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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.035
wR factor = 0.091
Data-to-parameter ratio = 17.5

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

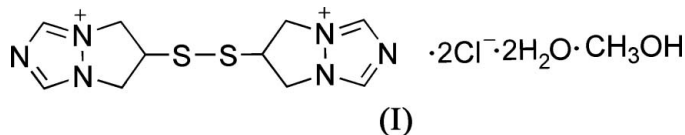
6,6-Dithiobis(6,7-dihydro-5H-pyrazolo[1,2-a]-
[1,2,4]triazolium) dichloride methanol solvate
dihydrate

The title compound, $\text{C}_{10}\text{H}_{14}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_4\text{O} \cdot 2\text{H}_2\text{O}$, was synthesized by the intermolecular cyclization of bis(4-pyrazolidinyl) disulfide dihydrochloride and ethyl formimidate hydrochloride. The water molecules form hydrogen bonds with each other and the chloride counter-ions. One chloride counter-ion is also involved in $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonding with the methanol solvent molecule.

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Comment

The title compound, (I), is an important intermediate in the synthesis of biapenem which is one of the most effective antibacterial drugs (Kumagai *et al.*, 1998) in the anti-infective chemotherapy field.



The molecular structure of (I) is shown in Fig. 1. There is extensive $\text{O}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonding within the crystal structure involving water, chloride and methanol (Table 1).

Experimental

A mixture of bis(4-pyrazolidinyl) disulfide dihydrochloride (28 g, 0.1 mol), ethyl formimidate hydrochloride (109 g, 1 mol) and KHCO_3 (20 g, 0.2 mol) was added to Hwater (1 l) at 273 K, and the mixture was stirred for 10 min. After adjusting to $\text{pH} = 2$ with 6 M HCl, the acidic reaction mixture was evaporated to dryness *in vacuo*. The solid residue was recrystallized from methanol to give the title compound, (I) (m.p. 556–557 K). $^1\text{H NMR}$ (D_2O , 270 MHz): δ 4.70–4.85 (m, 6H), 4.85–5.00 (m, 4H), 8.90 (s, 4H); ESI MS m/z 317.04 [$(M - \text{Cl})^+$]. 1 g of (I) was dissolved in methanol (200 ml) and ethyl acetate (200 ml); the solution was kept at room temperature for 15 d. Natural evaporation gave colorless single crystals of (I) suitable for X-ray analysis.

Crystal data

$\text{C}_{10}\text{H}_{14}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_4\text{O} \cdot 2\text{H}_2\text{O}$
 $M_r = 421.37$
Monoclinic, $P2_1/c$
 $a = 9.942$ (3) Å
 $b = 14.854$ (4) Å
 $c = 13.175$ (4) Å
 $\beta = 107.502$ (4) $^\circ$
 $V = 1855.5$ (9) Å^3
 $Z = 4$

$D_x = 1.508 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1021 reflections
 $\theta = 3.4\text{--}26.1^\circ$
 $\mu = 0.60 \text{ mm}^{-1}$
 $T = 293$ (2) K
Block, colorless
 $0.24 \times 0.22 \times 0.18 \text{ mm}$

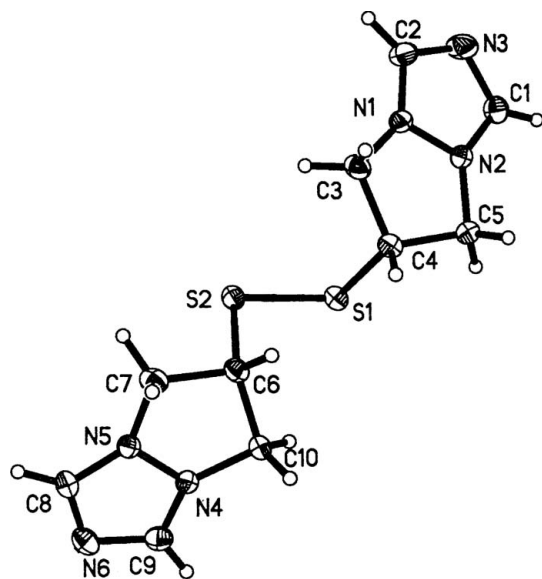


Figure 1

The molecular structure of the cation in (I), shown with 30% probability ellipsoids.

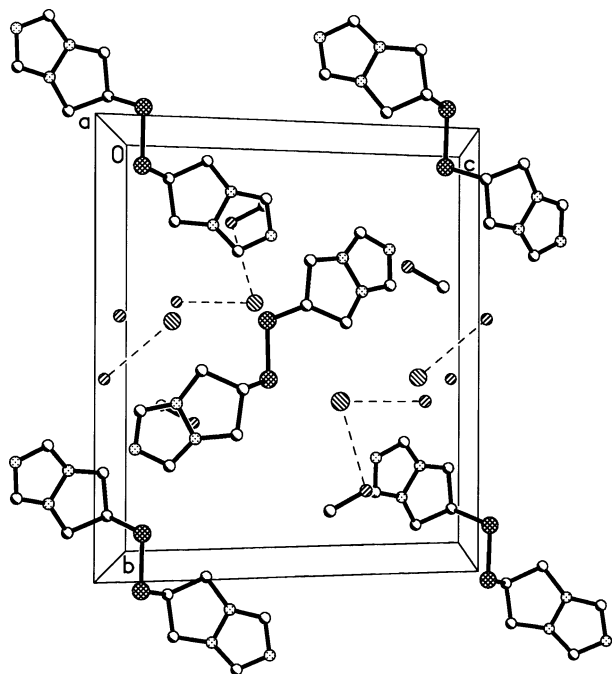


Figure 2

The crystal structure of (I), viewed along the *a* axis. H atoms have been omitted. Dashed lines indicate hydrogen bonds.

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.804$, $T_{\max} = 0.900$
 10653 measured reflections

3826 independent reflections
 2941 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 26.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -18 \rightarrow 16$
 $l = -12 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.091$
 $S = 1.02$
 3826 reflections
 219 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.6565P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...Cl2	0.82	2.32	3.13	166
O2—H2A...O3	0.97	1.90	2.84	163
O2—H2B...Cl1 ⁱ	0.90	2.29	3.17	165
O3—H3C...Cl2	0.93	2.18	3.08	165
O3—H3D...Cl1	0.89	2.43	3.31	169

Symmetry code: (i) $-x + 1, -y, -z + 1$.

H atoms were positioned geometrically, with C—H = 0.93–0.98 \AA , and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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References

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 Kumagai, T., Tamai, S., Abe, T., Matsunaga, H., Hayashi, K., Kishi, I., Shiro, M. & Nagao, Y. (1998). *J. Org. Chem.* **63**, 8145–8149.
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