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catena-Poly[piperazinium di-μ-sulfido-gallium]

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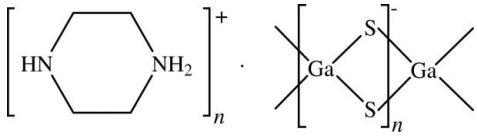
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.022; wR factor = 0.026; data-to-parameter ratio = 21.6.

The structure of the title compound, $\{(C_4H_{11}N_2)[GaS_2]\}_n$, which was prepared under solvothermal conditions, consists of one-dimensional $[GaS_2]^-$ chains of edge-sharing GaS_4 tetrahedra, separated by monoprotonated piperazinium cations. The crystal packing is consolidated by N—H···N and N—H···S hydrogen bonds.

Related literature

For related literature, see: Zheng *et al.* (2003); Bu, Zheng & Feng (2004); Peters & Krebs (1982); Bronger *et al.* (1987). The isostructural gallium selenide, $\{(C_4H_{11}N_2)[GaSe_2]\}_n$, was described by Bu, Zheng, Wang *et al.* (2004). Related structures containing one-dimensional $[GaS_2]^-$ chains were described by Vaqueiro (2006*a*,*b*). A fragment of a gallium selenide chain, $[Ga_6Se_{14}]^{10-}$, was reported by Deiseroth & Fu-Son (1981).



Experimental

Crystal data

$(C_4H_{11}N_2)[GaS_2]$
M_r = 221.00
Monoclinic, $P2_1/c$
a = 6.0798 (5) Å
b = 16.2655 (13) Å
c = 8.3611 (8) Å
β = 104.827 (5)°
V = 799.31 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.88 mm^{-1}
T = 298 K
0.20 × 0.12 × 0.08 mm

Data collection

Bruker-Nonius APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.554, T_{max} = 0.733
11588 measured reflections
2644 independent reflections
1772 reflections with $I > 3\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.026
S = 1.04
1772 reflections
82 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ga1—S2^{i}	2.3078 (5)	Ga1—S2	2.2984 (5)
Ga1—S3^{ii}	2.2877 (5)	Ga1—S3	2.2771 (5)
S2^{i}—Ga1—S3^{ii}	112.84 (2)	S2^{i}—Ga1—S3	118.656 (19)
S2^{i}—Ga1—S2	96.215 (17)	S3^{ii}—Ga1—S3	97.608 (17)
S3^{ii}—Ga1—S2	115.89 (2)	S2—Ga1—S3	116.89 (2)

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $-x+1, -y+1, -z+2$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H41···N7^{iii}	1.00	1.95	2.898 (2)	158
N4—H42···S2	1.00	2.71	3.6072 (19)	150
N7—H72···S2^{iv}	1.00	2.32	3.2842 (18)	162

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2412).

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supplementary materials

Acta Cryst. (2007). E**63**, m1700 [**doi:10.1107/S1600536807023598**]

catena-Poly[piperazinium di-μ-sulfido-gallium]

P. Vaqueiro and M. L. Romero

Comment

Solvothermal synthesis has been increasingly used for the preparation of a variety of sulfides containing the main group elements tin, germanium, arsenic, antimony and indium. By contrast, few solvothermally prepared gallium sulfides are known. Initial studies (Zheng *et al.*, 2003) suggested that there was large degree of similarity between the structural chemistry of solvothermally prepared indium and gallium sulfides. However, while the vast majority of reported structures for indium sulfides are based on supertetrahedral clusters (Bu, Zheng & Feng, 2004), recent work on gallium sulfides has resulted in the preparation of materials containing a variety of building units, including the one-dimensional $[GaS_2]^-$ chains observed in the title compound, (I).

The local coordination and the atom labelling scheme for the title compound is depicted in Figure 1. The structure of $\{(C_4H_{11}N_2)[GaS_2]\}_n$ contains GaS_4 tetrahedra, linked together by sharing non-adjacent edges to form one-dimensional $[GaS_2]^-$ chains, as shown in Figure 2. The $[GaS_2]^-$ chains, which run parallel to the *a*-axis, are separated by monoprotonated piperazinium cations. As shown in Figure 3, each piperazinium cation exhibits hydrogen-bonding interactions with sulfur atoms in the $[GaS_2]^-$ chains as well as with other piperazinium cations (Table 2).

