

## Two crystals of doubly protonated melaminium salts: melaminium bis(trifluoroacetate) trihydrate and melaminium bis(trichloroacetate) dihydrate

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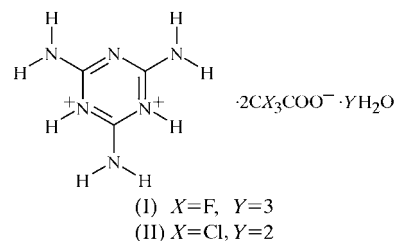
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Crystals of 2,4,6-triamino-1,3,5-triazine-1,3-dium bis(trifluoroacetate) trihydrate,  $C_3H_8N_6^{2+} \cdot 2CF_3COO^- \cdot 3H_2O$ , and 2,4,6-triamino-1,3,5-triazine-1,3-dium bis(trichloroacetate) dihydrate,  $C_3H_8N_6^{2+} \cdot 2CCl_3COO^- \cdot 2H_2O$ , both contain doubly protonated melamine rings that lie on crystallographic twofold axes. In the former structure, one water molecule also lies on a twofold axis. While the trifluoroacetate compound crystallizes in a centrosymmetric space group, the trichloroacetate is non-centrosymmetric, so it is useful as a material for non-linear optics. The efficiency of second harmonic generation is about three times greater than that of KDP ( $KH_2PO_4$ ). A combination of ionic and donor–acceptor hydrogen-bond interactions link the melaminium(2+) residues with trifluoroacetate or trichloroacetate ions and water molecules to form a three-dimensional network.

### Comment

The present study is a continuation of our investigations into the characterization of the hydrogen-bonding system formed by melamine in the solid state (Perpétuo & Janczak, 2005). Melamine and its derivatives and organic and inorganic complexes or salts can develop well defined non-covalent supramolecular architectures *via* multiple hydrogen bonds, since they contain complementary arrays of hydrogen-bonding sites (Desiraju, 1990; MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). In order to expand the understanding of the solid-state physical–organic chemistry of compounds that form multiple  $N-H \cdots N$ ,  $N-H \cdots O$  and  $O-H \cdots O$  hydrogen-bonding systems, we present here the solid-state structure of melaminium bis(trifluoroacetate) trihydrate, (I), and melaminium bis(trichloroacetate) dihydrate, (II).

Both crystals contain melamine protonated at two of the three ring N atoms (Figs. 1 and 2); the ring has a crystallographic twofold axis, and thus half of the melaminium(2+) ring is independent. The melaminium ring in both crystals is



almost planar, but shows significant distortion from an ideal hexagonal form; the internal  $C-N-C$  angle at the non-protonated N atom is significantly smaller than the  $C-N-C$  angles at the protonated N atoms (Tables 1 and 3). The differences between the internal  $C-N-C$  angles within the melaminium ring residue correlate with the steric effect of the lone-pair electrons and are fully consistent with the valence-shell electron-pair repulsion theory (Gillespie, 1963, 1992). As a result of the protonation of the melamine ring at two of the three ring N atoms, the internal  $N-C-N$  angle involving only protonated N atoms is significantly smaller than the  $N-C-N$  angles involving both protonated and non-protonated N atoms. The *ab initio* gas-phase geometry calculated for the isolated doubly protonated melaminium(2+) cation shows similar correlation between the internal  $C-N-C$  and  $N-C-N$  angles within the ring (Drozd & Marchewka, 2005). Thus, the ring distortions of the protonated melaminium residue result mainly from the protonation and, to a lesser degree, from the hydrogen-bonding system and the crystal packing. Protonation of the melamine ring also modifies the  $C-N$  bonds within the ring when compared with the neutral melamine crystal structure (Varghese *et al.*, 1977). The  $C-N$  bonds involving the protonated N atoms are slightly longer than the other  $C-N$  bonds within the ring. Thus, there is evidence for a partially localized double-bond form, in which, for example, the bond order of  $N2-C4$  is greater than that of

