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Distant Copper–Copper Interactions in a Metal-Organic Compound in the Solid State: Hexakis[(μ₃-4,6-dimethylpyrimidine-2-thiolato-*N*:*S*:*S*)copper(I)] Dihydrate

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Abstract

In the hexameric complex of the title compound, [Cu(C$_6$H$_7$N$_2$S)]$_6$.2H$_2$O, each of the six Cu^I atoms exhibits highly distorted square-pyramidal coordination geometry with two adjacent Cu^I atoms and two thiolate S atoms occupying the basal positions, and an azomethine N atom at the apex. The molecule consists of two centrosymmetrically related distorted tricapped trigonal prisms, formed by three Cu^I and three thiolate S atoms. The three planar tridentate C$_6$H$_7$N$_2$S ligands

are almost normal to their corresponding basal planes. Each thiolate S atom bridges two Cu^I atoms, the ligand thus coordinating to form two five-membered open envelopes. In the hexamer, the six Cu^I atoms are in a perfect chair conformation and this hints at a distant Cu^I···Cu^I interaction.

Comment

The discovery of the antibacterial, antiviral and antimicrobial properties (Rosenfield, Mascharak & Arora, 1987) of 4,6-dimethylpyrimidine-2-thiol (4,6Me$_2$Pm-2SH) and its metal complexes, and the use of copper–sulfur compounds (Krebs & Henkel, 1991) as models for copper–cysteine centres in metalloproteins like plastocyanin and azurin (Freeman, 1980), prompted the synthesis and structural investigation of the title complex. The crystal structure of [Cu(4,6Me$_2$Pm2S)]$_6$.2H$_2$O, (IV), is presented here and the metal coordination and nature of the bonding are discussed.

(IV)
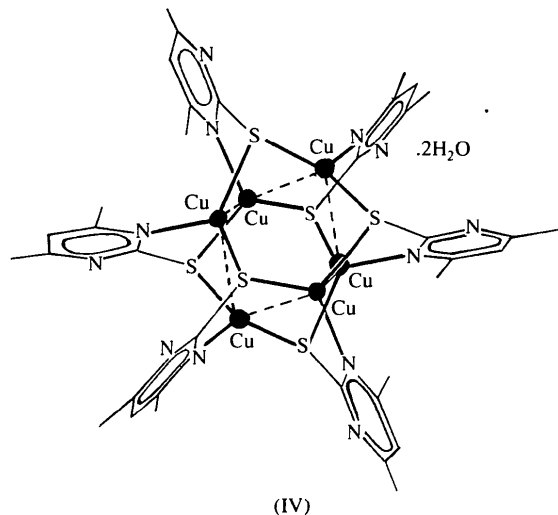
The structure (Fig. 1) consists of discrete centrosymmetric hexamers of (4,6-dimethylpyrimidine-2-thiolato)copper(I) and water of crystallization. The coordination geometry of the molecule (Table 2) is best described in terms of two centrosymmetrically related distorted tricapped trigonal prisms with bases Cu(1)···Cu(2^i)···Cu(3) and S(1)···S(2^i)···S(3). Each Cu^I atom, near the centre of the rectangular faces of the prism, exhibits highly distorted square-pyramidal coordination geometry with two adjacent Cu^I and two thiolato S atoms occupying the basal positions, and an azomethine N atom at the top of the pyramid. Each basal plane is planar to within ±0.018 (2) Å and the Cu^I atoms deviate above the plane by 0.836 (1), 0.733 (1) and 0.814 (1) Å. The Cu^I—N [2.021 (5)–2.044 (5) Å] and Cu(1)—S [2.239 (2)–2.264 (2) Å] distances are within normal ranges.
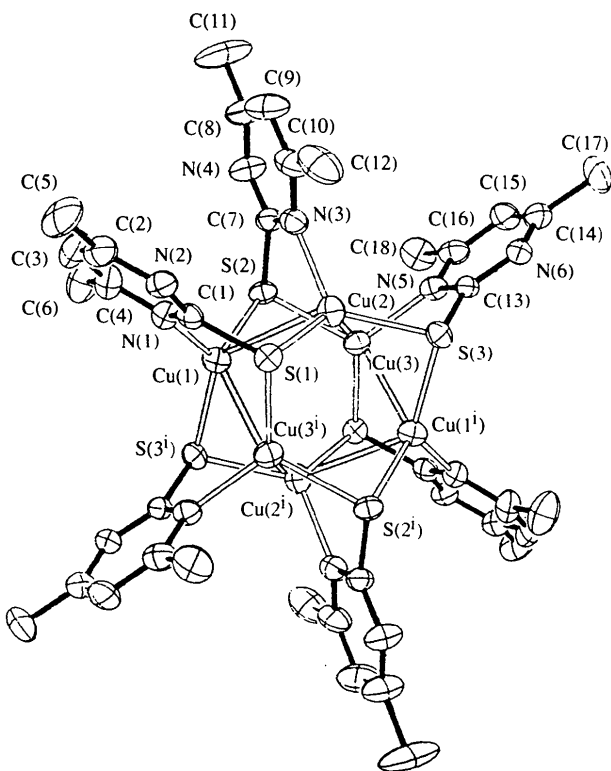
Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atom-numbering scheme. For non-H atoms, 50% probability ellipsoids are shown; O and H atoms are omitted for clarity. Symmetry code: (i) $-x$, $-y$, $-z$.

