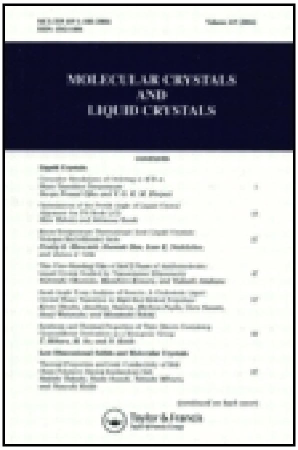

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Unusual Trisulphide Linkage in Bromine-Thiourea Reaction: Crystal Structure of Formamidinium Trisulphide Complex with Bromine

Abhaya D. Tol [a], Arun D. Natu [a] & Vedavati G. Puranik [b]

[a] Department of Chemistry, Postgraduate and Research Centre, Abasaheb Garware College, Pune, Maharashtra, India

[b] Center for Materials Characterization, National Chemical Laboratory, Pune, Maharashtra, India

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Abhaya D. Tol
Arun D. Natu
Department of Chemistry, Postgraduate and Research Centre,
Abasaheb Garware College, Pune, Maharashtra, India

Vedavati G. Puranik
Center for Materials Characterization, National Chemical Laboratory,
Pune, Maharashtra, India

A new complex of formamidinium trisulphide with bromine has been synthesized. Single-crystal X-ray analysis of this compound revealed a novel trisulphide linkage in the formamidinium trisulphide moiety. The crystals belong to orthorhombic space group Fdd2 with $a = 14.9119(15)$, $b = 16.5241(17)$, $c = 8.5114(9)$ Å, $V = 2097.3(4)$ Å^3, $R_1 = 0.0326$, *and* $wR_2 = 0.0846$ *for 2666 reflections. All four amine groups are hydrogen linked to four different formamidinium trisulphide molecules through bromine atoms, making a beautiful three-dimensional network of hydrogen bonds, which stabilize the crystal structure.*

Keywords: bromine; crystal structure; formamidinium trisulphide; thiourea

INTRODUCTION

The formation of salts of formamidinium disulphide from thiourea by oxidizing agents such as bromine is well known [1–5]:

$$2\ (H_2N)_2\ CS = [(H_2N)_2C - S - S - C(NH_2)_2]^{++} + 2e^-$$

An alcoholic medium was used by Claus [1] to obtain a colorless product, dithiocarbamide dibromide **I**. Later, this compound was

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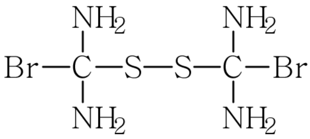
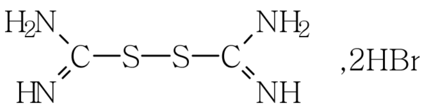
Address correspondence to Arun D. Natu, Department of Chemistry, Postgraduate and Research Centre, Abasaheb Garware College, Karve Road, Pune 411004, Maharashtra, India. E-mail: arunnatu@hotmail.com; arun.natu@gmail.com

identified by Fichter *etal.* [6,7] as Storch's base [8] or the formamidine disulphide **II**:



$$\mathrm{Br{-}C(NH_2)_2{-}S{-}S{-}C(NH_2)_2{-}Br}$$

I



II

There has been great discussion by Sahasrabudhey [5,9–11]regarding the disulphide nature of the salts. He argues that they were not disulphides, but monomeric compounds derived from a single thiourea molecule. Olav Foss *et al.* [12] have shown by the X-ray crystallographic work that the disulphide nature of the salts exists in the crystalline state, which is also preserved in solution.

Further, they have investigated the action of bromine with thiocarbamide (thiourea) in inert solvents such as $CHCl_3$, CCl_4, or CS_2 and obtained a deep red or orange product. On drying, this gave a yellow powder of bromine addition compound, which fumed copiously in moist air, giving out hydrobromic acid vapors. The compound decomposed at 180°C, and even in the presence of a large excess of bromine, the same compound was obtained. Olav Foss *et al.* [12] prepared the formamidinium disulphide dibromide by slowly adding the equivalent amount of bromine to a 20% aqueous solution of thiourea under cooling in ice water.

Here we report a different approach in which an unusual reaction of bromine with thiourea in aqueous solution at room temperature has been carried out. When excess bromine was added to an aqueous solution of thiourea, a white solid was separated. The melting point of this solid was 206°C, different from thiourea (180°C) as observed by mixed melting point. It was soluble in water, methanol and ethanediol but insoluble in chloroform, carbon tetrachloride, and acetone. The reaction was slightly exothermic.

