

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub>
S(1)	0.3882 (1)	0.0374	0.1650 (1)	0.046 (1)
S(2)	0.0090 (1)	0.0366 (1)	0.4312 (1)	0.063 (1)
S(3)	0.9326 (1)	-0.2501 (1)	0.1069 (1)	0.062 (1)
N(1)	0.6201 (2)	-0.0464 (2)	0.0997 (1)	0.051 (1)
N(2)	0.1745 (2)	0.0920 (2)	0.2551 (1)	0.051 (1)
N(3)	0.3619 (2)	-0.0785 (1)	0.3424 (1)	0.045 (1)
N(4)	0.6368 (2)	-0.1709 (1)	0.2408 (1)	0.044 (1)
C(1)	0.4712 (2)	-0.0816 (1)	0.2585 (1)	0.042 (1)
C(2)	0.4465 (3)	-0.1544 (2)	0.4382 (1)	0.058 (1)
C(3)	0.4003 (3)	-0.3011 (2)	0.4270 (2)	0.068 (1)
C(4)	0.4918 (3)	-0.3618 (2)	0.3336 (2)	0.066 (1)
C(5)	0.7085 (3)	-0.2897 (2)	0.3050 (1)	0.056 (1)
C(6)	0.7255 (2)	-0.1507 (2)	0.1459 (1)	0.047 (1)
C(7)	0.1803 (2)	0.0217 (2)	0.3383 (1)	0.048 (1)
C(8)	0.6482 (4)	-0.0020 (2)	-0.0040 (1)	0.065 (1)
C(9)	0.4791 (5)	-0.0771 (3)	-0.0862 (2)	0.089 (1)
C(10)	0.0155 (3)	0.2059 (2)	0.2264 (1)	0.060 (1)
C(11)	0.1037 (4)	0.3286 (2)	0.2873 (2)	0.084 (1)

Table 2. Selected geometric parameters (Å, °)

S(1)—C(1)	1.7149 (13)	N(2)—C(7)	1.291 (2)
S(1)—N(1)	1.8765 (13)	N(3)—C(11)	1.346 (2)
S(1)—N(2)	1.9032 (14)	N(3)—C(7)	1.428 (2)
S(2)—C(7)	1.6819 (13)	N(4)—C(1)	1.342 (2)
S(3)—C(6)	1.6797 (14)	N(4)—C(6)	1.428 (2)
N(1)—C(6)	1.300 (2)		
C(1)—S(1)—N(1)	83.44 (6)	N(4)—C(1)—S(1)	117.06 (9)
C(1)—S(1)—N(2)	83.33 (6)	N(3)—C(1)—S(1)	117.18 (10)
N(1)—S(1)—N(2)	166.77 (6)	N(1)—C(6)—N(4)	108.51 (12)
C(6)—N(1)—S(1)	116.61 (9)	N(1)—C(6)—S(3)	128.63 (11)
C(7)—N(2)—S(1)	115.82 (11)	N(4)—C(6)—S(3)	122.87 (11)
C(1)—N(3)—C(7)	114.20 (12)	N(2)—C(7)—N(3)	109.34 (11)
C(1)—N(4)—C(6)	114.31 (11)	N(2)—C(7)—S(2)	128.59 (12)
N(4)—C(1)—N(3)	125.75 (12)	N(3)—C(7)—S(2)	122.07 (11)

Data collection was carried out using standard Enraf-Nonius routines. Data reduction was performed using the PC version of *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined using *SHELXL93* (Sheldrick, 1993). During refinement cognizance was taken of the non-centrosymmetric space group of the compound. Refinement of the Flack (1983) absolute structure parameter gave a value of -0.12950, indicating that this is the 'correct' absolute structure of the compound. Refinement of the enantiomorphic structure resulted in slightly higher figures of merit and an absolute structure parameter of 0.55 (5). H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter. The labelled structure diagram was produced using *SCHAKAL88* (Keller, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Three BEDT-TTF Salts

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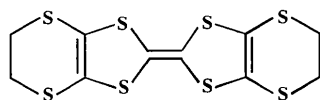
## Abstract

The crystal structures of 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium hexafluorophosphate chloroacetyl chloride solvate, (1), C<sub>10</sub>H<sub>8</sub>S<sub>8</sub><sup>1/2+</sup>·½PF<sub>6</sub><sup>-</sup>·½C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>O, 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium hexafluorophosphate tetrahydrofuran solvate, (2), C<sub>10</sub>H<sub>8</sub>S<sub>8</sub><sup>+</sup>·PF<sub>6</sub><sup>-</sup>·½C<sub>4</sub>H<sub>8</sub>O, and 3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium perchlorate, (3), C<sub>10</sub>H<sub>8</sub>S<sub>8</sub><sup>+</sup>·ClO<sub>4</sub><sup>-</sup>, have been determined. Compounds (1) and (2) crystallize in the *P* $\bar{1}$  space group. The structure of (1) consists of layers of BEDT-TTF ions separated by planes of PF<sub>6</sub><sup>-</sup> ions and chloroacetyl chloride molecules. The BEDT-TTF ions are stacked in a face-to-face manner with short S··S contacts linking these stacks. Compound (2) consists of layers of BEDT-TTF face-to-face dimers with PF<sub>6</sub><sup>-</sup> ions and tetrahydrofuran (THF) molecules filling cavities separating these layers. As in compound (1), there are short S··S contacts between dimers resulting from the side-by-side mode of packing. Compound (3) crystallizes in the *C2/m* space group and consists of layers of BEDT-TTF ions, stacked in a staggered side-by-side manner with one type of S··S contact, separated by layers of perchlorate ions.