The inner core of the molecule can be adequately described in terms of four rigid six-membered puckered rings in chair conformations and two kinds of copper–copper distances. Those bridged by an S atom average 3.178 Å and those not bridged average 2.808 Å, and are similar to those observed in Cu₄{SC(NH₂)₂}₆⁴⁺ (Griffith, Hunt & Amma, 1976) and [Cu₂(C₄H₈NOS)₂]₂ (Kuroda-Sowa, Munakata, Miyazaki & Maekawa, 1994). The average Cu^I—Cu^I distance of 2.808 Å is comparable with those reported so far for Cu^I complexes, but there is still some uncertainty about whether or not d^{10} metal atoms mutually interact (Cotton, Fenz, Matusz & Poli, 1988) in the solid state. But, in the present case, the formation of a puckered six-membered ring with the Cu^I atoms in a perfect chair conformation, as frequently encountered in cyclohexane systems, suggests that the Cu^I—Cu^I bond is more than a mere possibility. This is substantiated by the packing of the molecules, forming the hexameric complex in the solid state. The formation of a perfect chair may also be favoured so that the high-energy eclipsing interaction between the S atoms attached to any two consecutive Cu^I atoms may be avoided. No such significant Cu^I—Cu^I interactions are observed in the monohydrate (Castro *et al.*, 1992) of the same compound in the solid state.

The heterocyclic (4,6Me₂Pm2SH) ligands are all planar (within ±0.08 Å) and almost normal (average 91.7°) to their corresponding basal planes of the coordination polyhedron, displaying molecular geometry very close to that observed in the monohydrate and in other related complexes (Table 3). Each Cu^I atom is almost coplanar with the ligand plane [deviations 0.013 (1), −0.195 (1) and −0.005 (1) Å]. Each thiolate S atom bridges two Cu^I atoms (average Cu^I—S—Cu^I 90°) and thus the ligand behaves as a tridentate donor. The differences in the bonding of Cu^I to the ligands are, therefore, related to the internal geometry of the hexameric title complex; this effect was not observed in related (4,6Me₂Pm2S) metal complexes, where stable four-membered N,S-chelate rings are formed.

In the hexamer, there are two molecules of water of crystallization [U_{eq}(O1) = 0.202 (6) Å²]. The water H atoms were not located experimentally, but the O(1)···N(4)($-x-1/2$, $y+1/2$, $-z+1/2$) distance of 2.971 (11) Å is consistent with the existence of an intermolecular hydrogen bond which may stabilize the molecular packing. The closest intermolecular non-H atom contact in the structure is C(5)···O(1)($-x+1/2$, $y-1/2$, $-z+1/2$) of 3.37 (1) Å.

Experimental

4,6-Dimethylpyrimidine-2-thiol hydrochloride (4,6Me₂Pm-2SH.HCl) was synthesized by the standard technique (Seth, 1994). The yellow crystalline compound was then dissolved in ethanol, basified and complexed with CuCl₂.2H₂O. The resulting mixture was then allowed to stand for several hours at 297 K during which a deep-yellow crystalline product settled out. This was filtered and dried *in vacuo* over silica gel. Single crystals of the complex were grown by slow evaporation of its solution from a 1:1 mixture of chloroform and alcohol at room temperature. Elemental analysis is in agreement with the empirical formula C₆H₇N₂SCu.H₂O: found C 32.5, H 3.9, N 12.8, S 14.4, O 7.5, Cu 28.9%. The ¹H NMR spectrum of the uncomplexed pyrimidine using CDCl₃ as solvent (TMS as internal standard) shows a singlet (6H) at δ = 2.4 p.p.m. assignable to the six protons of the two methyl groups, while in the case of the Cu complex, two distinct singlets (3H each) at δ = 2.3 and 2.5 p.p.m. are observed under the same experimental conditions, indicating the existence of the complex in a monomeric state in solution. This was confirmed by the determination of its molecular weight in CHCl₃ solution. The IR spectrum of the complex exhibits no N—H stretch in the 3200–3100 cm⁻¹ region, indicating that the ligand coordinates to the metal as a thiol. An alcoholic solution of the compound is non-conducting and the complex is diamagnetic both in solution as well as in solid state, revealing that Cu is present in the +1 oxidation state. The crystal density D_m was measured by flotation in bromoform/xylene.