EXPERIMENTAL

Synthesis

In a typical experiment, thiourea (1 g) was dissolved in distilled water (5 ml), and concentrated bromine (15 drops) was slowly added to it. The temperature of the reaction mixture increased up to 65°C. A white solid separated in about 30 min, which was filtered, washed with mother liquor, and dried (0.80 g). This solid melted at 206°C. It was soluble in water, methanol, and ethane diol but insoluble in acetone, carbon tetrachloride, and chloroform. In ethyl acetate, it probably decomposed to give an orange color to the solution. This solid was dissolved in absolute methanol and allowed to crystallize in a refrigerator. Beautiful needle-shaped single crystals of this compound were obtained by slow evaporation of the solution in methanol.

Crystal Structure Determination

Colorless crystals of approximate size $0.21 \times 0.08 \times 0.06$ mm, were used for data collection on a Bruker Smart Apex CCD diffractometer using Mo K_α radiation with a fine-focus tube, 50 kV, and 30 mA. Crystal-to-detector distance was 6.05 cm, 512×512 pixels/frame, hemisphere data acquisition. Total scans = 3, total frames = 1212, oscillation/frame $-0.3°$, exposure/frame = 15.0 s/frame, maximum detector swing angle $= -30.0°$, beam center = (260.2, 252.5), in-plane spot width = 1.24, SAINT integration, θ range = 1.56 to 25.0°, completeness to θ of $25.0° = 99.7\%$. SADABS correction applied, $C_2 H_8 Br_2 N_4 S_3$, $M = 344.12$. Crystals belong to orthorhombic space group Fdd2, $a = 14.9119(15)$, $b = 16.524\ (2)$, $c = 8.5114\ (9)$ Å, $V = 2097.3(4)$ Å^3, $Z = 8$, $D_c = 2.180\ \mathrm{mg\ m^{-3}}$, $\mu\ (\mathrm{MoK_\alpha}) = 8.278\ \mathrm{mm^{-1}}$, T = 295(2) K, 2644 reflections measured, 958 unique $[I > 2\sigma(I)]$, R = 0.0326, wR2 = 0.0846. All the data were corrected for Lorentzian, polarization, and absorption effects. SHELX-97 (ShelxTL) [13] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in Table 1. The crystal structure data have been deposited with Cambridge Crystallographic Database (CCDC No. 610122).

RESULTS AND DISCUSSION

The final positional coordinates with equivalent isotropic thermal parameters for all the nonhydrogen atoms are listed in Table 2, the bond lengths and angles are given in Table 3, and torsion angles are given in Table 4.

X-ray analysis revealed a novel trisulphide linkage in the formamidinium trisulphide moiety along with bromine ion. Figure 1 shows the ORTEP diagram of the cation. This is the first type of trisulphide linkage reported so far from the reaction of bromine with thiourea. The thiourea groups N–H–CS–NH are almost planar. The conjugation

TABLE 1 Crystal Data and Structure Refinement for $C_2H_8Br_2N_4S_3$

Parameter	Value
Empirical formula	$C_2H_8Br_2N_4S_3$
Formula weight	344.12
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Fdd2
Unit cell dimensions	a = 14.9119(15) Å
	b = 16.5241(17) Å
	c = 8.5114(9) Å
Volume	2097.3(4) $Å^3$
Z, calculated density	8, 2.180 Mg/m^3
Absorption coefficient	8.278 mm^{-1}
F (000)	1328
Crystal size	0.21 × 0.08 × 0.06 mm
Theta range for data collection	3.02 to 25.49°
Limiting indices	$-16 \leq h \leq 18$, $-20 \leq k \leq 12$, $9 \leq 1 \leq 10$
Reflections collected/unique	2644/958 [R (int) = 0.0394]
Completeness to theta = 25.49	100.0%
Max. and min. transmission	0.6365 and 0,.2753
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	958/1/51
Goodness of fit on F^2	1.092
Final R indices [I > 2sigma(I)]	$R_1 = 0.0326$, $wR_2 = 0.0846$
R indices (all data)	$R_1 = 0.0331$, $wR_2 = 0.0848$
Absolute structure parameter	0.054(16)
Largest diff. peak and hole	0.600 and −0.680 $e \cdot A^{-3}$

of lone electron pairs of nitrogen atoms with Pi electrons of C=S double bond is usually illustrated by the resonance structures **III**, **IV**, and **V**. When the C−S bond length is closer to single-bond distance,

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $C_2H_8Br_2N_4S_3$

Atom	x	y	z	U(eq)
Br	7871(1)	3754(1)	5367(1)	43(1)
S (1)	7500	2500	– 1200(2)	39(1)
S (2)	8411(1)	3043(1)	268(2)	45(1)
N (1)	8506(3)	4544(3)	1245(5)	45(1)
N (2)	7349(3)	4314(3)	– 463(6)	45(1)
C (1)	8029(3)	4061(3)	353(6)	34(1)

