

Nicolet (1987). *XEMP* (part of Nicolet X-ray program system). Nicolet Analytical X-ray Instruments, Madison, Wisconsin, USA.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Siemens (1994). *XP. Molecular Graphics Program*, version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
 Stoe & Cie (1991a). *DIF4. Diffractometer Control Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1991b). *REDU4. Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
 Tsuji, R., Komatsu, K., Takeuchi, K., Shiro, M., Cohen, S. & Rabinovitz, M. (1993). *J. Phys. Org. Chem.* **6**, 435–444.

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Bis(2,4-diaminopyrimidinium) Sulfate Monohydrate, 2C₄H₇N₄⁺·SO₄²⁻·H₂O[†]

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Abstract

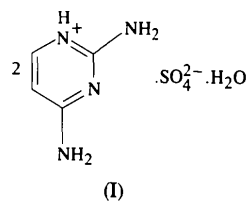
The asymmetric unit of the crystal consists of one sulfate ion, one water molecule and two 2,4-diaminopyrimidine (DAP) molecules stacked parallel to the *b* direction with average perpendicular separations of 3.310 (4) and 3.343 (4) Å, respectively. The tilt angle between the least-squares planes of the two DAP molecules in the asymmetric unit is 2.1 (1)°. The structure is stabilized by stacking forces, N—H···N hydrogen bonds and N—H···O hydrogen bonds.

Comment

2,4-Diaminopyrimidines and condensed pyrimidine systems are strong antagonists of folic acid (Hitchings, Elion, Vanderwerff & Falco, 1948; Hitchings, Falco, Vanderwerff, Russel & Elion, 1952) and some of these compounds possess growth-inhibitory properties affecting various living systems. It has also been found that 2,4-diaminopyrimidine has strong growth-inhibitory activity against *C. albicans*; the activities of 2,4,5,6-tetraamino- and 2,4,6-triaminopyrimidine are much weaker in that respect (Mukherjee, 1968). Therefore,

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in continuation of our structural studies of nucleic acid components (Banerjee, Dattagupta, Saenger & Rabczenko, 1977; Banerjee, Saenger, Lesyng, Kazimierzczuk & Shugar, 1978; Biswas, Iitaka, Shugar & Banerjee, 1989), the structure of the title compound, (I), was determined.



The structure consists of columnar stacks of DAP molecules and linear arrays of alternating SO₄²⁻ ions and water molecules, both running in the *b* direction (Fig. 2). Both the DAP molecules (*A* and *A'*) are planar, the largest deviations from the least-squares planes of the appropriate ring atoms being 0.039 (4) Å for N2 and 0.032 (4) Å for N2' and N4'. The atoms N1 and N1' are protonated. The average perpendicular distance between successive molecules of a stack alternates between 3.310 (4) and 3.343 (4) Å. Significant base-stacking interaction is obvious from the degree of overlap between adjacent base molecules (Fig. 2) and the short stack contacts C2'···C4 (3.310 Å) and C6'···C2 (3.391 Å).

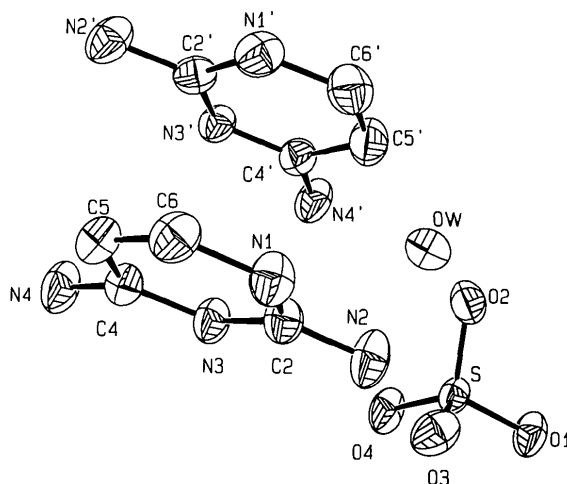


Fig. 1. ORTEP (Johnson, 1965) plot of the contents of the unit cell showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level for non-H atoms. H atoms have been omitted for clarity.