Crystal data

[Cu(C₆H₇N₂S)]₆.2H₂O   Mo $K\alpha$ radiation
M_r = 1252.47 λ = 0.71073 Å

	x	y	z	U_{eq}
C(15)	−0.3942 (6)	0.0447 (5)	0.2203 (6)	0.073 (3)
C(16)	−0.3476 (6)	0.0028 (4)	0.1488 (6)	0.064 (3)
C(17)	−0.3847 (7)	0.1573 (4)	0.3474 (7)	0.113 (5)
C(18)	−0.3998 (6)	−0.0680 (4)	0.0961 (6)	0.086 (4)
O(1)	−0.2072 (7)	0.2921 (4)	0.2158 (8)	0.202 (6)

Monoclinic
$P2_1/n$
$a = 11.914\,(2)$ Å
$b = 17.960\,(2)$ Å
$c = 11.997\,(2)$ Å
$\beta = 106.67\,(1)^\circ$
$V = 2459.2\,(7)$ Å^3
$Z = 2$
$D_x = 1.691$ Mg m^{-3}
$D_m = 1.71$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 7.5{-}15^\circ$
$\mu = 2.85$ mm^{-1}
$T = 294$ K
Plate
$0.42 \times 0.38 \times 0.36$ mm
Yellow

Data collection

Siemens *P4/PC* diffractometer
ω scans
Absorption correction:
  ψ scan (Kopfmann & Huber, 1968)
  $T_{min} = 0.511$, $T_{max} = 0.632$
3907 measured reflections
3809 independent reflections

2501 observed reflections
  $[|F_o| > 4\sigma(|F_o|)]$
$R_{int} = 0.028$
$\theta_{max} = 25^\circ$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 20$
$l = -13 \rightarrow 13$
3 standard reflections
  frequency: 60 min
  intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.037$
$S = 1.054$
2501 reflections
281 parameters
H-atom parameters not refined
$w = 1.3357/[\sigma^2(F_o) + 0.000139F_o^2]$
$(\Delta/\sigma)_{max} = 0.009$

$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction:
  *SHELX*76 (Sheldrick, 1976)
Extinction coefficient:
  −0.0003 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu(1)	0.09194 (6)	−0.10394 (4)	0.04438 (6)	0.0528 (3)
Cu(2)	0.04963 (6)	0.01888 (4)	0.17871 (6)	0.0551 (3)
Cu(3)	−0.16450 (7)	−0.02878 (4)	0.02465 (6)	0.0528 (3)
S(1)	0.23548 (13)	0.03341 (8)	0.16939 (12)	0.0467 (5)
S(2)	−0.06930 (13)	−0.13359 (8)	0.09851 (12)	0.0486 (6)
S(3)	−0.06903 (13)	0.11826 (8)	0.14620 (13)	0.0482 (6)
N(1)	0.2452 (4)	−0.1151 (3)	0.1726 (4)	0.050 (2)
C(1)	0.3000 (5)	−0.0526 (3)	0.2199 (5)	0.045 (2)
N(2)	0.3987 (4)	−0.0495 (3)	0.3082 (4)	0.053 (2)
C(2)	0.4485 (6)	−0.1151 (5)	0.3483 (6)	0.068 (3)
C(3)	0.3968 (6)	−0.1805 (4)	0.3043 (7)	0.081 (3)
C(4)	0.2934 (6)	−0.1797 (4)	0.2158 (6)	0.070 (3)
C(5)	0.5638 (5)	−0.1112 (5)	0.4414 (6)	0.099 (4)
C(6)	0.2313 (7)	−0.2496 (4)	0.1634 (7)	0.105 (4)
N(3)	0.0388 (4)	−0.0621 (3)	0.2949 (4)	0.054 (2)
C(7)	−0.0197 (5)	−0.1238 (4)	0.2522 (5)	0.054 (3)
N(4)	−0.0403 (6)	−0.1801 (3)	0.3129 (5)	0.080 (3)
C(8)	0.0058 (9)	−0.1767 (5)	0.4293 (7)	0.102 (4)
C(9)	0.0698 (8)	−0.1170 (6)	0.4792 (6)	0.104 (4)
C(10)	0.0861 (6)	−0.0596 (5)	0.4114 (6)	0.072 (3)
C(11)	−0.0191 (10)	−0.2406 (6)	0.4991 (7)	0.189 (7)
C(12)	0.1548 (7)	0.0091 (5)	0.4576 (6)	0.110 (4)
N(5)	−0.2488 (4)	0.0256 (3)	0.1244 (4)	0.049 (2)
C(13)	−0.2001 (5)	0.0892 (3)	0.1734 (5)	0.044 (2)
N(6)	−0.2414 (5)	0.1327 (3)	0.2427 (4)	0.059 (2)
C(14)	−0.3399 (7)	0.1093 (4)	0.2657 (6)	0.069 (3)