## Comment

Cation radical salts of the organic donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are of current interest as several compositions are examples of conducting and superconducting molecular solids (Adrian &

Cowan, 1992; Cowan & Wiygul, 1986; Kresin & Little, 1990; Parkin *et al.*, 1983; Williams *et al.*, 1987, 1990, 1992; Yagubskii *et al.*, 1984). Frequently, stacks or sheets of donor ions are separated by a network of counterions and conductivity in these materials results from intermolecular overlap between the organic donor molecules. Several different packing motifs are known in BEDT-TTF cation radical salts, some of which give rise to conductivity or superconductivity, while others result in semiconducting or insulating materials. There are a number of examples of BEDT-TTF cation radical salts having the same counterion and stoichiometry that are isolated in different crystal morphologies. Among the first counterions to be used in the preparation of BEDT-TTF cation radical salts were  $\text{PF}_6^-$  (Kobayashi, Kato *et al.*, 1983; Kobayashi, Mori *et al.*, 1983) and  $\text{ClO}_4^-$  (Kobayashi *et al.*, 1984; Kobayashi, Kobayashi *et al.*, 1983) ions. As none of the known (BEDT-TTF) $\text{PF}_6$  salts (Bu, Cisarova & Coppens, 1992*a,b,c*; Bu, Cisarova, Coppens, Lederle & Naughton, 1992; Kobayashi, Kato *et al.*, 1983; Kobayashi, Mori *et al.*, 1983) or (BEDT-TTF) $\text{ClO}_4$  salts (Kobayashi *et al.*, 1984; Kobayashi, Kobayashi *et al.*, 1983) is superconducting, we have attempted to isolate  $\text{PF}_6^-$  and  $\text{ClO}_4^-$  salts having new BEDT-TTF packing motifs by preparing ternary structures through the purposeful incorporation of small neutral molecules into the crystal lattice. Two of the title compounds, (BEDT-TTF) $_2\text{PF}_6 \cdot \text{ClCH}_2\text{COCl}$ , (1), and (BEDT-TTF) $\text{PF}_6 \cdot \text{THF}$ , (2), are examples of new ternary structures.



BEDT-TTF

- (1) (BEDT-TTF) $_2\text{PF}_6 \cdot \text{ClCH}_2\text{COCl}$   
 (2) (BEDT-TTF) $\text{PF}_6 \cdot \frac{1}{2}\text{THF}$   
 (3)  $\varepsilon$ -(BEDT-TTF) $\text{ClO}_4$

In a similar attempt to prepare new  $\text{ClO}_4^-$  salts, the dication salt (BEDT-TTF)( $\text{ClO}_4$ ) $_2$  was isolated from solvent mixtures containing  $\text{ClCH}_2\text{COCl}$  (Abboud, Cleveenger, de Oliveira & Talham, 1993). This material was the first example of a cation radical salt where BEDT-TTF is present only as a dication, and results from carrying out the electrocrystallization from an oxidizing solvent media (Abboud *et al.*, 1993). Using the same reaction conditions that produced the dication salt, we have isolated a monocation salt of BEDT-TTF, namely  $\varepsilon$ -(BEDT-TTF) $\text{ClO}_4$ , (3), which is the third structure reported here. This salt is isostructural with the recently reported complex  $\varepsilon$ -(BEDT-TTF) $\text{PF}_6$  (Bu, Cisarova & Coppens, 1992*b*).

The unit cell of compound (1) consists of  $\text{PF}_6^-$  ions located at a center of inversion ( $\frac{1}{2}, 0, 0$ ), with

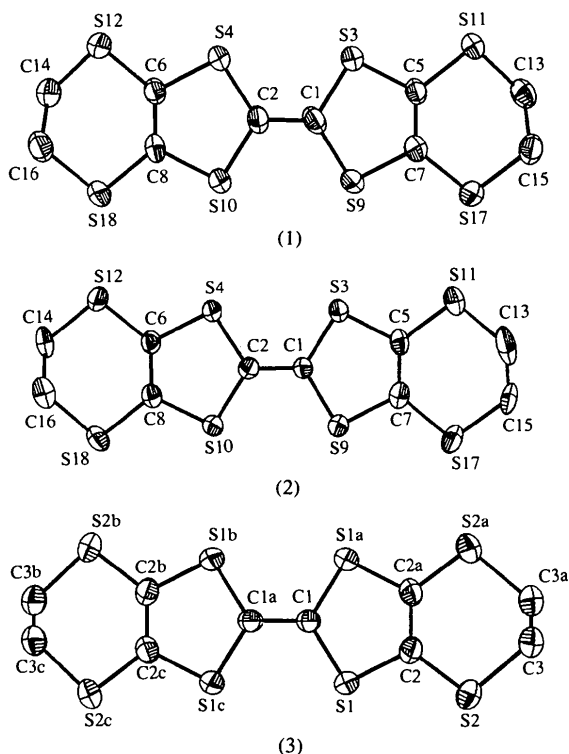


Fig. 1. Displacement ellipsoid drawings of the BEDT-TTF ions in compounds (1), (2) and (3), showing the atomic numbering schemes and 50% probability ellipsoids. H atoms and disorder have been omitted for clarity.

