A Centrosymmetric Organic Disulphide with a C–S–S–C Torsion Angle of 180°. The *X*-Ray Crystal and Molecular Structure of Chloro-(dipyrimidin-2-yl disulphide)copper(I) Monohydrate

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Summary In its complex with Cu^I, dipyrimidin-2-yl disulphide is centrosymmetric and planar with a C–S–S–C torsion angle of 180° and a long S–S bond, 2·113(1) Å.

CO-ORDINATION of a sulphur atom of an organic disulphide to a metal ion was first demonstrated in the crystal structure of chloro(diethyldisulphide)copper(I).[1] Some other Cu^I–disulphide complexes[2] also show such co-ordination. In order to investigate this effect further, we have prepared chloro(dipyrimidin-2-yl disulphide)copper(I) and determined its crystal structure. In this complex, although sulphur does not co-ordinate to Cu^I, the disulphide ligand is found in a conformation far from any reported previously.

Crystal data: $Cu(C_8H_6N_4S_2)Cl{\cdot}H_2O$, monoclinic, a = 11·916(3), b = 17·404(3), c = 6·643(2) Å, β = 116·58(2)°, U = 1233·3(4) $Å^3$, space group $C2/m$, M = 339·3, D_m = 1·82, D_c = 1·827 g cm^{-3}, R = 0·039 for 2401 reflections with $I > 2\sigma(I)$.

Intensity data were collected on a Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo-K_α radiation, (λ = 0·71073 Å). The temperature was maintained at 26 ± 1 °C throughout. Absorption and decay corrections were applied. The structure was solved using Patterson methods, and was refined using anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.†

The crystal structure consists of dipyrimidin-2-yl disulphide molecules bridging $\mathrm{Cu_2Cl_2}$ groups to form polymeric sheets. Within each sheet, each $\mathrm{Cu^I}$ ion co-ordinates to two nitrogen atoms from two different ligands, and to two chloride ions which bridge to another $\mathrm{Cu^I}$ to complete a planar four-membered $\mathrm{Cu_2Cl_2}$ ring. A water molecule hydrogen-bonds to each chloride ion. A portion of this structure, with its associated symmetry, is shown in the Figure.

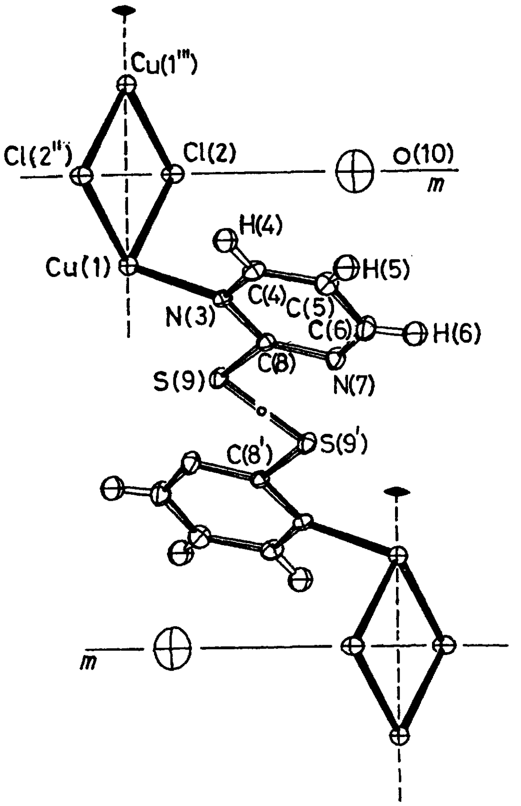

Figure. A portion of the polymeric sheet of chloro(dipyrimidin-2-yl disulphide)copper(I) monohydrate showing ellipsoids of 20% probability (C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1975). Mirror planes, two-fold axes, and an inversion centre are indicated.

