

## L-Cysteinium semioxalate

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Received 9 April 2008

Accepted 16 May 2008

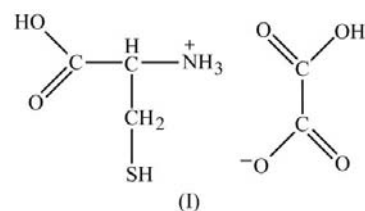
Online 21 May 2008

The title salt,  $C_3H_8NO_2^+ \cdot C_2HO_4^-$ , formed between L-cysteine and oxalic acid, was studied as part of a comparison of the structures and properties of pure amino acids and their cocrystals. The structure of the title salt is very different from that formed by oxalic acid and equivalent amounts of D- and L-cysteine molecules. The asymmetric unit contains an L-cysteinium cation and a semioxalate anion. The oxalate anion is only singly deprotonated, in contrast with the double deprotonation in the crystal structure of bis(DL-cysteinium) oxalate. The oxalate anion is not planar. The conformation of the L-cysteinium cation differs from that of the neutral cysteine zwitterion in the monoclinic and orthorhombic polymorphs of L-cysteine, but is similar to that of the cysteinium cation in bis(DL-cysteinium) oxalate. The structure of the title salt can be described as a three-dimensional framework formed by ions linked by strong O—H...O and N—H...O and weak S—H...O hydrogen bonds, with channels running along the crystallographic *a* axis containing the bulky  $-CH_2SH$  side chains of the cysteinium cations. The cations are only linked through hydrogen bonds *via* semioxalate anions. There are no direct cation–cation interactions *via* N—H...O hydrogen bonds between the ammonium and carboxylate groups, or *via* weaker S—H...S or S—H...O hydrogen bonds.

## Comment

Cysteine is the only widespread  $\alpha$ -amino acid that has a highly reactive sulfhydryl group (SH) in a side chain. Cysteine molecules easily form disulfide bridges, which play an important role in protein folding and in the stabilization of secondary, tertiary and quaternary structures. In biopolymers, such as proteins, the SH group can act as a proton donor in S—H...O and S—H...S interactions, or as a proton acceptor in N—H...S interactions. Studies of cysteine as an individual molecule in inert matrices (Dobrowolski *et al.*, 2007), as a zwitterion in solutions (Li & Thomas, 1991; Li *et al.*, 1992), in biomolecules (Kandori *et al.*, 1998), in different crystalline

polymorphs, in L- and DL-crystals and at various temperatures and pressures by spectroscopic and diffraction techniques (Harding & Long, 1968; Kerr & Ashmore, 1973; Kerr *et al.*, 1975; Görbitz & Dalhus, 1996; Luger & Weber, 1999; Moggach *et al.*, 2005, 2006; Kolesov *et al.*, 2008; Minkov, Chesalov *et al.*, 2008; Minkov, Krylov *et al.*, 2008) provide valuable information on the conformation of the cysteine fragment in relation to the intermolecular interactions of its  $-CH_2SH$  side chain. Considering cysteine cocrystallized in a neutral (zwitterionic) form, or in an ionic form with other species, can be a valuable extension of these studies, as was shown recently for bis(DL-cysteinium) oxalate (Drebushchak *et al.*, 2008). In the present communication, we report the structure of another oxalate of cysteine, but this time formed by only the L-enantiomer of the cation.



In the title structure, (I), the cysteine molecule is protonated but, in contrast with bis(DL-cysteinium) oxalate (Drebushchak *et al.*, 2008), only one of the protons has been transferred from the oxalic acid to the weaker acid, cysteine, so that a semioxalate ion is formed (Fig. 1). This cocrystal of L-cysteine and oxalic acid can be classified as a salt.

The conformation of cysteine is very sensitive to its crystalline environment and varies from structure to structure, being less sensitive to the degree of protonation (Fig. 2). As for all amino acids with small side chains, cysteine usually exists as two basically different conformers, *gauche+* (N—C—C—S torsion angle *ca* 60°) and *gauche-* (N—C—C—S torsion angle *ca* -60°). As an exception, one can mention one of the two crystallographically independent molecules in the monoclinic polymorph of L-cysteine, in which the N—C—C—S torsion angle is 170.15 (7)° and the conformation is termed *trans* (Harding & Long, 1968; Görbitz & Dalhus, 1996). Thus,