the  $\text{ClCH}_2\text{COCl}$  molecules of crystallization disordered around another center of inversion ( $0, \frac{1}{2}, 0$ ). The  $\text{PF}_6^-$  ions and  $\text{ClCH}_2\text{COCl}$  molecules form planes that separate sheets of the BEDT-TTF donor ions. Fig. 2 shows the packing mode in the crystal. The BEDT-TTF donors lie approximately in the (021) plane and form an angle of  $6.1(2)^\circ$  with it. Ions of BEDT-TTF stack in the  $[1\bar{1}0]$  direction forming an angle of  $87.8(4)^\circ$  between the long axis of BEDT-TTF and the stack axis. No significant  $\text{S} \cdots \text{S}$  interactions are observed between ions of each stack. However, stacks are linked by short  $\text{S} \cdots \text{S}$  contacts as a result of the side-by-side arrangement of the BEDT-TTF ions. The shortest distance is  $3.595(4) \text{ \AA}$ , which is comparable to twice the van der Waals radius of the S atom ( $3.70 \text{ \AA}$ ; Bondi 1964). The BEDT-TTF ion is planar except for the terminal  $\text{CH}_2$  units. The donor-ion packing is different from that observed in other 2:1 BEDT-TTF: $\text{PF}_6$  salts (Bu *et al.*, 1992, 1992*c*; Kobayashi, Kato *et al.*, 1983; Kobayashi, Mori *et al.*, 1983), but is similar to the donor arrangement found in  $\beta'$ -(BEDT-TTF) $_2\text{AuBr}_2$  (Kurmoo *et al.*, 1986).  $\beta'$ -(BEDT-TTF) $_2\text{AuBr}_2$  is a molecular metal, but no superconducting transition has been observed down to 1.5 K. Conductivity measurements on (BEDT-TTF) $_2\text{PF}_6 \cdot \text{ClCH}_2\text{COCl}$  have not yet been performed due to the small size of the crystals that were isolated.

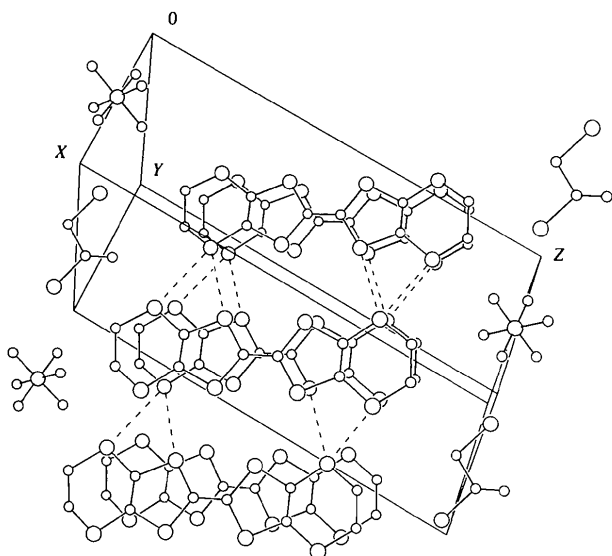


Fig. 2. Packing diagram of (1). Dashed lines represent S...S intermolecular interactions and disorder has been omitted for clarity.

The plane of the BEDT-TTF ion in compound (2) lies nearly in the *ab* plane, making a dihedral angle of  $12.3(2)^\circ$  with it. The structure is layered with each layer composed of face-to-face BEDT-TTF dimers that are separated from each other by cavities containing the counterion and THF molecules (which are disordered about inversion centers). There are no short S...S contacts within the face-to-face dimers, but between dimers S...S distances are  $3.530(3)$  and  $3.564(3)$  Å, which are within twice the van der Waals radius of the

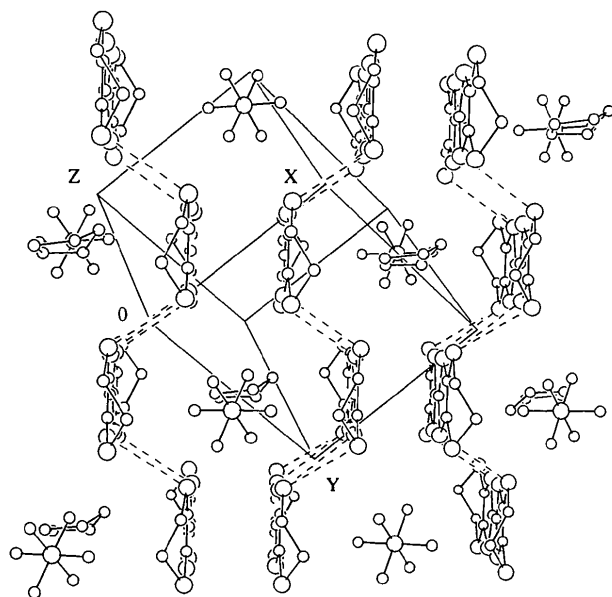


Fig. 3. Packing diagram of (2). Dashed lines represent S...S intermolecular interactions and disorder has been omitted for clarity.

S atom. The side-by-side interactions result in a zigzag network of dimer ions within each layer. The BEDT-TTF ethylene groups are ordered and puckered away from the adjacent ion within the dimer.