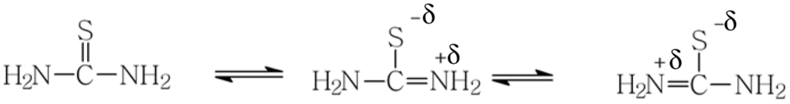
Note. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

TABLE 3 Bond Lengths (Å) and angles (deg) for $C_2\,H_8\,Br_2\,N_4\,S_3$

Parameter	Value
Bond Length	
S (1)–S (2)	2.0524(16)
S (1)–S (2)#1	2.0524(16)
S (2)–C (1)	1.778(5)
N (1)–C (1)	1.311(7)
N (2)–C (1)	1.298(7)
Angle	
S (2)–S (1)–S (2)#1	104.98(11)
C (1)–S (2)–S (1)	103.08(17)
N (2)–C (1)–N (1)	122.5(5)
N (2)–C (1)–S (2)	122.2(4)
N (1)–C (1)–S (2)	115.2(3)

Note. Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, $-y+1/2$, z.

the thiourea structure is better represented by polar structures IV and V [14].



III **IV** **V**

In the present structure, the C–S distance is 1.778 (5) Å, whereas N (1)–C (1) = 1.311 (7) Å and N (2)–C (1) = 1.298 (7) Å, which can be shown in the next structure.

TABLE 4 Torsion angles (deg) for $C_2\,H_8\,Br_2\,N_4\,S_3$

Angle	Value
S (2)#1–S (1)–S (2)–C (1)	−97.21(18)
S (1)–S (2)–C (1)–N (2)	−3.1(5)
S (1)–S (2)–C (1)–N (1)	179.6(3)

Note. Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, $-y+1/2$, z.

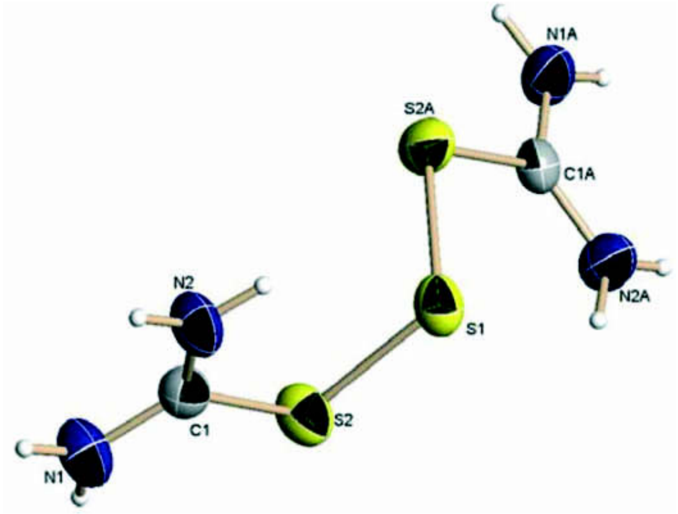
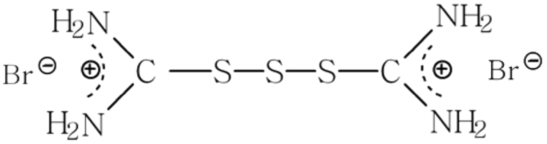
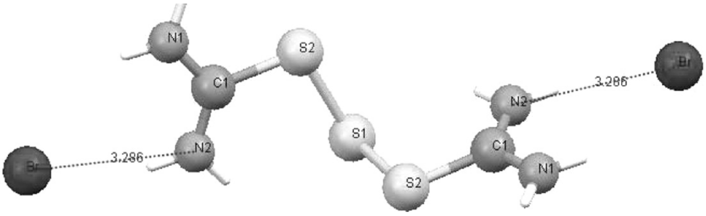


FIGURE 1 ORTEP diagram of the molecule. The ellipsoids are drawn at 50% probability.





In the symmetrical molecule of formamidinium trisulphide, the sulfur atom lies on the symmetry. Here, S–S–S bond angle is 105°, which is comparable to two other trisulphides reported in literature [15] (*viz.*, hexachlorodimethyltrisulphide and dicyanotrisulphide have S–S–S bond angles of 106° and 102° respectively).