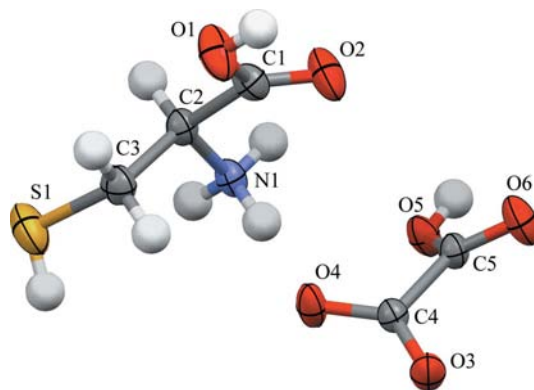
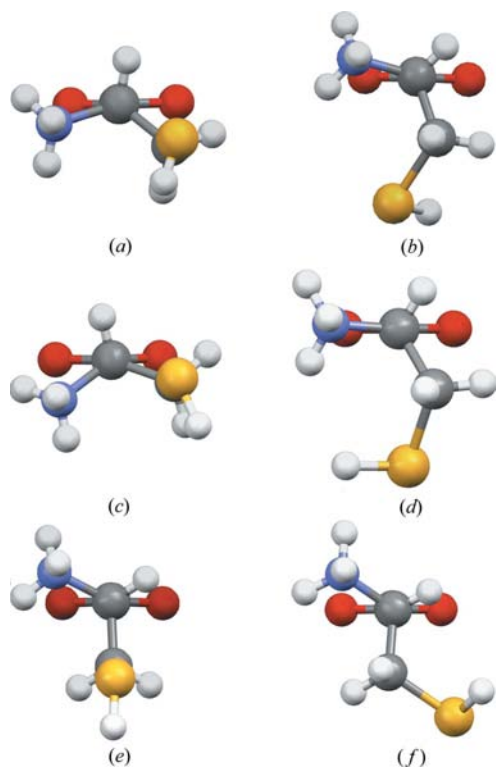


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.



**Figure 2**

The conformation of L-cysteine in different crystalline environments: (a) L-cysteinium oxalate; (b) orthorhombic L-cysteine; (c) bis(DL-cysteinium) oxalate; (d) and (f) two crystallographically independent molecules in monoclinic L-cysteine; (e) DL-cysteine.

the conformation of the side chain in the orthorhombic (Kerr & Ashmore, 1973; Kerr *et al.*, 1975) and monoclinic (Harding & Long, 1968; Görbitz & Dalhus, 1996) polymorphs of L-cysteine is *gauche+* [N—C—C—S torsion angles of 65.3 (2) and 74.39 (10)°, respectively; Figs. 2(b) and 2(d)]. In the structure of (I), the cysteine cation has a *gauche-* conformation, which was previously only observed for L enantiomers in racemic crystals of DL-cysteine (Luger & Weber, 1999) and bis(DL-cysteinium) oxalate (Drebushchak *et al.*, 2008) [N—C—C—S torsion angles of -62.3 (2) and -60.27 (13)°, respectively; Figs. 2(c) and 2(f)].

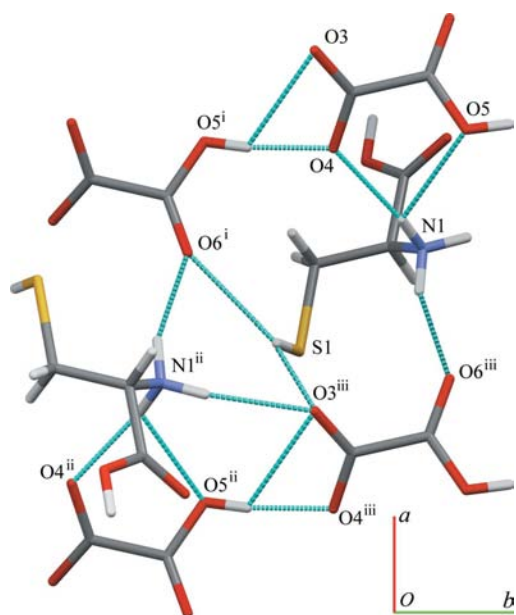
In contrast with the structure of bis(DL-cysteinium) oxalate, the oxalate anion in (I) is not planar, the angle between the planes of the two carbonyl groups being 38.6 (3)°. Although the planar conformation of an isolated oxalate ion is known to be energetically less advantageous than the twisted one (Dewar & Zheng, 1990), in more than 80% of the known crystal structures of metal oxalates, semioxalates and oxalic acid itself, the oxalate fragment is planar (Boldyreva *et al.*, 1996; Naumov *et al.*, 1997). In the crystal structures of oxalates of amino acids, twisted oxalate ions are observed more frequently. In DL-threoninium oxalate (Nandhini *et al.*, 2001), the value of the angle between the COO planes in the semioxalate ion [33.8 (3)°] is very close to that in (I). In the 16 hits of structures containing an amino acid and an oxalate ion from a recent version of the Cambridge Structural Database (CSD,

