Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The structures of the α-alums $RbCr(SO_4)_2\cdot 12H_2O$ and $CsCr(SeO_4)_2\cdot 12H_2O$ at 293 and 12 K

Brian N. Figgis,[a]* Philip A. Reynolds[b] and Alexandre N. Sobolev[a]

[a]Chemistry Department, University of Western Australia, Nedlands, WA 6907, Australia, and [b]Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia
Correspondence e-mail: bnf@crystal.uwa.edu.au

Received 6 December 1999
Accepted 2 April 2000

The crystal structures of the α-alums rubidium chromium bis(sulfate) dodecahydrate, $RbCr(SO_4)_2\cdot 12H_2O$, and caesium chromium bis[tetraoxoselenate(VI)] dodecahydrate, $CsCr(SeO_4)_2\cdot 12H_2O$, have been determined by X-ray diffraction at 293 and 12 K. The metal atoms lie on $\overline{3}$ sites and the anions lie on threefold rotation axes. The accurate and extensive data sets lead to much more precise determinations than are available from earlier work, particularly at 12 K. The changes in the atomic displacement parameters between 293 and 12 K correspond to the respective predominances of intermolecular and intramolecular vibrational effects.

Comment

The alums $M^{I}M^{III}(XO_4)_2\cdot 12H_2O$, like Elpasolites and Tutton salts, have played a significant role in research in physics and chemistry. In particular, the systems have been invaluable for examination of metal ions in various well defined site symmetries in native and doped single crystals.

There are many previous structural studies of alums by X-ray diffraction at room temperature. They adopt the space group $Pa\overline{3}$ and occur in α, β and γ forms. $RbCr(SO_4)_2\cdot 12H_2O$ has been studied only by film methods (Ledsham & Steeple, 1969) and $CsCr(SeO_4)_2\cdot 12H_2O$ somewhat more accurately (Armstrong *et al.*, 1990). In these two studies, the X—O and M—O bond length s.u.'s vary in the range 0.003–0.006 Å. Lower temperatures are of considerable interest to spectroscopic studies such as those of Tregenna-Piggott & Best (1996) and Tregenna-Piggott *et al.* (1997), and some others we have in hand, and serve to improve the accuracy of the structural determination.

There have been a number of neutron diffraction studies of both α- and β-alums at 15 K which show no abnormal behaviour or phase change resulting from the lowering in temperature. There is increased accuracy, not only in hydrogen, but also non-hydrogen, parameters compared to room-temperature X-ray studies (Best & Forsyth, 1990*a*,*b*, 1991; Best *et al.*, 1993).

We have determined the crystal structures of two α-alums of interest by X-ray diffraction at 293 and 12 K. The results illustrate the much improved accuracy, involving a factor mostly much greater than two in s.u.'s for non-H atoms which result from the lower temperature of the measurements. The crystal geometries are all typical of alums. The angle between the Cr—O bond and the unit-cell axis varies from 4.6 to 6.1°, the O11—M^{I}—O11′ angle varies from 65.7 to 66.2°, and the water molecules are twisted well out of the CrO_4 planes by an average value of 21 (3)° (Figs. 1*a* and 1*b*). These are distinct from the angles near 0 and 60° observed for β-alums (Beattie *et al.*, 1981).

The Cr—O bond lengths we observe apparently lengthen, due to reduced libration, from 1.960 (2) to 1.966 (1) Å as we lower the temperature from 293 to 12 K. This length agrees with that in the neutron determination of $CsCr(SO_4)_2\cdot 12H_2O$ of 1.961 (2) Å (Best & Forsyth, 1990*b*). Of the alums measured at low temperatures, the distortions of the CrO_6 fragments from octahedral stereochemistry that we observe in our compounds at 12 K are greater than the average observed by neutron diffraction.

The atomic displacement parameters at 12 K (Fig. 1*b*) show no evidence of intermolecular effects. It is well known that zero-point motion, such as we are seeing here, is dominated by intramolecular vibrational modes (Willis & Pryor, 1975). Thus, we can make the following predictions: (i) for Cr, S or Se, and Rb or Cs we should see relatively small (0.006–0.008 Å^2) and isotropic displacement ellipsoids; (ii) the O principal axes should be aligned with local bonding symmetry; (iii) terminal atoms (O1–O2) should be relatively isotropic perpendicular to the bond, and because of the relative frequencies of bond stretching and bending, motion perpendicular to the bond