The co-ordination geometry about $\mathrm{Cu^I}$ is distorted tetrahedral with bond angles ranging from 95·7—142·2°. The two nitrogen atoms and the two chloride ions act as σ-donors, and there is co-operative $d\rightarrow\pi^*$ back-donation of electron density from the filled $\mathrm{Cu^I}$ d orbitals into the lowest-lying π^* molecular orbital of each pyrimidine ring. The $\mathrm{Cu^I}$–N bond length, 1·966(3) Å, appears to be one of the shortest distances yet reported for $\mathrm{Cu^I}$ bonded to an unsaturated nitrogen atom in a cyclic ligand. The mean $\mathrm{Cu^I}$–N bond length in such compounds is *ca.* 2·04 Å.

The pyrimidine rings in the complex are quite planar (maximum deviation, 0·014 Å). Most of the bond distances and angles in the pyrimidine rings are close to the corresponding values in both the free ligand[3,4] and in crystalline pyrimidine.[5] However, the N(3)–C(4), N(3)–C(8), and C(4)–C(5) bonds in the co-ordinated ring (see Figure), those involving or near the co-ordinated nitrogen atom, are slightly longer (from 2σ to 4σ) than the corresponding bonds in the free ligand, and may be the result of back-donation of electron density from both $\mathrm{Cu^I}$ and sulphur atoms into the empty π^* orbitals of the pyrimidine rings. Also, a σ-polarization of the ring by $\mathrm{Cu^I}$ *via* the co-ordinated nitrogen is likely to have contributed to these small bond lengthenings.

The most surprising structural feature of the chloro(dipyrimidin-2-yl disulphide)copper(I) complex is the conformation of the co-ordinated ligand. Dipyrimidin-2-yl disulphide has a C–S–S–C torsion angle of exactly 180° by symmetry; this is 46·4° more than the largest value reported so far for an organic disulphide.[6] The long S–S bond, 2·113(1) Å, is consistent with a plausible extension of the relationship between S–S bond lengths and C–S–S–C torsion angles in acyclic and saturated cyclic disulphides observed by Hordvik.[7] He observed that the longest S–S bonds occur when the electron repulsion between sulphur lone pairs is at a maximum, *i.e.* when C–S–S–C is 0 or 180°.

The unusual 180° C–S–S–C torsion angle in the complex is stabilized by: (a) a π system which extends over the entire planar disulphide ligand (the entire ligand is planar to within 0·08 Å); and (b) the near absence of electron repulsion between the S $3p_\pi$ lone pairs and the adjacent-ring nitrogen lone pairs. This repulsion is large in the free ligand, whose C–S–S–C torsion angle of *ca.* 84° [3,4] is quite normal. Crystal packing forces may be important in stabilizing the C–S–S–C = 180° conformation.

Because the C–S bond length in the complex, 1·759(3) Å, is shorter than that in the free ligand, 1·782 Å (mean),[3,4] the co-ordinated disulphide ligand has a greater degree of thione character. This is indicative of a weak π system which extends over the entire planar disulphide molecule (conjugation across the S–S bond is small). It is consistent with the observation that the predominant tautomer of the thiol, 2-mercaptopyrimidine, the precursor of dipyrimidin-2-yl disulphide, is predominantly in the thione form.[8] According to simple bonding arguments, this extended π system leaves the sulphur atoms with a net partial positive charge. This analysis is strongly supported by recent CNDO/2 calculations by Gillbro[9] of the total energy of the $\mathrm{HSSH^+}$ and $\mathrm{MeSSMe^+}$ cation radicals, which indicate that the conformer with a 180° torsion angle is the most stable, and that the spin density (ρ) of the un-

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

paired electron in $HSSH^+$ and $MeSSMe^+$ is localized mainly in the $3p_{\pi}$ orbital of each sulphur atom with $\rho = 0{\cdot}53$ and $0{\cdot}52$, respectively.

This work was supported by the National Institutes of Health. We are indebted to the University of Hawaii Computing Center for assistance.

(*Received, 2nd March* 1979; *Com.* 209.)

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