Version 5.29 of January 2008; Allen, 2002), eight oxalate ions are planar, 16 more have an angle between the COO planes of less than 10°, seven have this angle between 20 and 30°, and one has this angle close to 90° (Chandra *et al.*, 1998). The total number of oxalate and semioxalate ions included in these statistics (32) exceeds the number of crystal structures (16), since in many crystal structures there are several independent oxalate ions and semioxalate ions.

There is no obvious correlation between the deprotonation of an oxalate ion and its twist. For example, in L-arginine hydrogen oxalate, the angle between the COO planes in the semioxalate ion is about 10°, whereas in DL-arginine hydrogen oxalate it is *ca* 90° (Chandra *et al.*, 1998). It is also of note that in L- and DL-arginine hydrogen oxalates, the semioxalate ion is formed, and this fact shows that it is not obvious that a DL salt should have a completely deprotonated oxalate ion and an L salt a semioxalate ion, as is observed for L-cysteinium oxalate (this work), bis(DL-cysteinium) oxalate (Drebushchak *et al.*, 2008), DL-serinium oxalate dihydrate (Alagar *et al.*, 2002), bis(glycinium) oxalate (Chitra & Choudhury, 2007) and glycinium oxalate (Subha Nandhini *et al.*, 2001).

The different species in the crystal structure of (I) are linked by hydrogen bonds to give a three-dimensional network (Figs. 3 and 4). Each semioxalate anion is linked to two other semioxalate anions and five cysteinium cations. Atoms O4 and O5 of the carboxyl groups of the semioxalate anion form a bifurcated hydrogen bond with the NH<sub>3</sub> group of a neighboring cysteinium cation (Fig. 3). Hydrogen bonds link cysteinium cations with semioxalate anions, but there are no direct cation–cation interactions *via* N—H...O hydrogen bonds between the NH<sub>3</sub> and carboxylic acid groups, or *via* weaker S—H...S or S—H...O hydrogen bonds, in which the side groups are involved (Figs. 3 and 4). The structure is formed by ribbons of two types, each representing the arrangement of the semioxalate anions and L-cysteinium cations within planes parallel to the *ab* plane. The first type of ribbons consists of infinite chains of semioxalate ions, which are linked by the shortest hydrogen bonds in the structure [O5—H5O...O4<sup>i</sup>; symmetry code: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ] and are extended along the crystallographic *b* axis. These chains of semioxalate ions are linked to each other *via* the -NH<sub>3</sub> and -SH groups of the cysteinium cations to form the ribbon (Fig. 3). In the second type of ribbon, L-cysteinium cations act as bridges, linking the ribbons of the first type together *via* hydrogen bonds formed between carboxyl groups of the semioxalate ions and -NH<sub>3</sub>, -SH and -OH groups of the cysteinium cations. Thus, the structure of (I) can be described as a three-dimensional framework formed by ions linked by strong hydrogen bonds, with channels along the crystallographic *a* axis containing the bulky -CH<sub>2</sub>SH side chains of the cysteinium cations (Fig. 4). These channels are very similar to those in the structure of pure orthorhombic L-cysteine (Kerr & Ashmore, 1973), which are preserved even under high hydrostatic pressure (Moggach *et al.*, 2006).

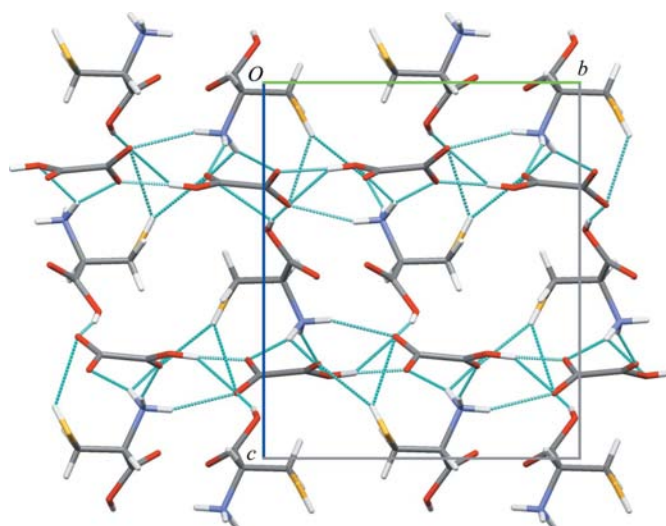
The only contact that seems to link two neighbouring cysteine cations directly is a short C—H...O contact (Table 2). Interestingly, neighbouring thiol groups in the structure of (I)