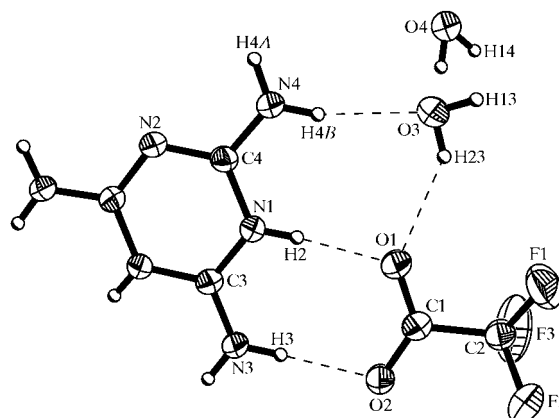
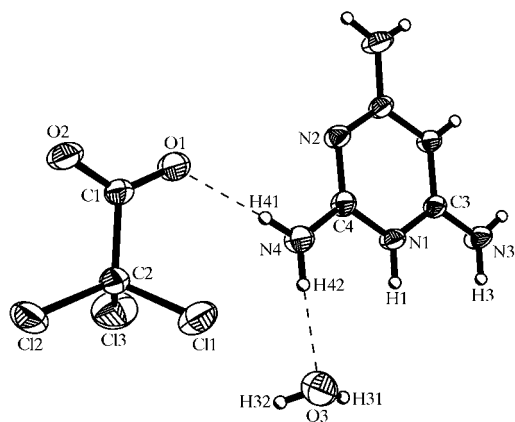


Figure 1

A view of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.

the other N—C (N1—C4 and N1—C3) bonds. Additionally, protonation of the triazine ring of melamine leads to shortening of the C—NH<sub>2</sub> bond in relation to the melamine molecule in the solid state (Varghese *et al.*, 1977), as well as in the gas phase (Drozd & Marchewka, 2005). A search of the Cambridge Structural Database (Version 5.27; Allen, 2002) for crystals containing a protonated melaminium residue yields over 30 structures, but only six of them contain doubly protonated melaminium(2+) residues; all of these six show melaminium ring distortions similar to those found for the title compounds.

The geometry of the trifluoroacetate ion, CF<sub>3</sub>COO<sup>−</sup>, is different from that of the trichloroacetate ion, CCl<sub>3</sub>COO<sup>−</sup>. The conformation of the anion in the crystals is well described by the O1—C1—C2—X1 torsion angle [ $X1 = F2$  in (I) and  $X1 = Cl2$  in (II)] and by the C1—C2 bond length. In the trifluoroacetate ion, this torsion angle is  $-160.0(1)^\circ$ , while in the trichloroacetate ion it is  $-179.0(1)^\circ$ , so atoms O1, C1, C2 and Cl2 are almost coplanar. Molecular orbital (MO) calculations using density functional theory and the B3LYP/6-31+G\*\* basis sets (Frisch *et al.*, 1998) performed for the isolated CCl<sub>3</sub>COO<sup>−</sup> ion show a minimum on the potential energy surface (PES) for the conformation observed in the crystal (O1—C1—C2—Cl2 =  $-179.9^\circ$ ), whereas MO calculations for the CF<sub>3</sub>COO<sup>−</sup> ion show a minimum on the PES for a more rotated conformation (O1—C1—C2—F2 =  $-175.2^\circ$ ); thus, in the crystal, the rotation of the COO<sup>−</sup> group with respect to CF<sub>3</sub> around the C1—C2 bond results from the hydrogen-bonding interactions. The C1—C2 bond length of 1.531(3) Å in CF<sub>3</sub>COO<sup>−</sup> is shorter than that in CCl<sub>3</sub>COO<sup>−</sup> [1.570(3) Å]. However, this bond in both crystals is longer than that found in non-substituted acetate crystals, such as melaminium acetate (Janczak & Perpétuo, 2001). The differences between the C1—C2 distances, as well as those between the C—F and C—Cl bond lengths, correlate well with the ionic radii of F and Cl (1.31 and 1.81 Å, respectively; Shannon, 1976) and their electronegativity (3.98 and 3.16 for F and Cl, respectively; Pauling, 1967). The lengthening of the C1—C2 bond in relation to that of the acetate ion (CH<sub>3</sub>COO<sup>−</sup>) results

