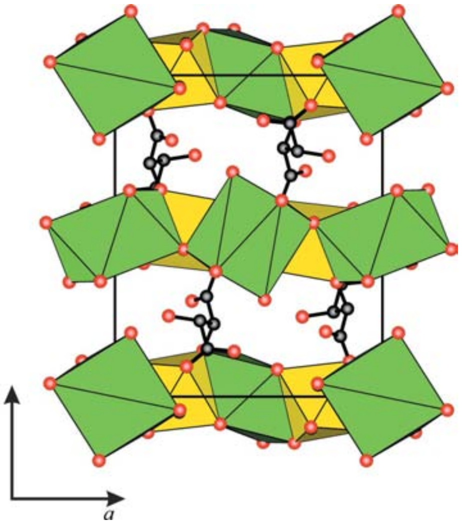


Figure 2
The packing of (I) in the unit cell, viewed along the crystallographic *c* axis. Coordination polyhedra of Rb are shown in mid-grey (green in the electronic version of the paper) and those of Na in pale grey (yellow).

In a careful analysis of absolute structure determinations by Flack & Shmueli (2007), it has been shown that not only the strongest resonant scatterers but all atoms in the unit cell must be taken into account. That publication introduces a parameter, Friedif, in order to make an *a priori* estimation of the Bijvoet differences on the basis of the composition of the crystal. For (I), we calculate Friedif as 1302×10^{-4} and 1096×10^{-4} for Zr and Mo radiation. A search for additional symmetry using the ADDSYM routine of *PLATON* (Spek, 2003) shows that the Rb and Na atoms have a centrosymmetric substructure [100% fit to space group *Pmmn* after an origin shift of $(\frac{1}{4}, \frac{1}{4}, 0)$]. This centrosymmetric substructure can be taken into account in the calculation of Friedif (Flack & Shmueli, 2007), which is then 1216×10^{-4} and 1024×10^{-4} for Zr and Mo radiation.

The Bijvoet differences for the 15 reflections reported in the original papers (see above) were recalculated with the present Mo radiation data of (I). Despite the different wavelength in the present experiment, all signs of $\Delta_{\rm obs}$ comply with the corresponding $\Delta_{\rm calc}$ values (Table 3). The magnitudes of $\Delta_{\rm obs}$ and $\Delta_{\rm calc}$ are also very similar, but the magnitudes are less important for the absolute structure determination. By using the same methodology and the same 15 reflections as in the 50-year old experiment we could confirm the absolute configuration of (I).

As introduced by Flack (1983), every noncentrosymmetric crystal structure can be refined as an inversion twin. The observed intensities *I* then have contributions from both individuals, $I(h,k,l,x) = (1-x)|\mathrm{F}(h,k,l)|^2 + x|\mathrm{F}(\overline{h},\overline{k},\overline{l})|^2$, and the Flack parameter x can be refined in the least-squares refinement together with other structural parameters, such as, for example, atomic coordinates and displacement parameters. The standard uncertainty u obtained from this refinement is a measure of the inversion-distinguishing power (Flack & Bernardinelli, 2000). To avoid an underestimation of u, we included TWIN/BASF cards in the instruction file. The refined value of x for (I) is −0.007 (6), confirming the enantiopurity of the crystal and the correct absolute structure. The standard uncertainty (< 0.04) is small enough to characterize the inversion-distinguishing power as strong.