**Figure 3**

Hydrogen bonding (dashed lines) between the semioxalate anions and L-cysteinium cations of (I). [Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $x - 1, y, z$ ]

do not form any S—H···S hydrogen bonds, the minimum distance between S atoms being 4.824 (2) Å. At the same time, there are very short S···O contacts of 3.339 (2) Å and longer contacts of 3.670 (2) Å (involving O atoms from the semioxalate ions), which can correspond to S—H···O hydrogen bonds being present in the structure, despite the disorder in the sulfhydryl group H atom, similar to the case of the orthorhombic polymorph of L-cysteine. The main difference between the hydrogen bonding in (I) and that in orthorhombic L-cysteine is that in (I) the SH group can donate its H atom to several O atoms of the COO groups. The occupancy of the position at which we have located the H atom of the SH group was estimated as 0.62, suggesting that other orientations of the SH groups in the structure are possible, and this co-existence of several types of local environments for the SH group is supported by IR spectroscopic data. For comparison, the shortest S···O distance hitherto observed in a cysteine-containing crystal structure is in orthorhombic L-cysteine at 30 K and has approximately the same value, 3.332 (1) Å (Moggach *et al.*, 2005). In the latter case, despite this short contact, no S—H···O hydrogen bonds are formed. Instead, the ordered thiol groups are thought to form S—H···S hydrogen bonds exclusively, as deduced from X-ray diffraction data (Moggach *et al.*, 2005). However, polarized single-crystal Raman spectroscopic data (Kolesov *et al.*, 2008) indicate the co-existence of several cysteine conformations and local SH group environments even at 3 K, with the S—H···S contacts obviously dominating.

The types of hydrogen bond formed by the SH groups can most reliably be determined from an analysis of the vibrational spectra (Li & Thomas, 1991; Li *et al.*, 1992; Minkov, Chesalov *et al.*, 2008; Kolesov *et al.*, 2008). A free thiol group in

**Figure 4**

A fragment of the crystal structure of (I), projected on to the *bc* plane. Hydrogen bonds are shown as dashed lines.

CCl<sub>4</sub> has an SH<sub>str</sub> vibration at 2585±5 cm<sup>-1</sup> (Li *et al.*, 1992); the SH<sub>str</sub> vibration of this group when involved in S—H···S hydrogen bonds is observed typically in the range 2500–2550 cm<sup>-1</sup>, and the same group forming S—H···O hydrogen bonds vibrates at higher frequencies, 2550–2585 cm<sup>-1</sup>, indicating that the S—H···O interaction is weaker than the S—H···S interaction, which is opposite to what could be expected from the electronegativity of the O and S atoms, probably because the same O atom is involved simultaneously in the formation of much stronger N—H···O hydrogen bonds (Kerr *et al.*, 1975). The SH<sub>str</sub> vibration in the IR spectrum of (I) is split into two bands, with maxima at 2593 and 2563 cm<sup>-1</sup>, which corresponds to one ‘free’ thiol group (or one forming a very weak S—H···O hydrogen bond, corresponding to the long S···O contact distance in the structure) and another which forms a short S—H···O contact, or several contacts equivalent in energy. For comparison, in the structure of bis(DL-cysteinium) oxalate, there is only one SH<sub>str</sub> band in the IR spectrum at 2576 cm<sup>-1</sup>, in agreement with the structural data showing ordered S—H···O hydrogen bonds [with an S···O distance of 3.6200 (15) Å] and no S—H···S hydrogen bonds, despite short [3.5176 (8) Å] S···S distances in the structure (Drebushchak *et al.*, 2008). In orthorhombic L-cysteine at ambient temperature, the thiol group is disordered between two types of contacts, S—H···S [S···S = 3.79 (2) Å] and S—H···O [S···O = 3.41 (2) Å] (Kerr *et al.*, 1975), and the corresponding frequencies in the IR spectrum are 2508 and 2551 cm<sup>-1</sup>, respectively (Minkov, Chesalov *et al.*, 2008).

