# Molecular Structure of [Bis-(2-pyridyl)disulphide]copper(I) Perchlorate Showing the $N_3S$ Co-ordination of Copper(I)

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*Summary* In its bis-(2-pyridyl)disulphide complex, $Cu^I$ has $N_3S$ co-ordination, similar to that expected for $Cu^I$-disulphide complexes in oxidases such as caeruloplasmin, rather than $N_2S_2$ or $N_4$ co-ordination.

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Disulphide linkages co-ordinated to readily reducible or oxidizable metal ions may constitute polynuclear two-or-more-electron redox sites with unusual potentials; such structures may be utilized by some metalloenzymes.[1] In the oxidized form (the resting state) of the copper oxidase caeruloplasmin, e.s.r.-inactive copper has been reported[2] to be $Cu^I$ with two $Cu^I$ ions co-ordinated to one organic disulphide group. The several $Cu^I$ complexes of organic disulphides which have been studied crystallographically show either $Cl_2S_2$ co-ordination,[3] or $N_2S_2$[4,5] co-ordination about tetrahedral $Cu^I$. In a protein, it is reasonable to expect, if the $Cu^I$ site is to survive many cycles of disulphide reduction-oxidation, that $Cu^I$ should co-ordinate to not more than one disulphide group, and that its other three ligands should be nitrogen or oxygen. We now report the molecular structure of [bis-(2-pyridyl)disulphide]copper(I) perchlorate, $[CuL_2]ClO_4$, in which $N_3S$ co-ordination has been specifically selected by $Cu^I$.

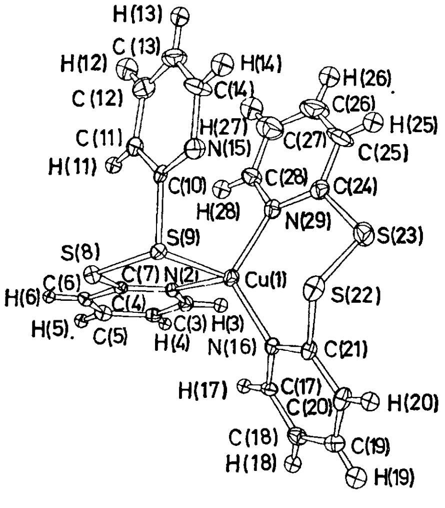

Figure 1 The structure of the $[Cu(C_{10}H_8N_2S_2)_2]^+$ ion. Ellipsoids of 15% probability are used.[9]

*Crystal data:* $C_{20}H_{16}N_4S_4ClO_4Cu$, $M = 603{\cdot}6$, triclinic, $a = 13{\cdot}898(12)$, $b = 21{\cdot}867(16)$, $c = 8{\cdot}278(4)$ Å, $\alpha = 92{\cdot}78(5)$, $\beta = 100{\cdot}79(6)$, $\gamma = 84{\cdot}37(6)°$, space group $P\bar{1}$, $Z = 4$, $D_m = 1{\cdot}666$, $D_c = 1{\cdot}643$, $R = 0{\cdot}051$ for 3079 reflections with $I > 3\sigma(I)$.

Intensity data were collected on a four-circle computer-controlled diffractometer with graphite-monochromated Mo–$K_\alpha$ radiation ($\lambda = 0{\cdot}71073$) at 22—23 °C. Absorption and decay corrections were applied. The structure was solved using Patterson methods, and refined using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were included at calculated positions.

The structure contains both isolated monomeric complexes of $CuL_2^+$, as shown in Figure 1, and the polymeric complex, $Cu_nL_{2n}^{n+}$, shown in Figure 2. In each case, $Cu^I$ is tetrahedrally co-ordinated by two ligands. One co-ordinates through its two pyridyl nitrogen atoms to $Cu^I$, forming a seven-membered ($\overline{\mathrm{SCNCuNCS}}$) chelate ring in the monomer and a bridge between two Cu$^{I}$ ions in the polymer; the disulphide group does not participate in co-ordination. In the other ligand, it is one pyridyl group which is excluded from co-ordination. The remaining pyridyl nitrogen and one sulphur atom of the disulphide group co-ordinate in both the monomeric and polymeric species, forming five-membered $(\overline{\mathrm{SCuNCS}})$ chelate rings. Either ligand could have co-ordinated like the other to give symmetric $N_4$ or $N_2S_2$ co-ordination about Cu$^{I}$, but this has not occurred, presumably because these co-ordination geometries are not preferred by Cu$^{I}$ for these particular donor atoms and potential chelate rings. Thus Cu$^{I}$ has demonstrated a preference for $N_3S$ co-ordination both in the monomer and the polymer, justifying one aspect of the proposed Cu$^{I}$ co-ordination in caeruloplasmin.

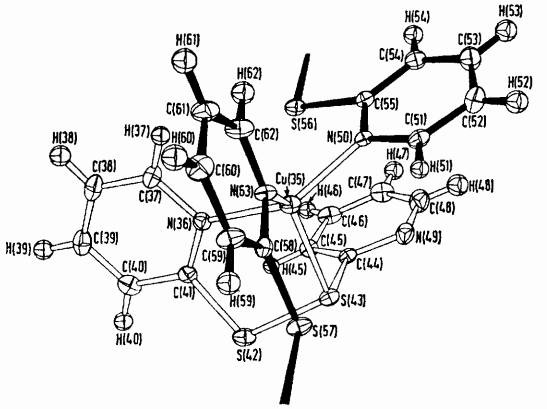

FIGURE 2 Partial structure of the polymeric complex, $[\mathrm{Cu}_n(\mathrm{C}_{10}\mathrm{H}_8\mathrm{N}_2\mathrm{S}_2)_{2n}]^{n+}$. The bridging ligand has been blackened in this figure. Ellipsoids of 15% probability are used.[9]

The disulphide bonds [2·032(4), 2·047(5), 2·025(4) and 2·026(4) Å] average 2·032(2) Å, which is slightly longer than the value of 2·016(2) Å found in the uncomplexed ligand.[6] The longest S–S bond is in the 7-membered chelate ring and the C–C–S–S and N–C–S–S torsion angles associated with it are uniquely far from 0° or 180°. The C–S–S–C torsion angles range from 81·1 to 93·3°, near to the expected value[7] of 90°. Like the previously reported structures of aliphatic disulphide complexes of Cu$^{I}$,[4,5] a significant lengthening of the disulphide bond is observed when bis(2-pyridyl) disulphide complexes to Cu$^{I}$, although it does not appear to depend upon whether a sulphur atom of the disulphide group participates in co-ordination.

The average Cu$^{I}$–S and Cu$^{I}$–N bond lengths are 2·418(2) and 2·024(5) Å, respectively. The average Cu$^{I}$–S bond distance is approximately equal to the sum of the tetrahedral covalent radii[8] of Cu$^{I}$ and S, and is about 0·1 Å longer than the average Cu$^{I}$–S distances found in cyclo-di-$\mu$-{bis-[2-(*NN*-dimethylamino)ethyl]disulphide}dicopper(I) tetrafluoroborate[4] and {bis-[2-(2-pyridyl)ethyl]disulphide}-copper(I) perchlorate,[5] indicating a weaker Cu$^{I}$–S interaction. The relatively short Cu$^{I}$–N bond lengths are consistent with possible metal to N $\pi$-backbonding, which is typical of Cu$^{I}$ to unsaturated N-complexes, and are nearly the same as those in the Cu$^{I}$ complex of bis-[2-(2-pyridyl)ethyl]disulphide.[5] The angles at Cu$^{I}$ range from 90° to 119° in the monomeric complex, and from 88° to 138° in the polymer.

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