Hooft *et al.* (2008) introduced a method that can be considered as a further development of the original Bijvoet idea. With this new approach, not only a small subset of 15 reflections is used, but the Bijvoet differences are calculated for all Bijvoet pairs present. By the application of Bayesian statistics, it is possible to extract valuable information from these differences, even in the case of weak anomalous scattering power. With this method, a value of y can be derived

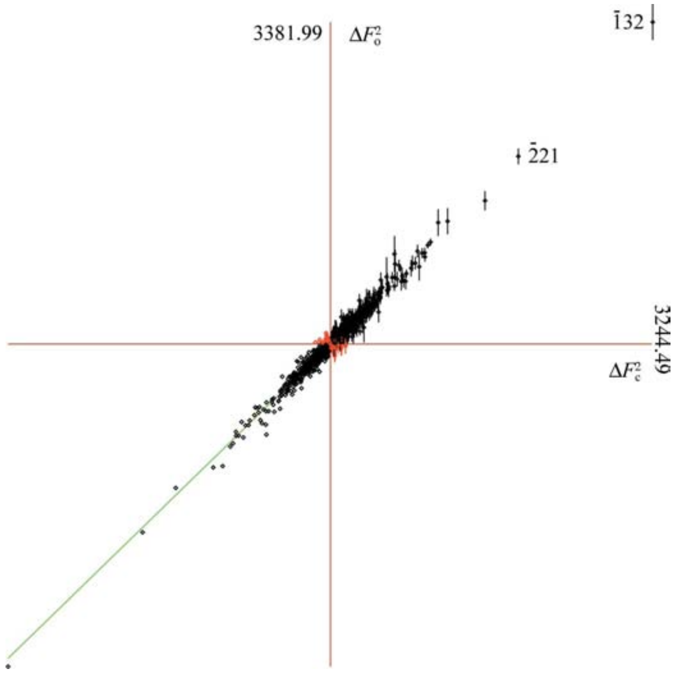


Figure 3
A scatter plot of Bijvoet differences, prepared using the program *PLATON* (Spek, 2003). Shown are 934 pairs where $\Delta_{obs} > 0.25\sigma(\Delta_{obs})$. 842 reflections confirming the absolute structure are shown in black. 92 reflections with the wrong sign (at the centre of the plot) are shown in grey (red in the electronic version of the paper).

from a probability distribution of differences $(\Delta_{obs} - \Delta_{calc})/\sigma_\Delta$; y has a physical range between 0.0 and 1.0, and its behaviour is thus comparable to that of the Flack x parameter. Because y is calculated from the F_o^2/F_c^2 listing, y is not part of the least-squares refinement and is thus not affected by correlations with the atomic parameters. For (I), we determine $y = -0.011$ (4), again confirming the enantiopurity and correctness of the absolute configuration. The completeness of Friedel pairs is 99.9%. A plot of 934 Bijvoet pairs with significant Bijvoet differences is shown in Fig. 3. Besides the confirmation of the absolute structure, this plot shows that the largest Bijvoet differences are for the reflections $\bar{1}32$ and $\bar{2}21$, which both have the correct sign. They do not belong to the selection of 15 reflections in the original Bijvoet experiment.

The program *DIRDIF2008* (Beurskens *et al.*, 2008) calculates a Bijvoet coefficient B for the 100 strongest Bijvoet pairs. Thereby B is a weighted average of the signs of the Bijvoet differences. The expected range of B is between -1.0 for the wrong and $+1.0$ for the correct assignment of the absolute configuration. For the calculation of B we used an atomic model with isotropic displacement parameters and without the contribution of H atoms. For (I), a value of 1.000 is obtained for B, which is another confirmation of the correct absolute configuration.

Experimental

A solution of (+)-tartaric acid (BDH Chemicals Ltd, Poole, England) in water was heated to 333 K, and an aqueous solution of equimolar amounts of sodium carbonate and rubidium carbonate was added dropwise. At first, rubidium hydrogen tartrate precipitated. Addition of the carbonate solution was continued until the evolution of CO_2 stopped and the initial precipitate had completely redissolved. This solution was then left at room temperature until a white solid formed. Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from a minimum amount of water.