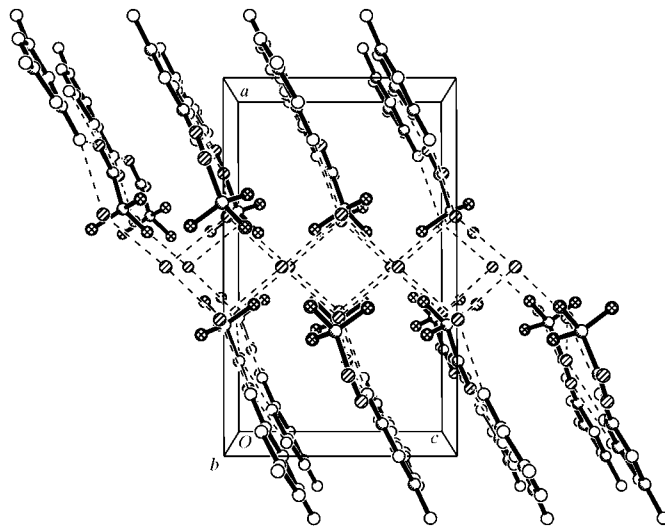


**Figure 2**

A view of (II), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.

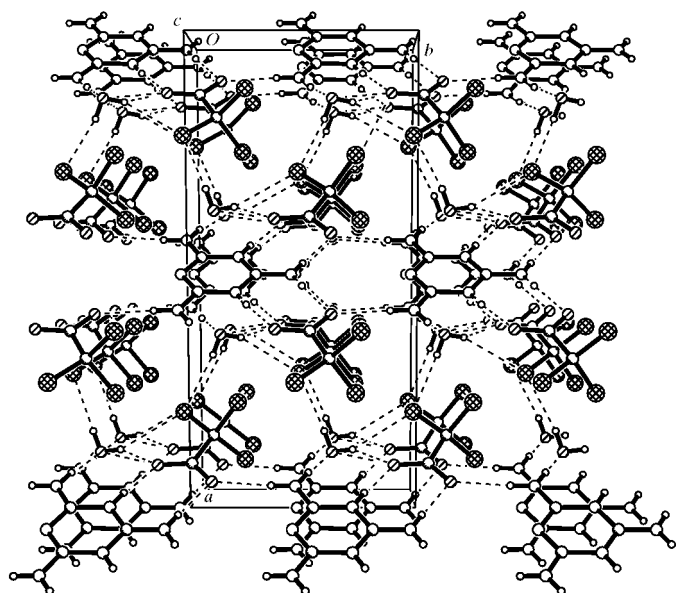
from the repulsion between the negatively charged O atoms and the three Cl or F atoms joined in the  $\alpha$ -position with respect to the COO<sup>−</sup> group. This effect is more pronounced in the gas-phase structures obtained by MO calculations, where C1—C2 is 1.588 Å in CF<sub>3</sub>COO<sup>−</sup> and 1.650 Å in CCl<sub>3</sub>COO<sup>−</sup> (Frisch *et al.*, 1998). The average C—F and C—Cl bond lengths in the crystal structure are 1.320 and 1.768 Å, respectively. These values correlate well with the values observed for  $Csp^3-F$  (1.314–1.332 Å) and for  $Csp^3-Cl$  (1.761–1.776 Å) (Allen *et al.*, 1987). The C—O bond lengths in the carboxylate group are intermediate between single  $Csp^2=O$  (1.308–1.320 Å) and double  $Csp^2-O$  bond values (1.214–1.224 Å; Allen *et al.* 1987) indicating delocalization of the charge on both O atoms of the COO<sup>−</sup> group.