Hydrogen-bonding parameters are given in Table 2. Fig. 2 shows that DAP molecules pair up (a characteristic feature of nucleobases) through two N—H···N type hydrogen bonds symmetrically disposed about a centre of inversion. Stacks of the base pairs form hydrophobic columns. Sulfate–water arrays, stabilized by OW—HW1···O2 and OW—HW2···O3 hydro-

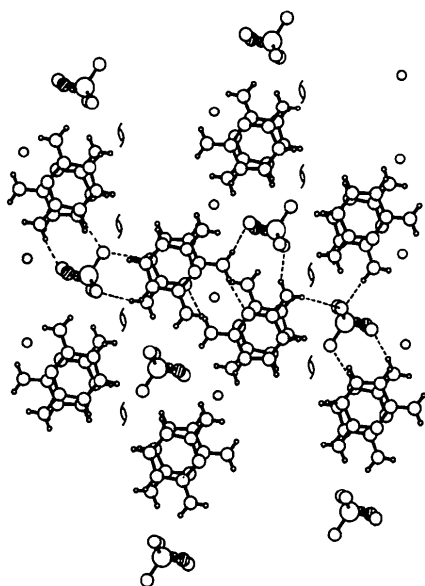


Fig. 2. The crystal packing viewed down the *b* axis. Hydrogen bonds are indicated by dashed lines. The O atoms of water molecules are shaded.

gen bonds and their symmetry equivalents, interconnect these columns through N—H···O hydrogen bonds. The distances along the *b* direction between successive water O atoms and S atoms are 3.393 (3) and 3.555 (3) Å.

Experimental

The title compound was prepared by reduction of the parent 6-chloro compound (Mukherjee, 1968).

Crystal data

$2C_4H_7N_4^+ \cdot SO_4^{2-} \cdot H_2O$

$M_r = 336.35$

Monoclinic

$P2_1/a$

$a = 20.992 (2) \text{ \AA}$

$b = 6.9480 (10) \text{ \AA}$

$c = 10.0830 (10) \text{ \AA}$

$\beta = 102.150 (10)^\circ$

$V = 1437.7 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.553 \text{ Mg m}^{-3}$

$D_m = 1.554 \text{ Mg m}^{-3}$

D_m measured by flotation in benzene/bromobenzene

Data collection

Enraf–Nonius CAD-4 diffractometer

ω - 2θ scans

Absorption correction: none

2762 measured reflections

2636 independent reflections

2561 observed reflections

$[I > 2\sigma(I)]$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 25\text{--}30^\circ$

$\mu = 2.394 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Thick prism

$0.45 \times 0.30 \times 0.12 \text{ mm}$

White

$R_{\text{int}} = 0.0418$

$\theta_{\text{max}} = 77.8^\circ$

$h = -26 \rightarrow 26$

$k = 0 \rightarrow 8$

$l = 0 \rightarrow 12$

3 standard reflections

monitored every 100

reflections

intensity decay: 1%

Refinement

Refinement on F^2

$R(F) = 0.0549$

$wR(F^2) = 0.1514$

$S = 1.096$

2632 reflections

200 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0855P)^2 + 1.0623P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.070$

$\Delta\rho_{\text{max}} = 0.349 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.776 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0048 (6)

