Table 3. *Comparison of mean bond lengths (Å) in related metal complexes*
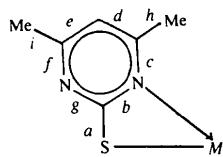
Bond	(I)	(II)	(III)	(IV)
a	1.732 (8)	1.728 (8)	1.71 (5)	1.76 (1)
b	1.350 (7)	1.357 (7)	1.38 (1)	1.337 (4)
c	1.352 (3)	1.347 (7)	1.36 (2)	1.35 (1)
d	1.384 (5)	1.390 (4)	1.40 (3)	1.370 (8)
e	1.387 (3)	1.376 (6)	1.39 (4)	1.359 (6)
f	1.33 (2)	1.347 (6)	1.34 (3)	1.346 (1)
g	1.33 (2)	1.327 (7)	1.33 (2)	1.33 (2)
h	1.48 (1)	1.49 (1)	1.50 (2)	1.49 (1)
i	1.50 (2)	1.503 (9)	1.54 (4)	1.505 (7)

References: (I) Seth (1994); (II) Cartweight *et al.* (1979); (III) Cotton *et al.* (1979); (IV) this work.

The positions of the Cu atoms were obtained from a Patterson function while successive weighted Fourier syntheses yielded the coordinates of all the remaining non-H atoms; non-H atoms were subjected to anisotropic refinement. All H atoms except those of the lattice water molecules were geometrically generated (C—H 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned appropriate isotropic displacement parameters and included in the structure-factor calculations. The water H atoms could not be located and were not included in the calculations. Anomalous-dispersion corrections for Cu were incorporated.

Program systems used: *XRAYARC* (Vickery, Bright & Mallinson, 1971) for Patterson syntheses; *NORMAL, EXFFT* and *SEARCH* sequences of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) for weighted Fourier syntheses; *SHELX*76 (Sheldrick, 1976) for refinement; *PARST*86 (Nardelli, 1983) for molecular geometry calculations; *ORTEP*II (Johnson, 1976) for molecular graphics.

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Bis(4,6-diamino-2-methylthiopyrimidinium) Tetrabromozincate(II)

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Abstract

The reaction of the pyrimidine base 4,6-diamino-2-methylthiopyrimidine (DAMTP) with zinc bromide in dilute hydrobromic acid resulted in the formation of single crystals of the title compound, $(C_5H_9N_4S)_2[ZnBr_4]$, $(HDAMTP)_2[ZnBr_4]$. The crystals contain isolated $[ZnBr_4]$ tetrahedra and non-coordinating pyrimidinium derivative cations which are linked to the anions *via* N—H···Br hydrogen bonds with donor–acceptor distances of 3.26 (1) Å.

Comment

Purines and pyrimidine derivatives are the main constituents of nucleic acids and play important roles in many biological systems. Among pyrimidine derivatives, thiopyrimidines are of great interest because of their wide-ranging biological activities. For example, 2-thiopyrimidine shows a strong bacteriostatic activity *in vitro* on *E. coli* (Holy, Votruba & Jost, 1974) and 6-amino-2-thiouracil is well known as an antiviral and chemotherapeutic agent (Lindsay, Nakagawa & Cohen, 1965).

The study of the metal complexes of heterocyclic thio derivatives is an area of great interest (Raper, 1985). Among this type of compounds, thiopyrimidines are important owing to their multiple potential sites for binding metal ions (Bret, Castan & Laurent, 1981; Cotton & Isley, 1981). As a continuation of our work on metal interactions with thiopyrimidine and thiopurine derivatives (Hueso, Moreno, Salas & Alvarez de Cienfuegos, 1991; Moreno, Romero, Salas & Sanchez, 1992; Romero *et al.*, 1993; Hueso *et al.*, 1993), we report here the crystal structure of the title compound, (I).


