Structure of Formamidine Disulphide

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Salts of formamidine disulphide result on oxidation of thiourea with halogens or other oxidizing agents [1-3]. Although the disulphide nature of the salts appears to be fairly well established, *e. g.*, from the careful study by Preisler and Berger [4] of the oxidation-reduction potential of the reversible thiourea-formamidine disulphide system, it has been claimed [5] that they are not disulphides, but monomeric compounds containing one thiourea unit only in the molecule.

The crystal structure of the diiodide of formamidine disulphide has now been determined. The results indicate the presence of an S—S bond and the correctness of the formamidine disulphide structure.

Formamidine disulphide diiodide, $[(H_2N)_2CS]_2I_2 \cdot H_2O$, was prepared from iodine and thiourea as described by Marshall [2]. The colourless salt, which turned out to be a monohydrate, was obtained as plates {100}, or as flat prisms bounded by {100} and, less developed, {001}. The axial lengths are, $a = 5.15$ Å, $b = 16.52$ Å, $c = 13.39$ Å (± 0.5 %). There are four formula units per unit cell; density, calc. 2.47, found 2.47 g/cm³. The space group, from systematic absences, is $D_{2h}^{10}-Pccn$, which has eightfold general positions, and centres of symmetry and twofold axes as special, fourfold positions.

Intensities of the 0*kl* and *hk*0 reflections were estimated visually from Weissenberg photographs taken with copper radiation, using crystals with cross-sections of 0.04 × 0.05 mm and 0.07 × 0.05 mm, respectively, in the case of the *a* and *c* axis photographs. Patterson, Fourier and Fourier difference projections along these axes, refined to reliability factors of $R = 8.8$ % and 9.7 %, respectively, for the 0*kl* and *hk*0 reflections, have led to the atomic coordinates given in Table 1.

Table 1. Atomic coordinates, in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z
I	0.072	0.0783	−0.1453
S	0.578	0.2192	−0.008
C	0.665	0.141	0.071
N_1	0.481	0.080	0.076
N_2	0.850	0.142	0.136
H_2O	0.250	0.250	0.214

The data of Table 1 give a length of 2.04 Å for the S—S bond, across the twofold axis at ($\frac{3}{4}$, $\frac{1}{4}$, z). The C—S—S bond angles are 98°, and the C—S—S/S—S—C dihedral angle, 104°. The disulphide group has thus normal dimensions. The shortest I—I approaches are 4.60 Å and 4.73 Å, across a twofold screw axis and a centre of symmetry, respectively, and the shortest I—S approaches are 3.91 Å and 3.95 Å.

Details of the structure of the diiodide will be published later.

The crystal structure of the corresponding dibromide [1], $[(H_2N)_2CS]_2Br_2 \cdot H_2O$, is being studied [6]. This salt is monoclinic, with $a = 8.61$ Å, $b = 5.12$ Å, $c = 12.40$ Å, $\beta = 99\frac{1}{2}°$, and two formula units per unit cell. The probable space group is C_{2h}^4-P2/c.

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