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

Cu(1)—Cu(2)	2.861 (1)	C(1)—N(1)	1.340 (7)
Cu(1)···Cu(2^i)	3.123 (1)	C(3)—C(4)	1.377 (9)
Cu(1)···Cu(3)	3.286 (1)	C(2)—C(3)	1.360 (11)
Cu(1)—Cu(3^i)	2.743 (1)	C(2)—N(2)	1.345 (9)
Cu(1)—S(2)	2.261 (2)	S(2)—C(7)	1.776 (6)
Cu(1)—S(3^i)	2.238 (2)	N(3)—C(10)	1.350 (8)
Cu(1)—N(1)	2.032 (4)	C(9)—C(10)	1.361 (13)
Cu(2)—Cu(3)	2.820 (1)	C(8)—C(11)	1.500 (14)
Cu(2)···Cu(3^i)	3.126 (1)	N(4)—C(7)	1.309 (9)
Cu(2)—S(1)	2.264 (2)	N(3)—C(7)	1.332 (8)
Cu(2)—S(3)	2.241 (2)	C(10)—C(12)	1.497 (11)
Cu(2)—N(3)	2.044 (5)	C(8)—C(9)	1.352 (13)
Cu(3)—S(1^i)	2.239 (2)	N(4)—C(8)	1.347 (9)
Cu(3)—S(2)	2.245 (2)	S(3)—C(13)	1.763 (7)
Cu(3)—N(5)	2.021 (5)	N(5)—C(16)	1.355 (9)
S(1)···S(3)	3.871 (2)	C(16)—C(18)	1.476 (10)
S(2)···S(1^i)	3.720 (2)	C(14)—C(17)	1.513 (12)
S(2)···S(3^i)	3.766 (3)	N(6)—C(13)	1.334 (8)
S(1)—C(1)	1.753 (6)	N(5)—C(13)	1.339 (7)
N(1)—C(4)	1.332 (8)	C(15)—C(16)	1.373 (11)
C(4)—C(6)	1.501 (10)	C(14)—C(15)	1.364 (11)
C(2)—C(5)	1.503 (8)	N(6)—C(14)	1.347 (10)
C(1)—N(2)	1.340 (6)		
Cu(2)—Cu(1)—Cu(3^i)	67.77 (3)	S(1)—C(1)—N(1)	118.7 (5)
Cu(2)—Cu(1)—N(1)	85.1 (1)	N(1)—C(1)—N(2)	125.4 (5)
Cu(3^i)—Cu(1)—S(2)	131.2 (1)	N(1)—C(4)—C(3)	120.0 (7)
Cu(3^i)—Cu(1)—N(1)	91.2 (1)	C(3)—C(4)—C(6)	122.6 (7)
S(2)—Cu(1)—N(1)	114.4 (2)	N(2)—C(2)—C(3)	120.9 (7)
Cu(2)—Cu(1)—S(2)	73.64 (4)	C(3)—C(2)—C(5)	123.0 (7)
Cu(2)—Cu(1)—S(3^i)	132.4 (1)	Cu(1)—S(2)—Cu(3)	93.7 (1)
Cu(3^i)—Cu(1)—S(3^i)	75.4 (1)	Cu(3)—S(2)—C(7)	107.9 (2)
S(2)—Cu(1)—S(3^i)	113.7 (1)	Cu(2)—N(3)—C(10)	126.4 (4)
S(3^i)—Cu(1)—N(1)	125.6 (1)	S(2)—C(7)—N(4)	116.2 (5)
Cu(1)—Cu(2)—Cu(3)	70.68 (3)	C(7)—N(3)—C(10)	116.3 (5)
Cu(1)—Cu(2)—S(3)	136.1 (1)	N(3)—C(10)—C(9)	120.4 (6)
Cu(3)—Cu(2)—S(1)	135.8 (1)	C(8)—C(9)—C(10)	119.7 (9)
Cu(3)—Cu(2)—N(3)	90.5 (1)	Cu(1)—S(2)—C(7)	102.6 (2)
S(1)—Cu(2)—N(3)	111.7 (2)	Cu(2)—N(3)—C(7)	117.3 (4)
Cu(1)—Cu(2)—S(1)	74.23 (4)	S(2)—C(7)—N(3)	117.6 (4)