(I)
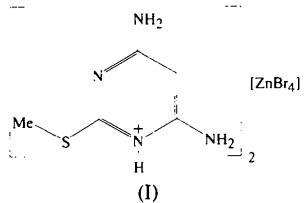
Fig. 1 shows a projection of the structure with the atomic numbering scheme. The asymmetric unit of the title compound comprises an isolated [ZnBr$_4$]$^{2-}$ anion and two crystallographically equivalent non-coordinating 4,6-diamino-2-methylthiopyrimidinium cations. The coordination polyhedron around the Zn atom is a distorted tetrahedron with Zn—Br distances ranging from 2.354 (4) (Zn—Br2) to 2.400 (6) Å (Zn—Br1) and Br—Zn—Br angles ranging from 105.2 (2) (Br1—Zn—Br1) to 114.3 (2)° (Br2—Zn—Br2). These distances and angles are in accordance with those found in analogous compounds, such as [N(CH$_3$)$_4$]$_2$[ZnBr$_4$] (Trouelan, Lefebvre & Derollez, 1984, 1985) and [MoL$_4$L'Br]$_2$[ZnBr$_4$] (Corfield, Baltusis & Lippard, 1981).

The pyrimidinium cations, probably protonated at N1, are planar to within 0.07 Å including the exocyclic atoms. The methyl C atom is coplanar (deviation 0.09 Å) with the rest of the molecule. Each cation is probably only linked *via* an N1—H$\cdots$Br hydrogen bond [3.26 (1) Å] to the [ZnBr$_4$] tetrahedron. The bond lengths and angles of the pyrimidinium moiety compare well with those found in 4,6-diamino-2-methylthiopyrimidinium hemitetrachlorozincate(II) (Romero *et al.*, 1990).

The thermal stability of this compound has been studied by thermogravimetric analysis and differential scanning calorimetry. The compound is thermally stable up to 523 K. At this temperature, fusion of the compound takes place. From the area of the associated endothermic effect (peak temperature 541 K) a value of 64 kJ mol^{-1} for the fusion enthalpy has been calculated.
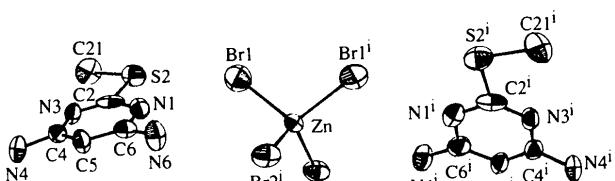
Fig. 1. View of the title compound. Displacement ellipsoids are shown at the 50% probability level. Symmetry code: (i) $x - y - 1$, $-2 - y$, $-\frac{1}{3} - z$.

Experimental

The title compound was prepared as follows. ZnCl$_2$ (20 mmol) was added to a solution of DAMTP (2 mmol) dissolved in 100 ml of water, then 60 mmol of KBr and 2 mml of concentrated HBr were added. The resulting solution was kept for 3 h in a thermostatic bath at 313 K. Crystals suitable for X-ray analysis were formed on standing the solution at room temperature for several days.

Crystal data
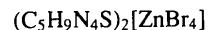
(C$_5$H$_9$N$_4$S)$_2$[ZnBr$_4$]	Mo $K\alpha$ radiation
$M_r = 699.4$	$\lambda = 0.7107$ Å
Trigonal	Cell parameters from 25
$P3_121$	reflections
$a = 8.790 (2)$ Å	$\theta = 15.90$–$21.43°$
$c = 24.831 (5)$ Å	$\mu = 9$ mm^{-1}
$V = 1661.7 (8)$ Å^3	$T = 295$ K
$Z = 3$	Prism
$D_x = 2.098$ Mg m^{-3}	$0.4 \times 0.4 \times 0.2$ mm
	Pale yellow

Data collection

Nonius CAD-4 diffractometer	868 observed reflections
	[$I > 3\sigma(I)$]
ω–4/3θ scans	$R_{int} = 0.041$
Absorption correction:	$\theta_{max} = 25°$
ψ scan (*SDP*; B. A. Frenz	$h = 0 \to 9$
& Associates Inc., 1982)	$k = 0 \to 9$
$T_{min} = 0.68$, $T_{max} = 0.99$	$l = 0 \to 29$
1220 measured reflections	3 standard reflections
1170 independent reflections	frequency: 60 min
	intensity decay: 1.5%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.2$
$R = 0.075$	$\Delta\rho_{max} = 1.0$ e Å^{-3}
$wR = 0.088$	$\Delta\rho_{min} = -1.4$ e Å^{-3}
$S = 4.7$	Extinction correction: none