The stoichiometry of compound (3) is 1:1 and the formal charge on BEDT-TTF is +1. The unit cell consists of two BEDT-TTF donors and two  $\text{ClO}_4^-$  ions, all located on  $2/m$  sites. The terminal  $\text{CH}_2$  units are disordered about the mirror plane and the  $\text{ClO}_4^-$  ions are disordered about a center of inversion. There is one short intermolecular S...S contact in the structure between the outer-ring S atoms [ $3.479(4)$  Å], with a staggered side-by-side mode of interaction giving rise to sheets of BEDT-TTF donors. This contact is shorter than in (BEDT-TTF)PF<sub>6</sub> (Bu *et al.*, 1992b) due to the smaller size of the  $\text{ClO}_4^-$  counterion compared with PF<sub>6</sub><sup>-</sup>. Compound (3) is isostructural with (BEDT-TTF)PF<sub>6</sub> (Bu *et al.*, 1992b) and (BEDSe-TSeF)PF<sub>6</sub> (Kato, Kobayashi, Kobayashi & Sasaki, 1985). Ions of BEDT-TTF lie in the  $(40\bar{1})$  plane and form stacks in a face-to-face mode with no significant intermolecular interaction. In each stack, the long axis of the BEDT-TTF ions makes an angle of  $38.7(4)^\circ$  with the stack axis.

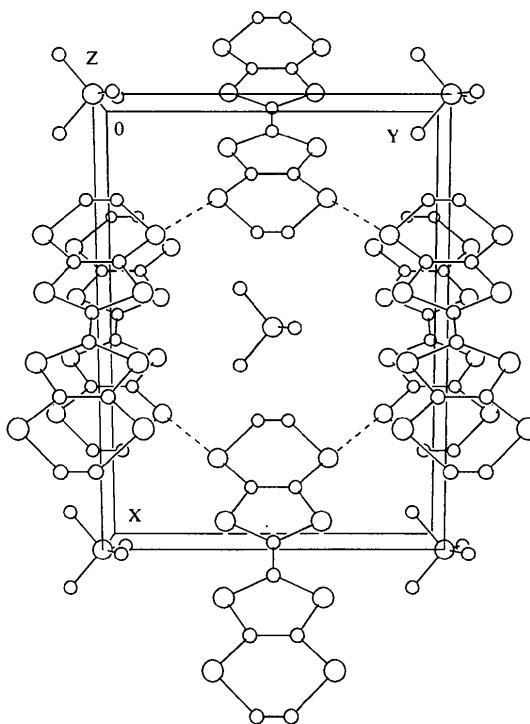


Fig. 4. Packing diagram of (3). Dashed lines represent S...S intermolecular interactions and disorder has been omitted for clarity.

Bond lengths and angles of the BEDT-TTF ions compare well with their counterparts in other crystal structures. The central  $\text{C1}=\text{C2}$  bond in compound (1) [ $1.367(7)$  Å] is shorter than its counterparts in

compounds (2) and (3) [1.379 (6) and 1.390 (7) Å, respectively]. This reflects the increase in the formal charge of BEDT-TTF from  $+\frac{1}{2}$  in compound (1) to +1 in compounds (2) and (3). As can be seen in Tables 2, 4 and 6, the bonds between S atoms and the central C atoms become shorter as the formal charge of the ions increases. The BEDT-TTF ions are planar, as expected, except for the CH<sub>2</sub> groups which, because of their *sp*<sup>3</sup> hybridization, lie above and below the plane of each ion.

## Experimental

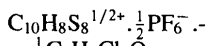
Compound (1), (BEDT-TTF)<sub>2</sub>PF<sub>6</sub>.ClCH<sub>2</sub>COCl, was isolated by standard electrocrystallization methods using two different sets of reaction conditions. In the first method, BEDT-TTF (Larsen & Lenoir, 1988) (12.5 mg) was placed in the working electrode compartment of a two-electrode H-cell containing 35 ml of  $1.6 \times 10^{-2}$  M tetrabutylammonium hexafluorophosphate in 3% CS<sub>2</sub>/ClCH<sub>2</sub>COCl. A current density of 1.5 μA cm<sup>-2</sup> was maintained between the working and counter electrodes, which were separated by two glass frits. Crystals were isolated after 20 d. In the second method, the same procedure was followed using 7 mg of BEDT-TTF and  $6 \times 10^{-2}$  M tetrabutylammonium hexafluorophosphate in 3% ClCH<sub>2</sub>COCl/benzonitrile as electrolyte. Crystals were obtained after 14 d.

Compound (2), (BEDT-TTF)PF<sub>6</sub>. $\frac{1}{2}$ THF, was isolated at the working electrode of a standard constant-current electrocrystallization cell. BEDT-TTF (7 mg) was placed in the working electrode arm of a two-electrode H-cell containing a total of 34 ml of  $6 \times 10^{-2}$  M tetrabutylammonium hexafluorophosphate in 5% CS<sub>2</sub>/THF. A current density of 1.5 μA cm<sup>-2</sup> was maintained between the working and counter electrodes, which were separated by two glass frits. Crystals were isolated after 14 d.

Compound (3), ε-(BEDT-TTF)ClO<sub>4</sub>, was again isolated in a constant-current electrocrystallization experiment. BEDT-TTF (9.5 mg) was placed in the anode compartment of a two-electrode H-cell containing a total of 30 ml of  $3 \times 10^{-2}$  M tetraethylammonium perchlorate in 15% ClCH<sub>2</sub>COCl/benzonitrile. The anode and cathode compartments were separated by two glass frits and a current density of 1.0 μA cm<sup>-2</sup> was maintained for 14 d, after which time crystals were harvested.

