

Disulphide Bond Cleavage in a Pyridine-containing Disulphide–Copper(II) System under Aerobic Conditions. X-Ray Crystal Structure Analysis of the Product, Diaquabis{ μ -2-[(2-pyridylmethyl)-amino]ethylsulphinato-O}dicopper(II) Dichloride

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The disulphide bond in a pyridine-containing disulphide was cleaved in the presence of copper(II) and dioxygen to give the copper(II) complex of the corresponding sulphinato, whose X-ray crystal structure analysis has disclosed a dimeric structure with the sulphinato oxygen atom bridging the copper(II) ions in a square-pyramidal environment.

Disulphides RSSR are known to undergo oxidative cleavage by electrophiles such as mercury(I) and silver(I) to form sulphinates RSO_2^- .¹ The reaction occurs *via* heterolytic cleavage to give RS^- and RS^+ ; the latter then forms RSO_2^- and the thiol RSH by reaction with water and subsequent disproportionation. Recent studies show that gold(III) reacts with disulphides, giving sulphonates and metallic gold.² Seff and his collaborators have made extensive synthetic and structural studies of copper(I) and copper(II) complexes of disulphides involving pyridine and other nitrogen donors^{3–7} and have found that the reaction of copper(II) with bis(2-pyridyl) disulphide gives the corresponding copper(I)-disulphide complex and a small amount of the copper(II)-2-pyridylsulphinato complex.⁶ This reaction occurred under a nitrogen atmosphere and was accompanied by a pH decrease. We here report the isolation and X-ray crystal structure analysis of the copper(II) complex of 2-[(2-pyridylmethyl)-amino]ethylsulphinato (PMS) formed by facile cleavage of the disulphide bond in the 2:1 Cu(II)-bis{2-[(2-pyridylmethyl)-amino]ethyl} disulphide (PMAD) system under aerobic conditions.

An aqueous solution (pH *ca.* 7) containing CuCl_2 and PMAD in the molar ratio of 2:1 was shaken under dioxygen, and the brown-green solution turned bright green. Greenish blue crystals of $[\text{Cu}(\text{PMS})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_2$ were isolated from the solution upon concentration *in vacuo* and addition of ethanol.

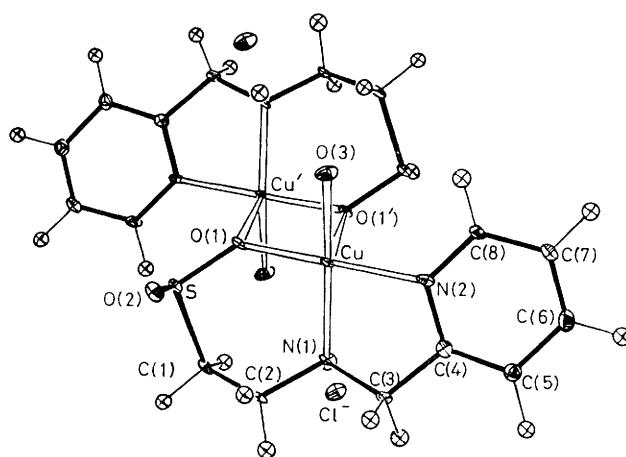


Figure 1. Molecular structure of $[\{\text{Cu}(\text{PMS})(\text{H}_2\text{O})\text{Cl}\}]_2$ showing ellipsoids of 50% probability.¹⁰ The relevant bond angles are: N(1)–Cu–N(2) 83.3(3), N(1)–Cu–O(1') 107.2(2), N(2)–Cu–O(3) 93.3(2), O(1')–Cu–O(3) 93.8(2), N(1)–Cu–O(3) 159.0(3), N(1)–Cu–O(1) 95.1(3), N(2)–Cu–O(1') 97.8(2), O(1)–Cu–O(3) 90.8(2), O(1)–Cu–O(1') 75.4(2), and N(2)–Cu–O(1) 172.2(3)°.

Crystal data: $(\text{C}_8\text{H}_{13}\text{ClCuN}_2\text{O}_3\text{S})_2$, $M = 632.54$, triclinic, space group $P\bar{1}$, $a = 7.139(1)$, $b = 8.586(2)$, $c = 10.072(2)$ Å,

$\alpha = 107.07(3)$, $\beta = 90.14(3)$, $\gamma = 102.94(3)^\circ$, $U = 573.6(1) \text{ \AA}^3$, $D_m = 1.828(2)$, $D_x = 1.837 \text{ g cm}^{-3}$, $Z = 1$. The structure was solved by direct methods⁸ and refined by block-diagonal least-squares to $R = 0.082$ using 1829 independent reflections. Hydrogen atom positions were obtained from a difference Fourier map.[†]

As shown in Figure 1, the complex is a centrosymmetric dimer comprising two square-planar CuN_2O_2 systems [Cu–N(1) 2.000(7), Cu–N(2) 1.960(7), Cu–O(1) 1.967(5), and Cu–O(3) 1.974(6) \AA] linked by $\text{Cu} \cdots \text{O}$ interactions to O(1) and O(1') [Cu–O(1') 2.353(5) \AA], which complete the square-pyramidal co-ordination. The Cu(II) \cdots Cu(II) separation is 3.426(2) \AA , which is comparable with a dimeric complex bridged through a single oxygen atom of the acetate ion [Cu(II) \cdots Cu(II) 3.445 \AA].⁹ The Cu(II) ion deviates slightly from the co-ordination plane towards the apical oxygen atom, probably owing to the bridge formation. Co-ordination through the negatively charged oxygen atom of the sulphinate group is also found in the monomeric 1:2 Cu(II)–2-pyridyl-sulphinato complex.⁶ The distances and geometry around O(3) indicate that there are two hydrogen bonds [O(3) \cdots O(2) ($1-x, 2-y, 1-z$) 2.611(9) and O(3) \cdots Cl[–] ($2-x, 2-y, 1-z$) 3.042(7) \AA] where O(3) acts as the hydrogen donor. These bonds stabilise the crystal structure, which is further stabilised by a weak hydrogen bond between N(1) and Cl[–] [3.203(7) \AA] and a stacking interaction between the pyridine rings with C(5) \cdots C(7) ($2-x, 2-y, -z$) 3.57(1) \AA .

The 2:1 Cu(II)–PMAD system absorbs *ca.* 2 mol of dioxygen per mol of PMAD (30 min, 30 °C), which may be used for (i) reoxidation of Cu(I) formed by the reaction with RSH and/or (ii) formation of the sulphinate group. It is interesting to

note in this connection that an iron-containing enzyme cysteine dioxygenase converts L-cysteine to L-cysteinesulphinic acid by directly incorporating dioxygen.¹¹ Experiments in our laboratory showed that the Cu(II)–bis(2-pyridyl) disulphide system does not absorb dioxygen, suggesting that the two sulphinates PMS and 2-pyridylsulphinato, may be formed by different pathways.

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