Cu(1)—Cu(2)—N(3)	83.8 (2)	N(3)—C(7)—N(4)	126.2 (6)
Cu(3)—Cu(2)—S(3)	73.8 (1)	N(3)—C(10)—C(12)	115.6 (6)
S(1)—Cu(2)—S(3)	118.5 (1)	C(9)—C(10)—C(12)	124.1 (8)
S(3)—Cu(2)—N(3)	121.7 (2)	N(4)—C(8)—C(11)	117.2 (7)
Cu(1^i)—Cu(3)—Cu(2)	68.28 (3)	C(9)—C(8)—C(11)	122.4 (9)
Cu(1^i)—Cu(3)—N(5)	90.7 (1)	C(7)—N(4)—C(8)	117.1 (6)
Cu(2)—Cu(3)—S(2)	74.7 (1)	N(4)—C(8)—C(9)	120.4 (7)
Cu(2)—Cu(3)—N(5)	88.6 (1)	Cu(2)—S(3)—Cu(1^i)	88.4 (1)
S(2)—Cu(3)—N(5)	116.9 (2)	Cu(1^i)—S(3)—C(13)	107.5 (2)
Cu(1^i)—Cu(3)—S(2)	132.9 (1)	Cu(3)—N(5)—C(16)	126.3 (4)
Cu(1^i)—Cu(3)—S(1^i)	77.1 (1)	S(3)—C(13)—N(6)	116.6 (5)
Cu(2)—Cu(3)—S(1^i)	133.9 (1)	C(13)—N(6)—C(14)	117.2 (5)
S(2)—Cu(3)—S(1^i)	112.1 (1)	N(5)—C(16)—C(15)	120.1 (6)
S(1^i)—Cu(3)—N(5)	122.0 (1)	C(14)—C(15)—C(16)	119.0 (7)
Cu(2)—S(1)—Cu(3^i)	87.9 (1)	N(6)—C(14)—C(15)	121.7 (7)
Cu(3^i)—S(1)—C(1)	108.9 (2)	C(13)—N(6)—C(14)	116.4 (6)
Cu(1)—N(1)—C(4)	125.0 (4)	Cu(2)—S(3)—C(13)	106.3 (2)
S(1)—C(1)—N(2)	115.8 (4)	Cu(3)—N(5)—C(13)	116.5 (4)
C(1)—N(1)—C(4)	117.6 (5)	S(3)—C(13)—N(5)	117.8 (5)
N(1)—C(4)—C(6)	117.4 (6)	N(5)—C(13)—N(6)	125.6 (5)
C(2)—C(3)—C(4)	119.7 (7)	N(5)—C(16)—C(18)	117.0 (6)
N(2)—C(2)—C(5)	116.1 (6)	C(15)—C(16)—C(18)	122.9 (7)
C(1)—N(2)—C(2)	116.3 (5)	C(15)—C(14)—C(17)	121.9 (7)
Cu(2)—S(1)—C(1)	102.7 (2)	N(6)—C(14)—C(17)	116.4 (7)
Cu(1)—N(1)—C(1)	117.4 (4)		

C(3)—C(4)—N(1)—Cu(1)	178.9 (5)
C(15)—C(16)—N(5)—Cu(3)	−178.6 (5)
C(9)—C(10)—N(3)—Cu(2)	−178.5 (6)

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

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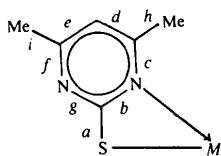
Bond	(I)	(II)	(III)	(IV)
a	1.732 (8)	1.728 (8)	1.71 (5)	1.76 (1)
b	1.350 (7)	1.357 (7)	1.38 (1)	1.337 (4)
c	1.352 (3)	1.347 (7)	1.36 (2)	1.35 (1)
d	1.384 (5)	1.390 (4)	1.40 (3)	1.370 (8)
e	1.387 (3)	1.376 (6)	1.39 (4)	1.359 (6)
f	1.33 (2)	1.347 (6)	1.34 (3)	1.346 (1)
g	1.33 (2)	1.327 (7)	1.33 (2)	1.33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