Crystal data

$Na^+\cdot Rb^+\cdot C_4H_4O_6^{2-}\cdot 4H_2O$
$M_r = 328.60$
Orthorhombic, $P2_12_12$
$a = 11.9764$ (4) Å
$b = 14.3836$ (3) Å
$c = 6.22447$ (16) Å
$V = 1072.25$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.70$ mm^{-1}
$T = 150$ (2) K
0.39 × 0.19 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min} = 0.161$, $T_{max} = 0.862$
15473 measured reflections
2477 independent reflections
2305 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.041$
$S = 1.04$
2477 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Absolute structure: Flack (1983), 1023 Bijvoet pairs
Flack parameter: -0.007 (6)

Table 1
Selected bond lengths (Å).

O1—Rb1	2.9279 (14)	Na1—O1	2.3571 (16)
O8—Rb1	3.1235 (17)	Na1—O3^{iv}	2.4646 (17)
O9—Rb1	2.9848 (19)	Na1—O5^{iv}	2.4914 (18)
O4—Rb2^{i}	2.9090 (15)	Na1—O7	2.3517 (18)
O5—Rb2	3.0804 (15)	Na1—O8^{v}	2.3742 (18)
O7—Rb2^{ii}	2.9067 (16)	Na1—O10	2.3670 (19)
O8—Rb2^{iii}	3.1485 (17)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O2	0.79 (3)	2.05 (3)	2.613 (2)	128 (3)
O6—H6···O10^{vi}	0.72 (3)	2.16 (3)	2.861 (3)	164 (3)
O7—H7*A*···O4^{ii}	0.82 (3)	2.07 (3)	2.860 (2)	164 (3)
O7—H7*B*···O6	0.86 (4)	1.94 (4)	2.796 (2)	176 (3)
O8—H8*A*···O3^{vii}	0.93 (4)	1.80 (4)	2.725 (2)	171 (3)
O8—H8*B*···O2^{viii}	0.79 (3)	1.99 (3)	2.774 (2)	171 (3)
O9—H9*A*···O4^{ix}	0.93 (3)	1.85 (3)	2.774 (2)	171 (3)
O9—H9*B*···O2^{x}	0.76 (3)	2.52 (3)	3.115 (2)	136 (3)
O9—H9*B*···O6^{iv}	0.76 (3)	2.52 (3)	3.156 (2)	142 (3)
O10—H10*A*···O1^{viii}	0.91 (3)	1.84 (3)	2.739 (2)	168 (2)
O10—H10*B*···O9^{i}	0.76 (3)	2.02 (3)	2.770 (3)	170 (3)

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

Table 3
Bijvoet differences in the crystal structure of (I).

Reflection	$F_o^2(h,k,l)$	$F_o^2(\bar{h},k,l)$	Δ_{obs}	$\sigma(\Delta_{obs})$	$F_c^2(h,k,l)$	$F_c^2(\bar{h},k,l)$	Δ_{calc}
141	6546.37	6761.12	−214.75	75.17	6569.55	6824.29	−254.74
151	6905.09	6486.45	418.64	79.90	6581.94	6134.25	447.69
161	4676.63	3719.27	957.36	55.10	4709.50	3760.50	949.00
171	761.51	917.89	−156.38	15.05	744.25	898.29	−154.04
181	2474.59	2033.86	440.73	32.86	2442.44	2019.21	423.23
191	817.16	631.86	185.30	17.95	825.31	627.54	197.77
1 10 1	3428.88	2730.17	698.71	58.52	3403.61	2783.06	620.55
1 11 1	571.83	722.81	−150.98	22.66	613.17	785.54	−172.37
261	13202.80	13029.56	173.24	156.80	13370.54	13033.50	337.04
271	376.87	188.15	188.72	7.71	379.07	186.61	192.46
281	10838.50	10497.45	341.05	126.49	10929.83	10576.59	353.24
291	2103.15	2072.87	30.28	32.10	2114.96	2051.87	63.09
2 10 1	2678.23	2703.29	−25.06	52.68	2747.83	2834.49	−86.66
2 11 1	2144.49	2128.70	15.79	48.85	2206.86	2149.25	57.61
2 12 1	4811.18	5154.51	−343.33	97.55	4675.26	5067.49	−392.23

Notes: The values of F_c^2 are taken from a *SHELXL97* (Sheldrick, 2008) refinement without a TWIN/BASF instruction. $\sigma^2(\Delta_{obs}) = \sigma^2[F_o^2(h,k,l)] + \sigma^2[F_o^2(\bar{h},k,l)]$.