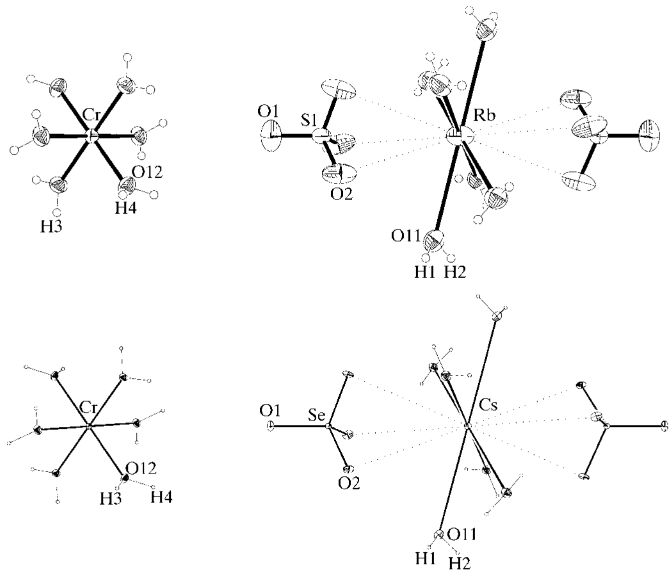

Figure 1
Environments of the atoms in (*a*) $RbCr(SO_4)_2\cdot 12H_2O$ at 293 K and (*b*) $CsCr(SeO_4)_2\cdot 12H_2O$ at 12 K. Displacement ellipsoids are shown at the 50% probability level.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

should exceed that parallel to it; (iv) the O12 displacement out of the approximate Cr—OH$_2$ plane should be larger than the plane motion. All these predictions are borne out by experiment. Since these motions are so small, this is an excellent internal test of the reliability of the measured diffraction intensities and their interpretation. We note that these requirements are *more* stringent than the bond rigidity tests that are commonly used at higher temperatures. The thermal motion at 293 K is greatly increased from 12 K (Fig. 1*a*).

Experimental

Single crystals of the alums were obtained by recrystallization from aqueous solutions.

$RbCr(SO_4)_2 \cdot 12H_2O$ at 293 K

Crystal data

$RbCr(SO_4)_2 \cdot 12H_2O$
$M_r = 545.78$
Cubic, $Pa\overline{3}$
$a = 12.296$ (2) Å
$V = 1859.1$ (5) Å^3
$Z = 4$
$D_x = 1.950$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 16.88$–$17.56°$
$\mu = 3.531$ mm^{-1}
$T = 293$ (2) K
Cube, pink
0.462 × 0.458 × 0.443 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: Gaussian (*Xtal*3.4; Hall *et al.*, 1994)
$T_{\min} = 0.360$, $T_{\max} = 0.420$
1655 measured reflections
557 independent reflections
444 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.01°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 0$
3 standard reflections every 100 reflections intensity decay: 0.5%

Table 1
Selected geometric parameters (Å, °) for $RbCr(SO_4)_2 \cdot 12H_2O$ at 293 K.

Rb—O11	3.082 (3)	S1—O1	1.442 (6)
Rb—O2	3.739 (4)	S1—O2	1.465 (3)
Cr—O12	1.960 (2)		
O11—Rb—O11$^{\rm i}$	65.68 (4)	O12—Cr—O12$^{\rm iii}$	89.13 (10)
O11—Rb—O11$^{\rm ii}$	114.32 (4)	O12—Cr—O12$^{\rm ii}$	90.87 (10)
O11—Rb—O2	61.17 (7)	O1—S1—O2	109.97 (15)
O2—Rb—O2$^{\rm ii}$	37.21 (7)	O2—S1—O2$^{\rm ii}$	108.96 (15)

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

Table 2
Hydrogen-bonding geometry (Å, °) for $RbCr(SO_4)_2 \cdot 12H_2O$ at 293 K.

D—H···A	D—H	H···A	D···A	D—H···A
O11—H1···O1$^{\rm i}$	0.813 (10)	2.011 (12)	2.821 (4)	175 (4)
O11—H2···O2$^{\rm ii}$	0.814 (10)	1.956 (14)	2.763 (4)	171 (5)
O12—H3···O2$^{\rm iii}$	0.822 (10)	1.800 (11)	2.621 (4)	178 (5)
O12—H4···O11$^{\rm iv}$	0.820 (10)	1.803 (12)	2.620 (4)	174 (4)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.080$
$S = 1.046$
557 reflections
55 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 4.4211P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0249 (15)

$RbCr(SO_4)_2 \cdot 12H_2O$ at 12 K

Crystal data

$RbCr(SO_4)_2 \cdot 12H_2O$
$M_r = 545.78$
Cubic, $Pa\overline{3}$
$a = 12.241$ (2) Å
$V = 1834.2$ (5) Å^3
$Z = 4$
$D_x = 1.976$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 16.88$–$17.56°$
$\mu = 3.578$ mm^{-1}
$T = 12$ (2) K
Cube, pink
0.462 × 0.458 × 0.443 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: Gaussian (*Xtal*3.4; Hall *et al.*, 1994)
$T_{\min} = 0.340$, $T_{\max} = 0.403$
4175 measured reflections
905 independent reflections
812 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 30.02°$
$h = -7 \rightarrow 17$
$k = -7 \rightarrow 17$
$l = -7 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: 0.5%

Table 3
Selected geometric parameters (Å, °) for $RbCr(SO_4)_2 \cdot 12H_2O$ at 12 K.