## Compound (1)

### Crystal data



$M_r = 513.6$

Triclinic

$P\bar{1}$

$a = 6.853$  (1) Å

$b = 7.878$  (1) Å

$c = 18.299$  (3) Å

$\alpha = 79.11$  (1)°

$\beta = 82.37$  (1)°

$\gamma = 68.96$  (1)°

$V = 903.2$  (2) Å<sup>3</sup>

$Z = 2$

$D_x = 1.888$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 40 reflections

$\theta = 10\text{--}11^\circ$

$\mu = 1.20$  mm<sup>-1</sup>

$T = 298$  K

Needle

$0.23 \times 0.18 \times 0.05$  mm

Black

### Data collection

Siemens P3m/V diffractometer

$\omega$  scans

Absorption correction:

analytical

$T_{\min} = 0.818$ ,  $T_{\max} =$

0.944

2607 measured reflections

2372 independent reflections

1675 observed reflections

$[F > 4\sigma(F)]$

$R_{\text{int}} = 0.02$

$\theta_{\text{max}} = 22.5^\circ$

$h = 0 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -19 \rightarrow 19$

4 standard reflections

monitored every 96

reflections

intensity decay: 1%

### Refinement

Refinement on  $F$

$R = 0.0397$

$wR = 0.0455$

$S = 1.42$

1675 reflections

232 parameters

$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.48$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
S3	0.1159 (2)	-0.7011 (2)	0.39846 (8)	0.0545 (8)
S4	-0.0151 (2)	-0.8244 (2)	0.57054 (7)	0.0528 (8)
S9	0.5088 (2)	-0.6921 (2)	0.44153 (8)	0.0538 (7)
S10	0.3734 (2)	-0.8082 (2)	0.61430 (8)	0.0548 (8)
S11	0.1955 (2)	-0.5932 (2)	0.23789 (8)	0.0485 (7)
S12	-0.1751 (2)	-0.9311 (2)	0.72175 (8)	0.0491 (7)
S17	0.6682 (2)	-0.5858 (2)	0.29025 (8)	0.0537 (8)
S18	0.2829 (2)	-0.8967 (2)	0.77571 (8)	0.0476 (7)
C1	0.2738 (8)	-0.7299 (8)	0.4697 (3)	0.045 (3)
C2	0.2166 (8)	-0.7811 (8)	0.5425 (3)	0.043 (2)
C5	0.2835 (8)	-0.6414 (7)	0.3271 (3)	0.037 (2)
C6	0.0216 (8)	-0.8713 (7)	0.6658 (3)	0.038 (2)
C7	0.4672 (8)	-0.6398 (7)	0.3470 (3)	0.039 (2)
C8	0.1998 (8)	-0.8612 (7)	0.6862 (3)	0.038 (2)
C13	0.4306 (8)	-0.5962 (8)	0.1806 (3)	0.047 (3)
C14	-0.0527 (9)	-1.0278 (8)	0.8085 (3)	0.046 (3)
C15	0.5468 (9)	-0.4863 (8)	0.2043 (3)	0.047 (3)
C16	0.0522 (9)	-0.9094 (8)	0.8324 (3)	0.048 (3)
P	1/2	0	0	0.0420 (9)
F1	0.4677 (6)	0.1264 (6)	0.0619 (2)	0.087 (2)
F2	0.2601 (6)	0.0432 (7)	0.0051 (3)	0.117 (3)
F3	0.5203 (10)	-0.1687 (6)	0.0618 (3)	0.137 (3)
Cl	0.2164 (2)	0.3545 (2)	-0.01639 (10)	0.0667 (8)
O	-0.0027 (15)	-0.522 (2)	0.0929 (5)	0.073 (5)
C	0.043 (5)	-0.481 (3)	0.0319 (15)	0.049 (11)
C'	0.042 (3)	-0.461 (2)	-0.0346 (10)	0.049 (9)

Table 2. Selected geometric parameters (Å, °) for (1)

C1—S3	1.735 (6)	C14—S12	1.800 (5)
C5—S3	1.733 (5)	C7—S17	1.741 (6)
C2—S4	1.734 (6)	C15—S17	1.788 (5)
C6—S4	1.744 (5)	C8—S18	1.745 (5)
C1—S9	1.736 (6)	C16—S18	1.795 (6)
C7—S9	1.738 (5)	C2—C1	1.364 (7)
C2—S10	1.741 (6)	C7—C5	1.361 (9)
C8—S10	1.748 (5)	C8—C6	1.356 (9)
C5—S11	1.742 (5)	C15—C13	1.516 (10)
C13—S11	1.797 (6)	C16—C14	1.516 (10)
C6—S12	1.731 (6)		
C1—S3—C5	95.6 (3)	C7—C5—S11	128.0 (4)
C2—S4—C6	95.8 (3)	S3—C5—S11	115.3 (3)
C1—S9—C7	95.3 (3)	C8—C6—S4	116.9 (4)