The compound reported here is isostructural to piperazinium gallium selenide, $\{(C_4H_{11}N_2)[GaSe_2]\}_n$ (Bu, Zheng, Wang *et al.*, 2004), which contains $[GaSe_2]^-$ chains. A gallium selenide containing six-gallium atom fragments, $[Ga_6Se_{14}]^{10-}$, of this type of one-dimensional chains has also been reported (Deiseroth & Fu-Son, 1981). Recently some solvothermally prepared gallium sulfides, $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ and $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni), which contain $[GaS_2]^-$ chains separated by monoprotonated 1,4-bis(3-aminopropyl)piperazine or $[M(en)_3]^{2+}$ complexes respectively, have also been described (Vaqueiro, 2006*ab*). Furthermore, the one-dimensional $[GaS_2]^-$ chains of the title compound are similar to those found in SiS_2 (Peters & Krebs, 1982) and in $KFeS_2$-type compounds (Bronger *et al.*, 1987). While all of these compounds contain $[MQ_2]^-$chains (M= Si, Fe, Ga; Q = S, Se) formed by edge-sharing MQ_4 tetrahedra, the packing of the chains differs significantly between these phases. This might be related to the presence of a hydrogen-bond network in some of these materials.

Experimental

A mixture of Ga_2S_3 (136.8 mg; 0.58 mmol), sulfur (148.5 mg; 4.64 mmol) and piperazine (1.290 g, 15 mmol) was loaded into a 23 ml Teflon-lined stainless steel autoclave. 3 ml of methanol were added to form a mixture with an approximate molar composition Ga_2S_3:*S*:piperazine:methanol of 0.58:4.64:15:74. After stirring the mixture, the container was closed, heated at 443 K for 10 days, and then cooled to room temperature at a cooling rate of 1 K min^{-1}. The product, which contained a

large number of colourless blocks of the title compound, was filtered, washed with methanol, deionized water and acetone and dried in air at room temperature.

Refinement

The hydrogen atoms were placed geometrically after each cycle of refinement (C—H = 1.00 Å, N—H = 1.00 Å) and U_{iso}(H) = 1.2U_{eq}(carrier), but not refined.

Figures

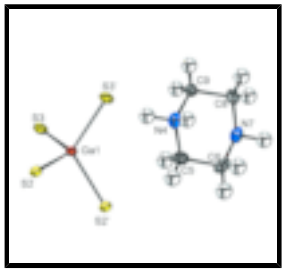

Fig. 1. **Figure 1.** Local coordination diagram for (I) showing the atom labelling scheme and displacement ellipsoids at 50% probability (arbitrary spheres for the H atoms).

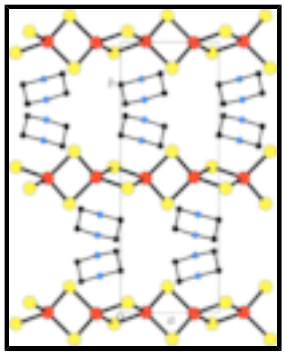

Fig. 2. **Figure 2.** View of the $\{(C_4H_{11}N_2)[GaS_2]\}_n$ structure along the [001] direction. Hydrogen atoms have been omitted for clarity.

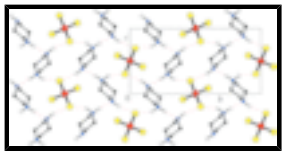

Fig. 3. **Figure 3.** View of the $\{(C_4H_{11}N_2)[GaS_2]\}_n$ structure showing the hydrogen-bond network (dashed lines).

catena-Poly[piperazinium di-μ-sulfido-gallium]

Crystal data

$(C_4H_{11}N_2)[GaS_2]$	F_{000} = 448
M_r = 221.00	D_x = 1.836 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: not measured K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 6.0798 (5) Å	Cell parameters from 2182 reflections
b = 16.2655 (13) Å	θ = 2.8–31.5°
c = 8.3611 (8) Å	μ = 3.88 mm^{-1}
β = 104.827 (5)°	T = 298 K