868 reflections
115 parameters
H atoms not located
$w = 1/\sigma^2(F_o)$

Atomic scattering factors
from *SDP* (B. A. Frenz &
Associates Inc., 1982)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_i.a_j.$$

	x	y	z	B_{eq}
Zn	−0.8440 (5)	−1	−1/6	2.91 (8)
Br1	−0.9179 (5)	−0.8162 (5)	−0.1145 (2)	6.72 (9)
Br2	−0.7942 (4)	−1.1908 (3)	−0.1126 (1)	4.76 (7)
N1	−0.611 (2)	−0.453 (2)	−0.0605 (8)	3.7 (5)
C2	−0.606 (3)	−0.373 (3)	−0.0124 (8)	3.5 (5)
N3	−0.484 (2)	−0.229 (2)	0.0041 (7)	3.2 (5)
C4	−0.350 (3)	−0.141 (3)	−0.0280 (9)	3.1 (5)
C5	−0.338 (3)	−0.198 (3)	−0.0789 (9)	3.7 (6)
C6	−0.472 (3)	−0.360 (3)	−0.095 (1)	4.0 (6)
S2	−0.8019 (9)	−0.5088 (9)	0.0242 (3)	4.8 (2)
C21	−0.752 (4)	−0.359 (4)	0.0812 (9)	5.3 (8)
N4	−0.215 (3)	0.004 (2)	−0.0079 (8)	4.2 (6)
N6	−0.476 (3)	−0.434 (3)	−0.1462 (8)	4.7 (6)

Table 2. *Selected geometric parameters* (Å, °)

Zn—Br1	2.400 (6)	N3—C4	1.31 (4)
Zn—Br2	2.354 (4)	C4—C5	1.38 (3)
N1—C2	1.37 (3)	C4—N4	1.33 (2)
N1—C6	1.37 (3)	C5—C6	1.38 (3)
C2—N3	1.25 (2)	C6—N6	1.42 (3)
C2—S2	1.78 (2)	S2—C21	1.83 (3)
Br1—Zn—Br1^i	105.2 (2)	N3—C4—C5	124 (2)
Br1—Zn—Br2^i	106.1 (2)	N3—C4—N4	116 (2)
Br1—Zn—Br2	112.4 (2)	C5—C4—N4	120 (2)
Br2—Zn—Br2^i	114.3 (2)	C4—C5—C6	117 (2)
C2—N1—C6	117 (2)	N1—C6—C5	119 (2)
N1—C2—N3	126 (2)	N1—C6—N6	118 (2)
N1—C2—S2	109 (2)	C5—C6—N6	123 (2)
N3—C2—S2	124 (2)	C2—S2—C21	96 (1)
C2—N3—C4	117 (2)		

Symmetry code: (i) $x - y - 1, -2 - y, -\frac{1}{3} - z$.

The high final R value of 0.075 is probably due to absorption problems [μ(Mo $K\alpha$) = 9 mm^{-1}]. All calculations were performed using the Enraf–Nonius *SDP* system (B. A. Frenz & Associates Inc., 1982) implemented on a DEC MicroVAX 3100-80 computer at the Centre de Diffractométrie Automatique, Université Lyon I. Molecular graphics were prepared using *SHELXTL-Plus* (Sheldrick, 1987).

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Bis(4-nitroanilinium) Tetrachlorocadmate

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Abstract

An aromatic cation-based perovskite-type layered crystal of bis(4-nitroanilinium) tetrachlorocadmate, $(C_6H_7N_2O_2)_2[CdCl_4]$, was obtained. X-ray diffraction analysis of a single crystal revealed it to have a layered structure consisting of alternating organic bilayers and inorganic sheets. Cd ions and Cl anions form six-coordinate octahedra whose equatorial corner anions are shared with the neighbouring octahedra. The organic bilayer has a 'tail-to-tail' structure, showing that the molecular arrangement is mainly determined by the inorganic layer structure, not by the intermolecular dipolar interaction of the 'push-pull' type molecule.

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