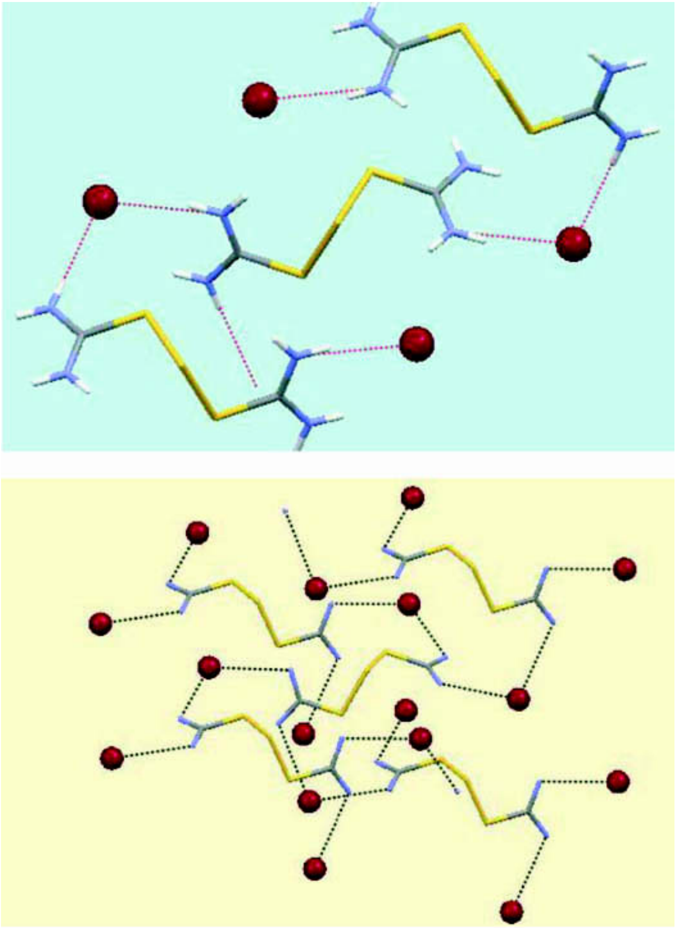


FIGURE 2 Zigzag H-bonding of N−H . . . Br.

TABLE 5 Analysis of Potential Hydrogen Bonds (Å)

Nr	Donor—H . . . . Acceptor	H . . . A	D . . . A	D-H . . . A
1	N (1)–H (1A)..Br^{i}	2.82	3.561(5)	145
2	N (1)–H (1B)..Br^{ii}	2.52	3.373(5)	170
3	N (2)–H (2A)..Br^{i}	2.46	3.286(5)	161
4	N (2)–H (2B)..Br^{iii}	2.70	3.407(5)	140

Note. Equivalent position code; ii = 1/4 + x, 3/4 − y, −1/4 + z; i = 3/2 − x, 1 − y, −1/2 + z; iii = −1/4 + x, 3/4 − y, −3/4+z.

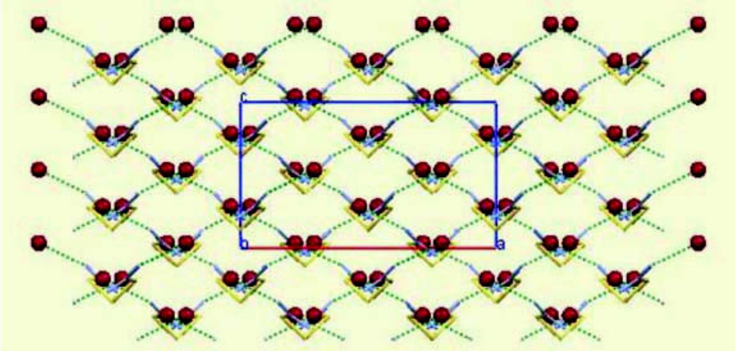
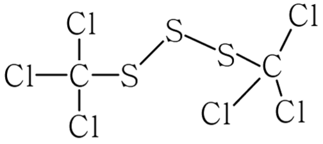
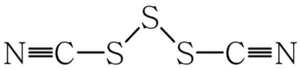


FIGURE 3 Packing of the molecules down the b-axis.



Hexachlorodimethyltrisulphide



Dicyanotrisulphide

Molecules are hydrogen bonded in a zigzag manner via N–H . . . Br bonding as shown in Fig. 2. All the four amino groups of formamidinium trisulphide moiety make hydrogen bonds with different symmetry-related molecules via bromine anions, forming a beautiful network of N–H . . . Br hydrogen bonds. The N–H . . . Br distances vary from 3.286(5) to 3.407(5) Å. There is an intramolecular H-bonding in N (2)–H (2B) . . . S (1), which is 3.071(5) Å (Table 5).

Both the hydrogens of the amino group make H-bonds with Br anion, and in turn the Br anion makes a bifurcated hydrogen bond. The structure is stabilized by a three-dimensional framework of hydrogen bonds. Formamidinium trisulphide cations look like bowls with the two bromine ions sitting inside the bowl and amino groups pointing outside when the packing of the molecules is seen down the b-axis (Fig. 3).

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