V = 799.31 (12) Å^3	Block, colourless
Z = 4	0.20 × 0.12 × 0.08 mm

Data collection

Bruker-Nonius APEX-2 CCD area-detector diffractometer	1772 reflections with $I > 3.00u(I)$
Monochromator: graphite	R_{int} = 0.025
T = 298 K	θ_{max} = 31.5º
ω/2θ scans	θ_{min} = 2.8º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −8→7
T_{min} = 0.554, T_{max} = 0.733	k = −23→23
11588 measured reflections	l = −12→12
2644 independent reflections	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.022	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = F /Fmax Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 1.32 -1.15 1.10 -0.477 [*P*rince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag. Watkin, D. (1994). *Acta Cryst.* A**50**, 411–437.]
$wR(F^2)$ = 0.026	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.04	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
1772 reflections	$\Delta\rho_{min}$ = −0.61 e Å^{-3}
82 parameters	Extinction correction: None
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ga1	0.25176 (3)	0.497823 (12)	0.99690 (2)	0.0164
S2	−0.06988 (7)	0.53947 (3)	0.80332 (6)	0.0200
S3	0.47634 (7)	0.40352 (3)	0.91380 (6)	0.0230
N4	0.2400 (3)	0.71296 (11)	0.7036 (2)	0.0272
C5	0.0475 (4)	0.72761 (15)	0.5606 (3)	0.0312
C6	0.0018 (4)	0.65667 (16)	0.4372 (3)	0.0322
N7	0.2128 (3)	0.63714 (11)	0.3850 (2)	0.0276
C8	0.4055 (4)	0.61672 (13)	0.5316 (3)	0.0295

C9	0.4449 (4)	0.68875 (13)	0.6515 (3)	0.0277
H41	0.2730	0.7645	0.7708	0.0330*
H42	0.1994	0.6680	0.7725	0.0330*
H51	0.0798	0.7781	0.5023	0.0382*
H52	−0.0918	0.7366	0.6011	0.0382*
H61	−0.1217	0.6727	0.3380	0.0385*
H62	−0.0468	0.6072	0.4903	0.0385*
H72	0.1830	0.5890	0.3081	0.0333*
H81	0.5465	0.6062	0.4941	0.0354*
H82	0.3665	0.5666	0.5878	0.0354*
H91	0.4969	0.7370	0.5966	0.0320*
H92	0.5663	0.6731	0.7521	0.0320*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.01204 (8)	0.01849 (9)	0.01931 (9)	0.00000 (6)	0.00510 (6)	−0.00066 (7)
S2	0.01562 (16)	0.0259 (2)	0.01824 (18)	0.00077 (16)	0.00391 (13)	0.00456 (16)
S3	0.01648 (17)	0.01957 (19)	0.0337 (2)	−0.00186 (16)	0.00780 (16)	−0.00880 (17)
N4	0.0356 (9)	0.0248 (8)	0.0221 (8)	−0.0025 (7)	0.0091 (7)	−0.0007 (6)
C5	0.0234 (9)	0.0401 (11)	0.0320 (10)	0.0026 (8)	0.0103 (8)	−0.0023 (9)
C6	0.0259 (9)	0.0430 (12)	0.0274 (10)	−0.0110 (8)	0.0063 (7)	−0.0027 (9)
N7	0.0353 (9)	0.0274 (8)	0.0207 (7)	−0.0051 (7)	0.0083 (7)	−0.0036 (6)
C8	0.0344 (10)	0.0239 (9)	0.0301 (10)	0.0049 (7)	0.0079 (9)	−0.0008 (7)
C9	0.0272 (9)	0.0237 (9)	0.0290 (9)	0.0012 (7)	0.0015 (7)	−0.0025 (7)

Geometric parameters (Å, °)