Atomic scattering factors

from *SHELXS86*

(Sheldrick, 1985)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N1	0.17292 (10)	-0.1598 (3)	0.2899 (2)	0.0376 (5)
C2	0.14645 (11)	-0.1069 (4)	0.1601 (2)	0.0325 (5)
N3	0.08319 (9)	-0.0639 (3)	0.1193 (2)	0.0336 (5)
C4	0.04522 (12)	-0.0811 (4)	0.2113 (3)	0.0347 (5)
C5	0.07079 (14)	-0.1370 (4)	0.3475 (3)	0.0404 (6)
C6	0.13473 (14)	-0.1752 (4)	0.3825 (3)	0.0397 (6)
N2	0.18552 (10)	-0.0987 (4)	0.0730 (2)	0.0428 (6)
N4	-0.01737 (10)	-0.0413 (4)	0.1709 (2)	0.0455 (6)
S	0.16068 (3)	0.18881 (9)	-0.28748 (5)	0.0310 (2)
O1	0.20196 (9)	0.1904 (3)	-0.3895 (2)	0.0418 (5)
O2	0.17984 (9)	0.3535 (3)	-0.1956 (2)	0.0446 (5)
O3 ⁺	0.16981 (10)	0.0103 (3)	-0.2098 (2)	0.0488 (5)
O4	0.09222 (8)	0.2087 (3)	-0.3568 (2)	0.0453 (5)
N1 ⁱ	0.14107 (12)	0.3334 (4)	0.3566 (2)	0.0410 (5)
C2 ⁱ	0.07707 (12)	0.3730 (4)	0.3006 (2)	0.0337 (5)
N3 ⁱ	0.05739 (10)	0.4218 (3)	0.1709 (2)	0.0334 (5)
C4 ⁱ	0.10177 (12)	0.4244 (4)	0.0929 (2)	0.0345 (5)
C5 ⁱ	0.16924 (13)	0.3864 (5)	0.1468 (3)	0.0439 (6)
C6 ⁱ	0.18626 (14)	0.3435 (4)	0.2785 (3)	0.0444 (6)
N2 ⁱ	0.03524 (12)	0.3606 (4)	0.3813 (2)	0.0450 (6)
N4 ⁱ	0.08244 (11)	0.4670 (4)	-0.0372 (2)	0.0457 (6)
OW	0.10663 (13)	-0.3231 (3)	0.6734 (2)	0.0591 (6)

Table 2. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N2—H21···O3	2.08	2.901 (3)	159
N4 ⁱ —H4 ⁱ 2···O2	2.15	2.954 (3)	156
N2—H22···O2 ⁱ	2.01	2.857 (3)	167
N1—H1···O1 ⁱ	1.97	2.807 (3)	162
N4—H42···O4 ⁱⁱ	2.14	2.928 (3)	153
N4—H41···N3 ⁱⁱⁱ	2.20	3.050 (3)	172
N2 ⁱ —H2 ⁱ 2···O4 ⁱⁱⁱ	2.02	2.861 (3)	167
N1 ⁱ —H1 ⁱ ···O1 ⁱⁱⁱ	1.97	2.792 (3)	161
OW—HW1···O3 ⁱⁱⁱ	2.11	2.800 (3)	133
N2 ⁱ —H2 ⁱ 1···OW ^{iv}	2.13	2.923 (3)	153
N4 ⁱ —H4 ⁱ 1···N3 ^{iv}	2.20	3.060 (3)	174
OW—HW2···O2 ^{vi}	1.98	2.881 (3)	172

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

The structure was solved using *SHELXS86* (Sheldrick, 1985) and refined using *SHELXL93* (Sheldrick, 1993) by full-matrix least-squares methods. H atoms were fixed from a difference Fourier map and were assigned the equivalent isotropic displacement parameters of the atoms to which they are attached. Geometrical parameters were calculated using *PARST* (Nardelli, 1983). All calculations were carried out on PC/AT(386) and MicroVaxII computers.