Rb—O11	3.039 (1)	S1—O1	1.479 (2)
Rb—O2	3.704 (1)	S1—O2	1.4798 (9)
Cr—O12	1.965 (1)		
O11—Rb—O11$^{\rm i}$	65.798 (15)	O12—Cr—O12$^{\rm iii}$	88.78 (4)
O11—Rb—O11$^{\rm ii}$	114.202 (15)	O12—Cr—O12$^{\rm ii}$	91.22 (4)
O11—Rb—O2	60.15 (2)	O1—S1—O2	109.77 (4)
O2—Rb—O2$^{\rm ii}$	38.00 (2)	O1—S1—O2$^{\rm ii}$	109.77 (4)

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

Table 4
Hydrogen-bonding geometry (Å, °) for $RbCr(SO_4)_2 \cdot 12H_2O$ at 12 K.

D—H···A	D—H	H···A	D···A	D—H···A
O11—H1···O1$^{\rm i}$	0.78 (3)	2.04 (3)	2.7933 (15)	162 (2)
O11—H2···O2$^{\rm ii}$	0.76 (2)	2.02 (2)	2.7541 (15)	166 (2)
O12—H3···O2$^{\rm iii}$	0.81 (3)	1.83 (3)	2.6321 (14)	171 (2)
O12—H4···O11$^{\rm iv}$	0.83 (3)	1.79 (3)	2.6087 (14)	171 (3)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.045$
$S = 1.094$
905 reflections
55 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2 + 1.4261P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0119 (4)

$CsCr(SeO_4)_2{\cdot}12H_2O$ at 293 K

Crystal data

$CsCr(SeO_4)_2{\cdot}12H_2O$
$M_r = 687.02$
Cubic, $Pa\overline{3}$
$a = 12.585$ (1) Å
$V = 1993.2$ (3) Å^3
$Z = 4$
$D_x = 2.289$ Mg m^{-3}
Mo $K\alpha$ radiation

Cell parameters from 14 reflections
$\theta = 16.40$–$17.06°$
$\mu = 6.110$ mm^{-1}
$T = 293$ (2) K
Prism, dark violet
0.65 × 0.64 × 0.63 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: Gaussian (*Xtal*3.4; Hall *et al.*, 1994)
$T_{\min} = 0.138$, $T_{\max} = 0.189$
1751 measured reflections
589 independent reflections
549 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.020$
$\theta_{\max} = 25.00°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 0$
3 standard reflections every 100 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.044$
$S = 1.259$
589 reflections
55 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 0.7907P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0166 (6)

Table 5
Selected geometric parameters (Å, °) for $CsCr(SeO_4)_2{\cdot}12H_2O$ at 293 K.

Cs—O11	3.232 (2)	Se—O1	1.627 (4)
Cs—O2	3.782 (2)	Se—O2	1.634 (2)
Cr—O12	1.963 (2)		
O11—Cs—O11^{i}	66.16 (3)	O12—Cr—O12^{iii}	89.13 (8)
O11—Cs—O11^{ii}	113.84 (3)	O12—Cr—O12^{ii}	90.87 (8)
O11—Cs—O2	59.79 (5)	O1—Se—O2	110.16 (8)
O2—Cs—O2^{ii}	41.13 (5)	O2—Se—O2^{ii}	108.77 (8)

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

Table 6
Hydrogen-bonding geometry (Å, °) for $CsCr(SeO_4)_2{\cdot}12H_2O$ at 293 K.

D—H···A	D—H	H···A	D···A	D—H···A
O11—H1···O1^{i}	0.811 (10)	2.018 (14)	2.811 (3)	166 (4)
O11—H2···O2^{ii}	0.815 (10)	1.949 (14)	2.753 (3)	169 (4)
O12—H3···O2^{iii}	0.817 (10)	1.821 (11)	2.635 (3)	175 (3)
O12—H4···O11^{iv}	0.822 (10)	1.803 (12)	2.620 (3)	173 (4)

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

Table 7
Selected geometric parameters (Å, °) for $CsCr(SeO_4)_2{\cdot}12H_2O$ at 12 K.