Ga1—S2^{i}	2.3078 (5)	C6—N7	1.491 (3)
Ga1—S3^{ii}	2.2877 (5)	C6—H61	1.000
Ga1—S2	2.2984 (5)	C6—H62	1.000
Ga1—S3	2.2771 (5)	N7—C8	1.500 (3)
N4—C5	1.463 (3)	N7—H72	1.000
N4—C9	1.475 (3)	C8—C9	1.521 (3)
N4—H41	1.000	C8—H81	1.000
N4—H42	1.000	C8—H82	1.000
C5—C6	1.525 (3)	C9—H91	1.000
C5—H51	1.000	C9—H92	1.000
C5—H52	1.000		
S2^{i}—Ga1—S3^{ii}	112.84 (2)	C5—C6—H61	109.402
S2^{i}—Ga1—S2	96.215 (17)	N7—C6—H61	109.413
S3^{ii}—Ga1—S2	115.89 (2)	C5—C6—H62	109.402
S2^{i}—Ga1—S3	118.656 (19)	N7—C6—H62	109.406
S3^{ii}—Ga1—S3	97.608 (17)	H61—C6—H62	109.466
S2—Ga1—S3	116.89 (2)	C6—N7—C8	111.02 (17)
Ga1^{i}—S2—Ga1	83.785 (17)	C6—N7—H72	109.088
Ga1^{ii}—S3—Ga1	82.392 (17)	C8—N7—H72	109.088

C5—N4—C9	111.17 (16)	N7—C8—C9	109.05 (16)
C5—N4—H41	109.046	N7—C8—H81	109.583
C9—N4—H41	109.042	C9—C8—H81	109.582
C5—N4—H42	109.048	N7—C8—H82	109.574
C9—N4—H42	109.048	C9—C8—H82	109.580
H41—N4—H42	109.470	H81—C8—H82	109.462
N4—C5—C6	113.51 (19)	C8—C9—N4	113.48 (17)
N4—C5—H51	108.449	C8—C9—H91	108.461
C6—C5—H51	108.456	N4—C9—H91	108.464
N4—C5—H52	108.445	C8—C9—H92	108.461
C6—C5—H52	108.458	N4—C9—H92	108.458
H51—C5—H52	109.469	H91—C9—H92	109.470
C5—C6—N7	109.74 (16)		

Symmetry codes: (i) −*x*, −*y*+1, −*z*+2; (ii) −*x*+1, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···N7^{iii}	1.00	1.95	2.898 (2)	158
N4—H42···S2	1.00	2.71	3.6072 (19)	150
N7—H72···S2^{iv}	1.00	2.32	3.2842 (18)	162

Symmetry codes: (iii) *x*, −*y*+3/2, *z*+1/2; (iv) −*x*, −*y*+1, −*z*+1.