An extensive set of hydrogen bonds (Tables 2 and 4) links the components of (I) and (II) into a continuous framework superstructure (Figs. 3 and 4). All H atoms of the doubly protonated melaminium residues in both structures form N—H...O hydrogen bonds. In (I), the melaminium residue acts as a donor in eight hydrogen bonds with four symmetrically equivalent CF<sub>3</sub>COO<sup>−</sup> ions and two water (O3) molecules, forming two-dimensional layers almost parallel to the (101) plane. The two O atoms of the trifluoroacetate ion act as acceptors in two hydrogen bonds; atom O1 interacts with a water molecule and with the H atom of a protonated N atom of the melaminium ring, while atom O2 links two translationally equivalent melaminium residues *via* the H atoms of amine groups. The two almost parallel N—H...O hydrogen-bonding interactions between the melaminium residues and CF<sub>3</sub>COO<sup>−</sup> ions are the strongest in the structure (Table 2). The water molecules are interconnected *via* O—H...O hydrogen bonds into chains along the [001] direction. In the chain, the O4 water molecule is surrounded by four O3 water molecules, which are related in pairs by the twofold axis upon which atom O4 lies. Atom O3 is hydrogen bonded to atom O4



**Figure 3**

A view of the crystal packing in (I), showing the chain of hydrogen-bonded water molecules that join the hydrogen-bonded melaminium-trifluoroacetate units into a three-dimensional superstructure.



**Figure 4**  
A view of the crystal packing in (II), showing the hydrogen-bonding interactions.

and to another O4 atom related by the inversion centre. In conclusion, the O4 water molecule has a tetrahedral-like geometry. The chains of water molecules join the melaminium and trifluoroacetate ions into a three-dimensional superstructure (Fig. 3). The melaminium ions are arranged parallel to one another and are separated by  $\sim 3.33$  Å in the [001] direction.

In (II), each melaminium residue acts as donor in eight N—H...O hydrogen bonds – with four  $\text{CCl}_3\text{COO}^-$  anions related by the twofold axis and by a unit translation along the  $b$  axis, and with two symmetrically equivalent water molecules – to form separate but interacting two-dimensional layers almost parallel to the  $(\bar{4}01)$  plane. These layers are separated by  $\sim 3.50$  Å. Both O atoms of the trichloroacetate ion act as acceptors in two almost linear bifurcated hydrogen bonds (Table 4). Atom O1 is involved in hydrogen bonds with two amine groups of two symmetry-equivalent melaminium cations, while atom O2 accepts hydrogen bonds from the protonated ring N atom and from one water molecule. This same water molecule also takes part in two hydrogen bonds in which it acts as an acceptor for an amine group of the melaminium ion and as a donor to Cl (O3—H32...Cl2<sup>viii</sup>; Table 4). In both (I) and (II), the non-protonated ring N atom with the lone pair does not form any hydrogen bonds.

The second harmonic generation (SHG) experiment was carried out using the Kurtz–Perry powder technique (Kurtz & Perry, 1968). The calibrated samples (melaminium trichloroacetate and KDP) were irradiated at 1064 nm by an Nd:YAG laser and the second harmonic beam power diffused by the sample (at 532 nm) was measured as a function of the fundamental beam power. SHG efficiency for melaminium bis(trichloroacetate) dihydrate is about three times greater than for KDP [ $d_{\text{eff}} \sim 3d_{\text{eff}}(\text{KDP})$ ].

## Experimental

Melamine was dissolved in 10% aqueous trifluoroacetic or trichloroacetic acid; after several days, colourless single crystals had formed, which proved to be suitable for single-crystal X-ray diffraction analysis.