C2—S10—C8	95.5 (3)	C8—C6—S12	128.6 (4)	C2	0.6452 (5)	1.1042 (4)	-0.0440 (3)	0.0305 (14)
C5—S11—C13	101.4 (3)	S4—C6—S12	114.5 (3)	C5	0.6364 (6)	1.2400 (5)	0.2275 (3)	0.0340 (15)
C6—S12—C14	101.5 (3)	S9—C7—S17	114.3 (4)	C6	0.7547 (5)	0.9464 (4)	-0.1827 (3)	0.0314 (14)
C7—S17—C15	101.6 (3)	S9—C7—C5	117.1 (4)	C7	0.5182 (6)	1.3343 (4)	0.1777 (3)	0.0344 (15)
C8—S18—C16	101.3 (3)	S17—C7—C5	128.6 (4)	C8	0.6347 (6)	1.0429 (4)	-0.2313 (3)	0.0311 (14)
C2—C1—S3	121.7 (5)	S10—C8—S18	114.6 (4)	C13	0.653 (2)	1.414 (2)	0.364 (2)	0.064 (5)
C2—C1—S9	122.9 (5)	S10—C8—C6	116.8 (4)	C13'	0.598 (4)	1.379 (3)	0.406 (2)	0.050 (8)
S3—C1—S9	115.3 (3)	S18—C8—C6	128.6 (4)	C15	0.476 (3)	1.479 (2)	0.3480 (12)	0.061 (5)
S4—C2—S10	115.0 (3)	C15—C13—S11	114.1 (4)	C15'	0.557 (5)	1.505 (3)	0.320 (3)	0.057 (10)
S4—C2—C1	123.0 (5)	S17—C15—C13	114.1 (4)	C14	0.804 (2)	0.8183 (14)	-0.3589 (8)	0.047 (4)
S10—C2—C1	121.9 (5)	S18—C16—C14	114.9 (4)	C14'	0.862 (4)	0.884 (5)	-0.383 (2)	0.052 (11)
C7—C5—S3	116.7 (4)			C16	0.763 (2)	0.9644 (13)	-0.4179 (6)	0.048 (4)
				C16'	0.685 (4)	0.919 (3)	-0.415 (2)	0.047 (9)
				P	0.0501 (2)	1.2792 (2)	0.65694 (11)	0.0457 (5)
				F1	0.0970 (5)	1.1197 (3)	0.6472 (3)	0.084 (2)
				F2	0.0050 (5)	1.4376 (3)	0.6672 (3)	0.086 (2)
				F3	-0.0804 (6)	1.2914 (5)	0.5690 (4)	0.122 (2)
				F4	-0.0884 (6)	1.2428 (5)	0.7458 (4)	0.122 (2)
				F5	0.1862 (5)	1.2649 (4)	0.7406 (3)	0.095 (2)
				F6	0.1886 (6)	1.3154 (4)	0.5648 (3)	0.097 (2)
				C22	0.9086 (9)	0.5240 (8)	0.0759 (5)	0.076 (3)
				C21	1.033 (4)	0.611 (2)	0.050 (2)	0.064 (7)
				C23	0.944 (3)	0.423 (3)	-0.019 (2)	0.079 (10)
				O	1.1740 (12)	0.5409 (10)	-0.0121 (8)	0.078 (4)

**Compound (2)***Crystal data* $M_r = 565.66$ 

Triclinic

 $P\bar{1}$  $a = 8.019 (2) \text{ \AA}$  $b = 9.889 (2) \text{ \AA}$  $c = 12.726 (2) \text{ \AA}$  $\alpha = 80.21 (2)^\circ$  $\beta = 85.31 (2)^\circ$  $\gamma = 81.69 (2)^\circ$  $V = 982.3 (4) \text{ \AA}^3$  $Z = 2$  $D_x = 1.912 \text{ Mg m}^{-3}$ *Data collection*

Siemens P3m/V diffractometer

 $\omega$  scans

Absorption correction: analytical

 $T_{\min} = 0.848$ ,  $T_{\max} = 0.923$ 

4869 measured reflections

4543 independent reflections

2711 observed reflections

 $[I > 2\sigma(I)]$ *Refinement*Refinement on  $F^2$  $R = 0.0453$  $wR = 0.0523$  $S = 1.57$ 

2711 reflections

300 parameters

 $w = 1/[\sigma^2(F) + 0.0004F^2]$ Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 32 reflections

 $\theta = 10\text{--}11^\circ$  $\mu = 1.05 \text{ mm}^{-1}$  $T = 298 \text{ K}$ 

Needle

 $0.40 \times 0.14 \times 0.08 \text{ mm}$ 

Black

 $R_{\text{int}} = 0.0453$  $\theta_{\text{max}} = 27.5^\circ$  $h = 0 \rightarrow 10$  $k = -12 \rightarrow 12$  $l = -16 \rightarrow 16$ 

4 standard reflections

monitored every 96

reflections

intensity decay: 1%

 $(\Delta/\sigma)_{\text{max}} = 0.001$  $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$ 

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

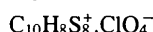
Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
S3	0.73517 (14)	1.11194 (12)	0.15623 (9)	0.0351 (4)
S4	0.79296 (14)	0.96086 (12)	-0.05253 (9)	0.0357 (4)
S9	0.4813 (2)	1.31718 (12)	0.04806 (9)	0.0382 (4)
S10	0.5325 (2)	1.16357 (11)	-0.15655 (9)	0.0354 (4)
S11	0.7045 (2)	1.2338 (2)	0.35502 (10)	0.0518 (5)
S12	0.8801 (2)	0.81018 (14)	-0.23185 (10)	0.0454 (4)
S17	0.3971 (2)	1.47592 (13)	0.22376 (11)	0.0528 (5)
S18	0.5739 (2)	1.06077 (14)	-0.36165 (9)	0.0450 (4)
C1	0.6213 (5)	1.1690 (4)	0.0449 (3)	0.0292 (14)