## Experimental

Crystals of L-cysteinium semioxalate were obtained by slow evaporation of a water–ethanol (3:1) solution of an equimolar ratio of L-cysteine and oxalic acid dihydrate under ambient conditions. Several crystals were tested and found to be built up of several domains slightly misoriented with respect to each other.

**Table 1**  
Selected geometric parameters (Å, °).

S1—C3	1.810 (2)	C2—C3	1.517 (2)
O2—C1—O1	124.86 (19)	O3—C4—O4	125.88 (15)
N1—C2—C3	112.22 (15)	C2—C3—S1	113.00 (13)
O2—C1—C2—N1	15.7 (2)	O6—C5—C4—O4	142.04 (19)
O2—C1—C2—C3	139.8 (2)	N1—C2—C3—S1	−64.76 (18)
O6—C5—C4—O3	−38.0 (3)	C1—C2—C3—S1	173.84 (13)

**Crystal data**

$C_3H_8NO_2S^+ \cdot C_2HO_4^-$	$V = 875.4 (2) \text{ \AA}^3$
$M_r = 211.20$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.0529 (11) \text{ \AA}$	$\mu = 0.37 \text{ mm}^{-1}$
$b = 10.2407 (12) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 12.1199 (15) \text{ \AA}$	$0.46 \times 0.38 \times 0.22 \text{ mm}$

**Data collection**

Stoe IPDS-2 diffractometer	6447 measured reflections
Absorption correction: numerical ( <i>X-SHAPE</i> ; Stoe & Cie, 2003)	2052 independent reflections
$T_{\min} = 0.834$ , $T_{\max} = 0.926$	1727 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{\max} = 0.18 \text{ e \AA}^{-3}$
$wR(F^2) = 0.072$	$\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
$S = 1.00$	Absolute structure: Flack (1983),
2052 reflections	with 854 Friedel pairs
128 parameters	Flack parameter: $-0.02 (9)$
H atoms treated by a mixture of independent and constrained refinement	

The selected crystal was found to be a twin with two large domains (two orientation matrices, where 58 and 39% of the reflections from the whole data set could be indexed and integrated). A small number of reflections could not be indexed with either of the two orientation matrices. The twin law for transforming  $hkl(1)$  to  $hkl(2)$  is: 0.99986, −0.00105, −0.00068; 0.00231, 0.99886, 0.05342; 0.00179, −0.07266, 0.99791. Structure solution and refinement were carried out using data corresponding solely to the major domain (data from the minor domain and overlaps were subtracted from the whole data set). This has led to the omission of some 13% of the unique reflections from the data set. Nonetheless, the data-to-parameter ratio has remained high. Attempts to refine the structure by including the overlapping reflections and correcting their intensities for the contribution from the minor domain gave worse results.

Methine and methylene H atoms were placed in geometrically calculated positions and constrained to ride on their parent atoms, with C—H = 0.98 and 0.97 Å, respectively. The H atoms of the NH<sub>3</sub> group were also constrained to an ideal geometry, with N—H = 0.89 Å, but were allowed to rotate freely about the N—C bond. The positions of the sulfhydryl and hydroxyl H atoms were found from difference Fourier maps and were refined freely. For all H atoms,  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{parent atom})$ . In order to locate the H atom of the SH group, a dummy SH<sub>3</sub> group was introduced. The occupancies of several possible H-atom positions were refined and eventually estimated as 0.6, 0.2 and 0.05 from the difference Fourier

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

$D-H \cdots A$	D—H	H···A	$D \cdots A$	$D-H \cdots A$
N1—H1N···O4	0.89	2.06	2.912 (2)	161
N1—H1N···O5	0.89	2.49	3.041 (2)	121
N1—H2N···O3 <sup>i</sup>	0.89	2.24	3.0977 (19)	161
N1—H3N···O6 <sup>ii</sup>	0.89	2.09	2.926 (2)	157
O1—H1O···O3 <sup>iii</sup>	0.89 (3)	1.71 (3)	2.587 (2)	170 (3)
O5—H5O···O4 <sup>i</sup>	0.85 (3)	1.69 (3)	2.5346 (18)	172 (2)
O5—H5O···O3 <sup>i</sup>	0.85 (3)	2.59 (2)	3.0796 (19)	118 (2)
S1—H1S···O3 <sup>ii</sup>	0.97 (3)	2.73 (3)	3.3387 (16)	121 (2)
S1—H1S···O6 <sup>iv</sup>	0.97 (3)	2.84 (3)	3.6702 (17)	144 (2)
C2—H2···O2 <sup>v</sup>	0.98	2.40	3.105 (2)	128

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

maps using *PLATON* (Spek, 2003). The location suggested in the present CIF corresponds to site occupancy 0.6, and the H atom at this position can form two S—H···O contacts, a longer and a shorter one, which agrees with the spectroscopic data.