## Compound (I)

### Crystal data

$\text{C}_3\text{H}_8\text{N}_6^{2+} \cdot 2\text{C}_2\text{F}_3\text{O}_2^- \cdot 3\text{H}_2\text{O}$   
 $M_r = 408.24$   
 Monoclinic,  $P2_1/c$   
 $a = 12.442$  (3) Å  
 $b = 8.3330$  (17) Å  
 $c = 7.6600$  (15) Å  
 $\beta = 90.14$  (3)°  
 $V = 794.2$  (3) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.707$  Mg m<sup>-3</sup>  
 $D_m = 1.70$  Mg m<sup>-3</sup>  
 $D_m$  measured by flotation in chloroform/bromoform  
 Mo  $K\alpha$  radiation  
 $\mu = 0.19$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Parallelepiped, colourless  
 $0.32 \times 0.18 \times 0.14$  mm

### Data collection

Kuma KM-4 diffractometer with CCD detector  
 $\omega$  scan  
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990b)  
 $T_{\text{min}} = 0.932$ ,  $T_{\text{max}} = 0.981$

9531 measured reflections  
 2076 independent reflections  
 1101 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$   
 $\theta_{\text{max}} = 29.5^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.105$   
 $S = 1.00$   
 2076 reflections  
 136 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.20$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.015 (3)

**Table 1**

Selected geometric parameters (Å, °) for (I).

N3—C3	1.317 (3)	O1—C1	1.236 (2)
C3—N1	1.3530 (18)	C1—C2	1.531 (3)
N1—C4	1.376 (2)	C2—F3	1.304 (2)
C4—N4	1.314 (2)	C2—F1	1.308 (2)
C4—N2	1.3278 (18)	C2—F2	1.346 (2)
O2—C1	1.217 (2)		
N1—C3—N1 <sup>i</sup>	118.4 (2)	C4—N2—C4 <sup>i</sup>	117.55 (19)
C3—N1—C4	119.59 (16)	O2—C1—O1	128.97 (17)
N2—C4—N1	122.27 (16)		

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

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H3...O2	0.868 (18)	1.915 (18)	2.7772 (17)	172.3 (17)
N1—H2...O1	0.838 (19)	1.86 (2)	2.684 (2)	169.4 (17)
N4—H4A...O2 <sup>ii</sup>	0.86	2.06	2.9134 (19)	171
N4—H4B...O3	0.86	2.05	2.895 (2)	165
O3—H13...O4 <sup>iii</sup>	0.82 (2)	2.14 (1)	2.8250 (16)	141 (2)
O3—H23...O1	0.82 (1)	2.11 (1)	2.8078 (18)	143 (2)
O4—H14...O3 <sup>iv</sup>	0.82 (1)	2.26 (2)	2.8157 (17)	126 (2)
O4—H14...F2 <sup>v</sup>	0.82 (1)	2.42 (2)	3.0581 (17)	135 (2)

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

## Compound (II)

## Crystal data

$C_3H_8N_6^{2+} \cdot 2C_2Cl_3O_2^- \cdot 2H_2O$   
 $M_r = 488.93$   
 Monoclinic,  $C2$   
 $a = 17.865$  (3) Å  
 $b = 8.465$  (2) Å  
 $c = 6.117$  (1) Å  
 $\beta = 100.22$  (1)°  
 $V = 910.4$  (3) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.784$  Mg m<sup>-3</sup>  
 $D_m = 1.78$  Mg m<sup>-3</sup>  
 $D_m$  measured by flotation in  
 chloroform/bromoform  
 Mo  $K\alpha$  radiation  
 $\mu = 0.98$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Parallelepiped, colourless  
 $0.32 \times 0.27 \times 0.21$  mm

## Data collection

Kuma KM-4 diffractometer with  
 CCD detector  
 $\omega$  scan  
 Absorption correction: analytical  
 face-indexed (SHELXTL;  
 Sheldrick, 1990b)  
 $T_{min} = 0.743$ ,  $T_{max} = 0.814$

6412 measured reflections  
 2229 independent reflections  
 2109 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.028$   
 $\theta_{max} = 28.5^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.085$   
 $S = 1.00$   
 2229 reflections  
 125 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 1.7329P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.010$   
 $\Delta\rho_{max} = 0.61$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.66$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0089 (10)  
 Absolute structure: Flack (1983),  
 997 Friedel pairs  
 Flack parameter: 0.08 (8)

Table 3

Selected geometric parameters (Å, °) for (II).