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

C1—S3	1.718 (4)	C7—S17	1.744 (5)
C5—S3	1.742 (5)	C15—S17	1.76 (2)
C2—S4	1.724 (4)	C15'—S17	1.93 (4)
C6—S4	1.742 (5)	C8—S18	1.741 (4)
C1—S9	1.717 (4)	C16—S18	1.83 (1)
C7—S9	1.740 (5)	C16'—S18	1.76 (3)
C2—S10	1.728 (4)	C2—C1	1.379 (6)
C8—S10	1.725 (4)	C7—C5	1.346 (6)
C5—S11	1.743 (5)	C8—C6	1.360 (6)
C13—S11	1.79 (2)	C15—C13	1.48 (3)
C13'—S11	1.76 (3)	C15'—C13'	1.53 (4)
C6—S12	1.735 (4)	C16—C14	1.51 (2)
C14—S12	1.759 (12)	C16'—C14'	1.48 (5)
C14'—S12	1.95 (2)		
C1—S3—C5	95.2 (2)	C7—C5—S11	127.0 (4)
C2—S4—C6	95.8 (2)	S3—C5—S11	116.3 (2)
C1—S9—C7	95.4 (2)	C8—C6—S4	116.4 (3)
C2—S10—C8	96.1 (2)	C8—C6—S12	129.5 (4)
C5—S11—C13	97.8 (7)	S4—C6—S12	114.1 (2)
C5—S11—C13'	107.6 (9)	S9—C7—S17	114.3 (2)
C6—S12—C14	102.9 (4)	S9—C7—C5	116.7 (3)
C6—S12—C14'	97.1 (12)	S17—C7—C5	129.1 (4)
C7—S17—C15	104.4 (6)	S10—C8—S18	115.8 (2)
C7—S17—C15'	96.6 (9)	S10—C8—C6	116.7 (3)
C8—S18—C16	98.2 (3)	S18—C8—C6	127.5 (3)
C8—S18—C16'	106.1 (9)	C15—C13—S11	118.1 (13)
C2—C1—S3	122.6 (3)	C15'—C13'—S11	114. (2)
C2—C1—S9	121.5 (3)	S17—C15—C13	116.4 (13)
S3—C1—S9	115.9 (3)	S17—C15'—C13'	113. (2)
S4—C2—S10	115.0 (3)	C16—C14—S12	113. (1)
S4—C2—C1	122.6 (3)	C16'—C14'—S12	113. (2)
S10—C2—C1	122.4 (3)	S18—C16—C14	113.6 (8)
C7—C5—S3	116.7 (3)	S18—C16'—C14'	114. (3)

**Compound (3)***Crystal data* $M_r = 484.09$ 

Monoclinic

 $C2/m$  $a = 14.172 (2) \text{ \AA}$  $b = 10.630 (2) \text{ \AA}$  $c = 5.751 (1) \text{ \AA}$  $\beta = 103.78 (1)^\circ$  $V = 841.4 (3) \text{ \AA}^3$  $Z = 2$  $D_x = 1.911 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 32

reflections

 $\theta = 10\text{--}11^\circ$  $\mu = 1.23 \text{ mm}^{-1}$  $T = 298 \text{ K}$ 

Plate

 $0.19 \times 0.16 \times 0.08 \text{ mm}$ 

Black

*Data collection*

Siemens P3m/V diffractometer	$R_{\text{int}} = 0.0163$
$\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: analytical	$h = 0 \rightarrow 18$
$T_{\text{min}} = 0.835$ , $T_{\text{max}} = 0.913$	$k = 0 \rightarrow 13$
1071 measured reflections	$l = -7 \rightarrow 7$
1032 independent reflections	4 standard reflections monitored every 96 reflections
791 observed reflections	intensity decay: 1%
$[I > 3\sigma(I)]$	

*Refinement*

Refinement on $F$	$(\Delta/\sigma)_{\text{max}} = 0.0001$
$R = 0.0488$	$\Delta\rho_{\text{max}} = 0.69 \text{ e } \text{\AA}^{-3}$
$wR = 0.0644$	$\Delta\rho_{\text{min}} = -0.86 \text{ e } \text{\AA}^{-3}$
$S = 2.26$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
791 reflections	
74 parameters	
$w = 1/[\sigma^2(F) + 0.0004F^2]$	

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (3)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
S1	0.42632 (7)	0.13702 (9)	1.2388 (2)	0.0434 (3)
S2	0.29653 (8)	0.16252 (10)	0.7574 (2)	0.0547 (4)
C2	0.3580 (2)	0.0642 (4)	0.9848 (6)	0.0383 (11)
C1	0.4685 (3)	0	1.3871 (9)	0.037 (2)
C3	0.2143 (8)	0.0452 (9)	0.549 (2)	0.056 (3)
C3'	0.1932 (6)	0.0784 (9)	0.653 (2)	0.048 (3)
C1	0	0	0	0.141 (3)
O1	-0.0845 (8)	0.0931 (10)	-0.050 (2)	0.121 (5)
O2	-0.0020 (10)	0.0615 (14)	-0.193 (4)	0.232 (12)

Table 6. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (3)

C2—S1	1.731 (3)	C2'—C2	1.365 (6)
C1—S1	1.721 (3)	C1''—C1	1.390 (7)
C2—S2	1.738 (3)	C3''—C3	1.502 (14)
C3—S2	1.918 (9)	C3'—C3'	1.502 (14)
C3'—S2	1.699 (9)		
C2—S1—C1	95.6 (2)	S1—C2—S2	116.5 (2)
C2—S2—C3	101.5 (3)	C1''—C1—S1	122.20 (14)
C2—S2—C3'	100.6 (3)	S1—C1—S1'	115.6 (3)
C2'—C2—S1	116.6 (2)	C3''—C3—S2	118.0 (7)
C2'—C2—S2	127.0 (2)	S2—C3'—C3'	111.3 (7)

Symmetry codes: (i)  $x, -y, z$ ; (ii)  $1 - x, -y, 3 - z$ .