Data collection: *X-AREA* (Stoe & Cie, 2007); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

This work was supported by a grant from RFBR (grant No. 06-03-90573), a grant from BRHE (grant No. RUX0-008-NO-06/BP2M08), the Innovation Project 'Education' from the Russian Ministry of Education and Science No. 456, and Integration Projects Nos. 49 and 110 of the Siberian Branch of the Russian Academy of Sciences.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3098). Services for accessing these data are described at the back of the journal.

**References**

- Alagar, M., Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2002). *Acta Cryst.* **E58**, o114–o116.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Boldyreva, E. V., Naumov, D. Yu., Podberezskaya, N. V. & Virovets, A. V. (1996). *J. Struct. Chem.* **37**, 550–578.
- Chandra, N. R., Prabu, M. M., Venkatraman, J., Suresh, S. & Vijayan, M. (1998). *Acta Cryst.* **B54**, 257–263.
- Chitra, R. & Choudhury, R. R. (2007). *Acta Cryst.* **B63**, 497–504.
- Dewar, M. J. S. & Zheng, Y.-J. (1990). *J. Mol. Struct. THEOCHEM*, **209**, 157–162.
- Dobrowolski, J. M., Jamroz, M. H., Kolos, R., Rode, J. E. & Sadlej, J. (2007). *Phys. Chem. Chem. Phys.* **8**, 1085–1094.
- Drebushchak, T. N., Bizyaev, S. N. & Boldyreva, E. V. (2008). *Acta Cryst.* **C64**, o313–o315.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Görbitz, C. H. & Dalhus, B. (1996). *Acta Cryst.* **C52**, 1756–1759.
- Harding, M. M. & Long, H. A. (1968). *Acta Cryst.* **B24**, 1096–1102.
- Kandori, H., Kinoshita, N., Shichida, Y., Maeda, A., Needlenan, R. & Lanyi, K. (1998). *J. Am. Chem. Soc.* **120**, 5828–5829.
- Kerr, K. A. & Ashmore, J. P. (1973). *Acta Cryst.* **B29**, 2124–2127.
- Kerr, K. A., Ashmore, J. P. & Koetzle, T. F. (1975). *Acta Cryst.* **B31**, 2022–2026.
- Kolesov, B. A., Minkov, V. S., Boldyreva, E. V. & Drebushchak, T. N. (2008). *J. Phys. Chem. B*. Submitted.

- Li, H. & Thomas, G. J. (1991). *J. Am. Chem. Soc.* **113**, 456–462.
- Li, H., Wurrey, C. J. & Thomas, G. J. (1992). *J. Am. Chem. Soc.* **114**, 7463–7469.
- Luger, P. & Weber, M. (1999). *Acta Cryst.* **C55**, 1882–1885.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Minkov, V. S., Chesalov, Yu. A. & Boldyreva, E. V. (2008). *J. Struct. Chem.* In the press.
- Minkov, V. S., Krylov, A. S., Boldyreva, E. V., Goryainov, S. V., Bizyaev, S. N. & Vtyurin, A. N. (2008). *J. Phys. Chem.* Submitted.
- Moggach, S. A., Allan, D. R., Clark, S. J., Gutmann, M. J., Parsons, S., Pulham, C. R. & Sawyer, L. (2006). *Acta Cryst.* **B62**, 296–309.
- Moggach, S. A., Clark, S. J. & Parsons, S. (2005). *Acta Cryst.* **E61**, o2739–o2742.
- Nandhini, M. S., Krishnakumar, R. V., Malathi, R., Rajan, S. S. & Natarajan, S. (2001). *Acta Cryst.* **E57**, o769–o771.
- Naumov, D. Yu., Boldyreva, E. V., Howard, J. A. K. & Podberezskaya, N. V. (1997). *Solid State Ionics*, **101–103**, 1315–1320.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Stoe & Cie (2003). *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (2007). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2001). *Acta Cryst.* **C57**, 115–116.
- Westrip, S. P. (2008). *publCIF*. In preparation. <http://journals.iucr.org/services/cif/publCIF>