C1—C2	1.765 (3)	C3—N3	1.302 (4)
C12—C2	1.773 (3)	C3—N1	1.346 (2)
C13—C2	1.768 (3)	N1—C4	1.377 (3)
C2—C1	1.570 (3)	N2—C4	1.324 (3)
C1—O1	1.233 (3)	N4—C4	1.315 (3)
C1—O2	1.234 (3)		
O1—C1—O2	127.9 (3)	C4—N2—C4 <sup>vi</sup>	117.5 (3)
N1 <sup>vi</sup> —C3—N1	118.1 (3)	N4—C4—N2	120.0 (2)
C3—N1—C4	120.0 (2)		

Symmetry code: (vi)  $-x, y, -z$ .

For both compounds, data collection: *KM-4 CCD Software* (Kuma, 2002); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL97*.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 $\cdots$ O2 <sup>vii</sup>	0.86	1.84	2.700 (3)	173
N3—H3 $\cdots$ O1 <sup>viii</sup>	0.86 (2)	1.98 (2)	2.841 (2)	174 (3)
N4—H41 $\cdots$ O1	0.86	2.12	2.977 (3)	177
N4—H42 $\cdots$ O3	0.86	2.03	2.872 (3)	164
O3—H31 $\cdots$ O2 <sup>vii</sup>	0.82 (2)	1.93 (2)	2.690 (3)	153 (4)
O3—H31 $\cdots$ Cl2 <sup>vii</sup>	0.82 (2)	2.76 (3)	3.374 (2)	133 (3)
O3—H32 $\cdots$ Cl2 <sup>viii</sup>	0.82 (2)	2.73 (2)	3.419 (2)	143 (4)

Symmetry codes: (vii)  $x, y + 1, z$ ; (viii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 2$ .

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3013). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.  
 Desiraju, G. R. (1990). In *Crystal Engineering. The Design of Organic Solids*. Amsterdam: Elsevier.  
 Drozd, M. & Marchewka, M. K. (2005). *J. Mol. Struct. (Theochem)*, **716**, 175–192.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Frisch, J. M. *et al.* (1998). *GAUSSIAN98*. Revision A3. Gaussian Inc., Pittsburgh, PA, USA.  
 Gillespie, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.  
 Gillespie, R. J. (1992). *Chem. Soc. Rev.* **21**, 59–69.  
 Janczak, J. & Perpétuo, G. J. (2001). *Acta Cryst.* **C57**, 873–875.  
 Krische, M. J. & Lehn, J. M. (2000). *Struct. Bonding*, **96**, 3–29.  
 Kuma (2002). *KM-4 CCD Software*. Version 173.1. Kuma Diffraction, Wrocław, Poland.  
 Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.  
 MacDonald, J. C. & Whitesides, G. M. (1994). *Chem. Rev.* **94**, 2383–2420.  
 Pauling, L. (1967). *The Chemical Bond: A Brief Introduction to Modern Structural Chemistry*, ch. 3. Ithaca, New York: Cornell University Press.  
 Perpétuo, G. J. & Janczak, J. (2005). *Acta Cryst.* **E61**, o287–o289.  
 Row, T. R. (1999). *Coord. Chem. Rev.* **183**, 81–100.  
 Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.  
 Sheldrick, G. M. (1990a). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1990b). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Sherrington, D. C. & Taskinen, K. A. (2001). *Chem. Soc. Rev.* **30**, 83–91.  
 Varghese, J. N., O'Connell, A. M. & Maslen, E. N. (1977). *Acta Cryst.* **B33**, 2102–2108.