For each structure, the  $\omega$ -scan width was symmetrically over  $1.2^\circ$  about the  $K\alpha_{1,2}$  maximum and the background was offset 1.0 and  $-1.0^\circ$  in  $\omega$  from the  $K\alpha_{1,2}$  maximum. The scan speed was a variable  $3\text{--}6^\circ \text{ min}^{-1}$ , depending upon intensity. The linear absorption coefficients were calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The structure of (1) was solved by direct methods. The  $\text{ClCH}_2\text{COCl}$  solvent molecule is disordered around a center of inversion. The site occupation factor of the O atom was fixed at 0.5, while those of the C and C' atoms were fixed at 0.6 and 0.4, respectively.

The structure of (2) was solved by direct methods. The  $\text{C}_4\text{H}_8\text{O}$  solvent molecule is disordered around a center of inversion. The site occupation factors of all of the atoms

were fixed at 0.5, except for atom C22 which is common to both and has a site occupation factor of 1. The  $\text{CH}_2$  units are disordered. The site occupation factors for the C13 and C15 methylene units refined to 0.66 (3), and consequently those of the C13' and C15' methylene units refined to 0.34 (3). The site occupation factors for the C14 and C16 methylene units refined to 0.72 (3), and consequently those of the C14' and C16' methylene units refined to 0.28 (3).

For compound (3), the systematic absences could not differentiate between space groups  $C2$ ,  $Cm$  and  $C2/m$ . The structure was solved in  $C2/m$  and refined in all three possible space groups. Only  $C2/m$  gave a full and good solution. Refinement in  $C2$  and  $Cm$  gave results that were not acceptable from a structural point of view. Chemically similar bonds were significantly different. Correlation factors were very high and a full solution was not obtained in either  $C2$  or  $Cm$ . The structure was refined by full-matrix least squares in the  $C2/m$  space group. The outer  $\text{CH}_2$  units are disordered about mirror planes and thus had their site occupation factors fixed at 0.5. The site occupation factors for atoms O1 and O2 of the disordered perchlorate ion were also fixed at 0.5.

The H atoms of all three structures were calculated in idealized positions ( $0.96 \text{ \AA}$ ), given fixed displacement parameters ( $0.08 \text{ \AA}^2$ ) and not refined.

For all compounds, data collection: *SHELXTL-Plus* (Sheldrick, 1990); cell refinement: *SHELXS76* (Sheldrick, 1976); data reduction: *SHELXTL-Plus*; program(s) used to solve structures: *SHELXTL-Plus*; program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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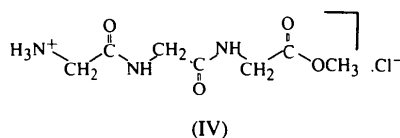
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MeGly<sub>3</sub> forms an infinite puckered sheet of hydrogen-bonded molecules related by a screw axis. Each molecule is held in the crystal structure by four hydrogen bonds involving NH<sub>3</sub><sup>+</sup>, NH and two CO groups.

### Comment

During a study of solid-state reactions of polypeptide esters, diglycyl-glycine methyl ester hydrochloride (MeGly<sub>3</sub>), (IV), was prepared according to the procedures of Sluyterman & Kooistra (1952) and Sluyterman & Veenedaal (1952). Its crystal structure was determined by single-crystal X-ray diffraction.



Diglycyl-glycine has seven rotational degrees of freedom (apart from C—NH<sub>3</sub> rotation); however, its conformation is determined mainly by strong intramolecular interactions such as the conjugation between the lone-pair electrons of an N atom and a neighbouring carbonyl group. This strong interaction favors a planar N—C(C)=O moiety and the number of free rotations is reduced to five. The molecule has several donors and acceptors of hydrogen bonds and the conformation of the molecule in the solid state is, therefore, also determined by intermolecular hydrogen bonds. A few crystal structures of compounds containing the diglycyl-glycine skeleton are known. Only three do not include metal cations (in the latter compounds the conformation is strongly influenced by interactions with the cation). The conformation and the hydrogen-bonding patterns have been compared for glycyl-glycyl-glycine hydrochloride, (I) (Lalitha & Subramanian, 1982), sarcosyl-glycyl-glycine, (II) (Glusker, Carrel, Berman, Gallen & Peck, 1977), glycyl-glycyl-glycine, (III) (Srikrishnan, Winiewicz & Parthasarathy, 1982), and the methyl ester of (I), the subject of the present study, (IV).

The expected most stable conformation is the same as found for alkanes, namely all-*trans*. Some torsion angles in compounds (I)–(IV) are compared in Table 3. Most of the torsion angles indicate the all-*trans* conformation found in alkanes. There are four exceptions that should be noted. In these cases, atoms are involved that are not constrained by the intramolecular interaction mentioned above (the resulting torsion angles are marked by a † in Table 3).

Each of the four compounds, (I)–(IV), includes three identical hydrogen-acceptor groups (C=O), two identical hydrogen-donor groups (NH) and a third which is either NH<sub>3</sub><sup>+</sup> or CH<sub>3</sub>NH<sub>2</sub><sup>+</sup>. The conformation of the molecule in the crystal and the possibility of hydrogen-bond

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## Hydrogen Bonding in Glycyl-glycyl-glycine Methyl Ester Hydrochloride

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### Abstract

The structure of the title compound, C<sub>7</sub>H<sub>14</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup>.Cl<sup>-</sup> (MeGly<sub>3</sub>), is described and compared to those of other compounds having the diglycyl-glycine moiety. Although the molecular structure of MeGly<sub>3</sub> is similar to that of the parent acid, its crystal structure is different.