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computational help and cooperation. SP thanks the CSIR (Government of India) for a Senior Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Banerjee, A., Dattagupta, J. K., Saenger, W. & Rabczenko, A. (1977). *Acta Cryst.* **B33**, 90–94.
 Banerjee, A., Saenger, W., Lesyng, B., Kazimierczuk, Z. & Shugar, D. (1978). *Acta Cryst.* **B34**, 2472–2477.
 Biswas, G., Iitaka, Y., Shugar, D. & Banerjee, A. (1989). *Nucleosides Nucleotides*, **8**, 1335–1343.
 Hitchings, G. H., Elion, G. B., Vanderwerff, H. & Falco, E. A. (1948). *J. Biol. Chem.* **174**, 765–767.
 Hitchings, G. H., Falco, E. A., Vanderwerff, H., Russel, P. B. & Elion, G. B. (1952). *J. Biol. Chem.* **199**, 43–45.
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Mukherjee, M. (1968). PhD thesis, University of Calcutta, India.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–97.
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Bromobis(diethyldithiocarbamato)-(4-methoxyphenyl)tellurium(IV)

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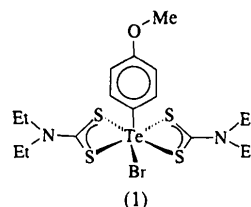
Abstract

The crystals of the Te^{IV} complex *p*-CH₃OC₆H₄Te(Et₂NCS₂)₂Br are isomorphous with those of the iodine and mixed iodine/bromine analogues previously investigated. The structure is pentagonal bipyramidal at the Te atom with four S atoms [Te—S 2.618–2.721 (1) Å] and the Br atom [Te—Br 2.943 (1) Å] in equatorial positions. The *p*-methoxyphenyl group is axial [Te—C 2.147 (3) Å]. The second axial position is approached by a Br atom of a centrosymmetrically related complex

[Te···Br 3.423 (1) Å, C—Te···Br 173.1 (1)°] so that the molecules are joined into centrosymmetric pairs by this weak secondary coordination.

Comment

The structure of the title complex, (1), is quite similar to the isomorphous structures of the iodo complex *p*-MeOC₆H₄Te(Et₂NCS₂)₂I, (2), and the mixed Br/I complex *p*-MeOC₆H₄Te(Et₂NCS₂)₂Br_{0.41}I_{0.59}, (3), investigated earlier (Husebye, Kudis & Lindeman, 1996a). Therefore, the discussion will focus only on those structural parameters of complex (1) which differ significantly from the corresponding structural parameters of (2) and (3), and are an effect of the halogen-atom replacement.



The Te atom in complex (1) has pentagonal bipyramidal coordination geometry with two bidentate dithiocarbamate ligands and a Br atom in the equatorial plane. There is an aryl group and a secondary bonded Br atom of a centrosymmetrically related complex in axial positions (Fig. 1), so that the molecules of (1) are connected into weakly bound dimers *via* two bridging bromine ligands. This secondary bonding is weaker than in the corresponding iodide [the Te—Br and Te···Br distances differ by 0.480 (1) Å in (1), whereas the Te—I and Te···I distances differ by 0.400 (1) and 0.394 (2) Å in (2) and (3), respectively], in full agreement with the weaker *trans* influence of Br as compared to I. However,

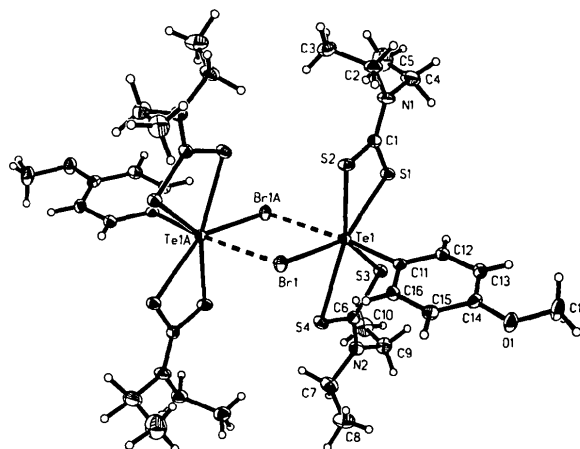


Fig. 1. Perspective view of (1) showing a pair of centrosymmetrically related molecules loosely associated by secondary Te···Br contacts (dashed lines). The displacement ellipsoids are drawn at the 50% probability level.