Fig. 1

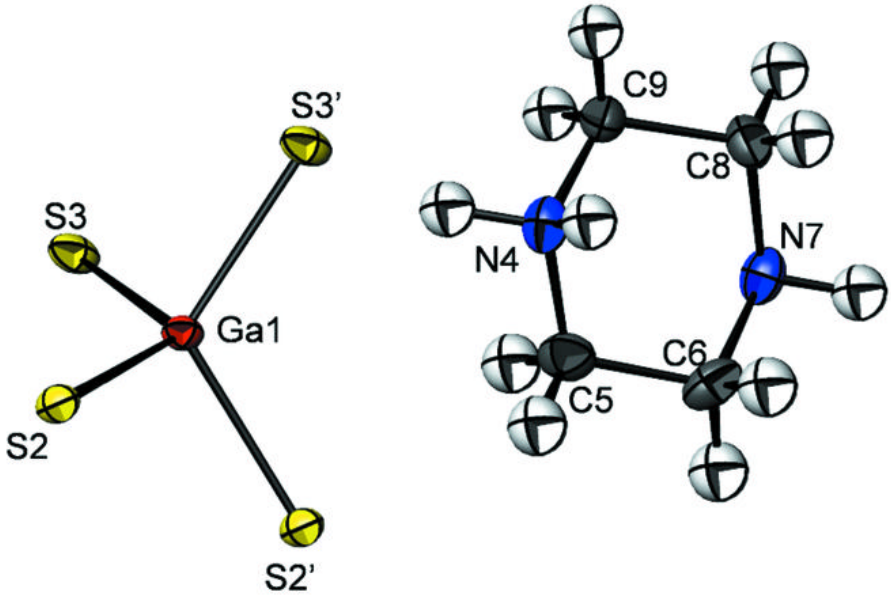

Fig. 2

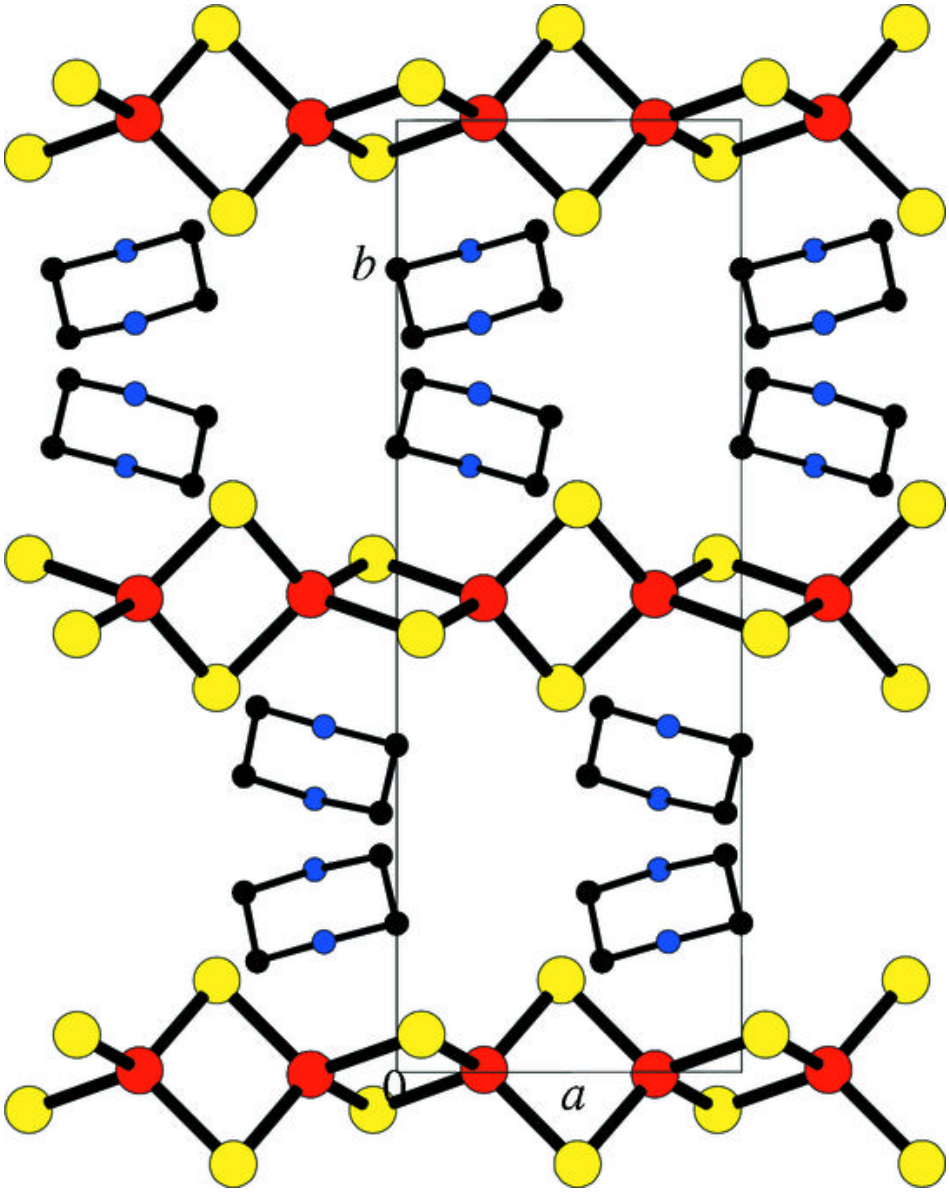

Fig. 3