All H atoms were located in difference Fourier maps. H atoms bonded to C atoms were kept fixed on their located positions, with U_{iso}(H) values of 0.05 Å^2, and C—H distances of 0.94 and 0.99 Å. H atoms bonded to O atoms were refined freely with isotropic displacement parameters, giving a range of O—H distances of 0.72 (3)–0.93 (4) Å. TWIN/BASF instructions were included in the refinement for the determination of the Flack (1983) parameter.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *PEAKREF* (Schreurs, 2008); data reduction: *EVAL15* (Xian *et al.*, 2006); program(s) used to solve structure: initial coordinates taken from the literature (Peerdeman, 1955); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *DRAWxtl* (Finger *et al.*, 2007); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO). We acknowledge Dr H. H. Kubbinga for initiating this study, Professor A. L. Spek for fruitful discussions and Professor J. D. Dunitz for encouraging us to publish the results.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3231). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Beevers, C. A. & Hughes, W. (1941). *Proc. R. Soc. London Ser. A*, **177**, 251–259.

Beurskens, P. T., Beurskens, G., de Gelder, R., Garcia-Granda, S., Gould, R. O. & Smits, J. M. M. (2008). *The DIRDIF2008 Program System*. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Bijvoet, J. M., Peerdeman, A. F. & van Bommel, A. J. (1951). *Nature* (*London*), **168**, 271–273.

Brożek, Z., Mucha, D. & Stadnicka, K. (1994). *Acta Cryst.* B**50**, 465–472.

Brożek, Z. & Stadnicka, K. (1994). *Acta Cryst.* B**50**, 59–68.

Coster, D., Knol, K. S. & Prins, J. A. (1930). *Z. Phys.* **63**, 345–369.

Deslattes, R. D., Kessler, E. G. Jr, Indelicato, P. & Lindroth, E. (2004). *International Tables for Crystallography*, Vol. C, 3rd ed., edited by E. Prince, pp. 200–212. Dordrecht: Kluwer Academic Publishers.

Finger, L. W., Kroeker, M. & Toby, B. H. (2007). *J. Appl. Cryst.* **40**, 188–192.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.

Flack, H. D. & Shmueli, U. (2007). *Acta Cryst.* A**63**, 257–265.

Hooft, R. W. W., Straver, L. H. & Spek, A. L. (2008). *J. Appl. Cryst.* **41**, 96–103.

Laugier, J. & Bochu, B. (2002). *SCATFAC*. Laboratoire des Matériaux et du Génie Physique, Grenoble, France.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Peerdeman, A. F. (1955). PhD thesis, Utrecht University, The Netherlands.

Peerdeman, A. F., van Bommel, A. J. & Bijvoet, J. M. (1951). *Proc. R. Acad. Amsterdam Ser. B*, **54**, 16–19.

Schreurs, A. M. M. (2008). *PEAKREF*. Utrecht University, The Netherlands.

Sheldrick, G. M. (2002). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Solans, X., Gonzalez-Silgo, C. & Ruiz-Pérez, C. (1997). *J. Solid State Chem.* **131**, 350–357.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Suzuki, E., Kabasawa, H., Honma, T., Nozaki, R. & Shiozaki, Y. (1996). *Acta Cryst.* B**52**, 976–981.

Suzuki, E., Muta, T., Nozaki, R. & Shiozaki, Y. (1996). *Acta Cryst.* B**52**, 296–302.

Waasmaier, D. & Kirfel, A. (1995). *Acta Cryst.* A**51**, 416–431.

Xian, X., Schreurs, A. M. M. & Kroon-Batenburg, L. M. J. (2006). *Acta Cryst.* A**62**, s92.