Cs—O11	3.202 (2)	Se—O1	1.641 (2)
Cs—O2	3.729 (2)	Se—O2	1.642 (1)
Cr—O12	1.966 (1)		
O11—Cs—O11^{i}	66.18 (2)	O12—Cr—O12^{iii}	88.97 (5)
O11—Cs—O11^{ii}	113.82 (2)	O12—Cr—O12^{ii}	91.03 (5)
O11—Cs—O2	58.92 (3)	O1—Se—O2	110.10 (5)
O2—Cs—O2^{ii}	41.98 (3)	O1—Se—O2^{ii}	110.10 (5)

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

$CsCr(SeO_4)_2{\cdot}12H_2O$ at 12 K

Crystal data

$CsCr(SeO_4)_2{\cdot}12H_2O$
$M_r = 687.02$
Cubic, $Pa\overline{3}$
$a = 12.522$ (3) Å
$V = 1963.5$ (8) Å^3
$Z = 4$
$D_x = 2.324$ Mg m^{-3}
Mo $K\alpha$ radiation

Cell parameters from 14 reflections
$\theta = 16.47$–$17.15°$
$\mu = 6.202$ mm^{-1}
$T = 12$ (2) K
Prism, dark violet
0.65 × 0.64 × 0.63 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: Gaussian (*Xtal*3.4; Hall *et al.*, 1994)
$T_{\min} = 0.132$, $T_{\max} = 0.188$
4443 measured reflections
963 independent reflections
916 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.033$
$\theta_{\max} = 29.98°$
$h = -7 \rightarrow 17$
$k = -7 \rightarrow 17$
$l = -7 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.042$
$S = 1.309$
963 reflections
55 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0122P)^2 + 2.1334P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0092 (3)

Table 8
Hydrogen-bonding geometry (Å, °) for $CsCr(SeO_4)_2{\cdot}12H_2O$ at 12 K.

D—H···A	D—H	H···A	D···A	D—H···A
O11—H1···O1^{i}	0.849 (10)	1.99 (2)	2.796 (2)	158 (4)
O11—H2···O2^{ii}	0.844 (10)	1.910 (12)	2.740 (2)	167 (3)
O12—H3···O2^{iii}	0.844 (10)	1.804 (11)	2.641 (2)	171 (3)
O12—H4···O11^{iv}	0.849 (10)	1.761 (10)	2.609 (2)	176 (3)

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

The room temperature and very low temperature data sets were collected on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henriksen *et al.*, 1986; Larsen, 1995). The temperature evolution of thermal motion is illustrated for the hexaaquachromium(III) and selenate molecular ions $CsCr(SeO_4)_2{\cdot}12H_2O$ in Fig. 1. The correction for the absorption by the beryllium shield was performed using the program *PROFIT* (Streltsov & Zavodnik, 1989).

For both compounds, data collection: local diffractometer control software; cell refinement: local diffractometer control software; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1983); software used to prepare material for publication: *SHELXTL*.

The authors thank Dr L. Dubicki of the Australian National University for providing the crystals of the alums. BNF and ANS are grateful to the Australian Research Council for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1280). Services for accessing these data are described at the back of the journal.

References

Armstrong, R. S., Beattie, J. K., Best, S. P., Braithwaite, G. P., Del Favero, P., Skelton, B. W. & White, A. H. (1990). *Aust. J. Chem.* **43**, 393–398.

Beattie, J. K., Best, S. P., Skelton, B. W. & White, A. H. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2105–2111.

Best, S. P. & Forsyth, J. B. (1990*a*). *J. Chem. Soc. Dalton Trans.* pp. 395–400.

Best, S. P. & Forsyth, J. B. (1990*b*). *J. Chem. Soc. Dalton Trans.* pp. 3507–3511.

Best, S. P. & Forsyth, J. B. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1721–1725.

Best, S. P., Forsyth, J. B. & Tregenna-Piggott, P. L. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2711–2715.

Hall, S. R., King, G. S. D. & Stewart, J. M. (1994). Editors. *Xtal*3.4 *User's Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Henriksen, K., Larsen, F. K. & Rasmussen, S. E. (1986). *J. Appl. Cryst.* **19**, 390–394.

Larsen, F. K. (1995). *Acta Cryst.* B**51**, 468–482.

Ledsham, A. H. C. & Steeple, H. (1969). *Acta Cryst.* B**25**, 398–400.

Sheldrick, G. M. (1983). *SHELXTL User's Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Streltsov, V. A. & Zavodnik, V. E. (1989). *Sov. Phys. Crystallogr.* **34**, 824–828.

Tregenna-Piggott, P. L.W. & Best, S. P. (1996). *Inorg. Chem.* **35**, 5730–5736.

Tregenna-Piggott, P. L.W., Best, S. P., O'Brien, M. C. M., Knight, K. S., Forsyth, J. B. & Pilbrow, J. R. (1997). *J. Am. Chem. Soc.* **119**, 3324–3332.

Willis, B. T. M. & Pryor, A. W. (1975). In *Thermal Vibrations in Crystallography*. Cambridge University Press.