The Preparation and Crystal Structure of Dichloro(3,5-diamino-1,2,4-dithiazolium)-Copper(I), $Cu(S_2C_2N_3H_4)Cl_2$. An Example of a Positively-charged Electron-donor Ligand

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Summary The compound dichloro(3,5-diamino-1,2,4-dithiazolium)copper(I) has been prepared and its crystal structure determined as a spiraling Cu–Cl–Cu chain of approximately tetrahedral Cu^I bound to three Cl atoms and a ring nitrogen.

Systems containing the S–S linkage and their interactions with metal ions are of considerable interest because of their close relationship to the interaction of metal ions with cystine in biological systems.[1] We have generated this linkage as part of a reaction of dithiobiuret with Cu^{II} chloride. This reaction gave a positively charged ring system, $(S_2C_2N_3H_4)$[4] and Cu^I is bound to this ring system *via* a ring nitrogen; this binding has not been observed previously.

This reaction between a 95% ethanol solution of $CuCl_2\cdot 2H_2O$ and an ether solution of dithiobiuret (Hdtb, $S_2C_2N_3H_5$) gives three crystalline products: (1) olive green (the material reported here), (2) yellow (under investigation), and (3) a blue material, the eventual end product in air, most likely $CuSO_4\cdot 5H_2O$.

The olive green product has the stoicheiometry $Cu(S_2C_2N_3H_4)Cl_2$. Diffraction-quality crystals have been isolated and found to be monoclinic, $P2_1/c$, $a = 6{\cdot}992(1)$ Å, $b = 7{\cdot}494(1)$ Å, $c = 16{\cdot}011(2)$ Å, $\beta = 110{\cdot}06(1)^\circ$ $D_m = 2{\cdot}22$ g cm^{-3}, $D_c = 2{\cdot}26$ g cm^{-3}, $Z = 4$. The crystal structure was solved by standard heavy-atom techniques and refined by full matrix least-squares, including anisotropic temperature factors for all non-hydrogen atoms to a current R value of 0·052.

The structure may be described as an infinite chain of chlorine-bridged Cu^I species (Figure). The co-ordination sphere of the metal is completed to four (approximately tetrahedral Cu^I) with a terminal Cu–Cl bond and a Cu–N bond to the central nitrogen of the 3,5-diamino-1,2,4-dithiazolium ring system.

This structure can be formulated as Cu^ICl_2 $[S_2C_2N_3H_4]^+$, or as $Cu^{II}Cl_2$ $[S_2C_2N_3H_4]$ in which the ligand is cyclized and uncharged. The former is a well documented result of mild oxidation[2] but the latter ring system is unknown and unexpected. We have also tried to find the Cu^{II} e.s.r. signal but without success.†

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† E.s.r. measurement was carried out by S. Shaffer in the laboratory of Professor C. P. Poole, Department of Physics, University of South Carolina.

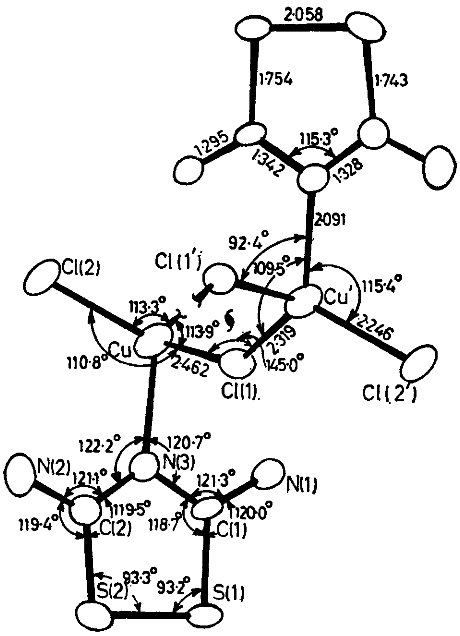

FIGURE. ORTEP drawing of the structure of dichloro(3,5-diamino-1,2,4-dithiazolium)copper(I), viewed down the infinite chain of bridge –Cu–Cl–Cu– atoms. The upper and lower halves in the figure are related by the screw axis (§) in the centre. Primes refer to atoms related by this operation. The estimated standard deviations for the bond distances are S–S ± 0·002, S–C ± 0·005, C–N ± 0·006, Cu–Cl ± 0·001, Cu–N ± 0·003 Å, and for the angles are Cu–Cl–Cu ± 0·04°, Cl–Cu–Cl ± 0·03°, Cl–Cu–N ± 0·10°, N–C–S ± 0·33°, C–N–C ± 0·35°.

It is clear not only from the bond angles about the ring nitrogen but also from the Cu–N(3)–(centre of S–S bond) angle of 165° that the ring nitrogen is three co-ordinate planar with one of the linkages being the Cu^{I}–N bond. Thus although the [$S_2C_2N_3H_4$] ring system is positively charged as in [$S_2C_2N_3H_4$]I,[3] it is still acting as an electron pair donor to Cu^{I}. This is unusual and the compound has not been reported by other workers who have described reactions between nitrogen substituted Hdtb and Cu^{II} salts.[4] We expected a compound such as Cu(Hdtb)Cl_2 to be formed, analogous to those found by Srivastava and Agarwal[4] or Ni(Hdtb)$_2$(ClO_4)$_2$·EtOH.[5] In the present case a proton has been lost in a non-aqueous medium, a surprising result. The heterocyclic ring is planar including the external nitrogens. The nitrogen is displaced 0·12 Å from the Cu–C(1)–C(2) plane. The observed ring distances and angles are normal[3] and the Cu–N distance is that expected for a Cu–N single bond. However, the Cl–Cu–Cl bridge is asymmetric in Cu–Cl distances without obvious reason. In addition, the Cu–Cl–Cu bridge angle is unusually large at 145°; it is neither close to 90° nor close to linear.

In this structure Cu^{I} is bound to nitrogen and not to sulphur although nitrogen is considered a relatively hard base and the disulphide linkage a relatively soft base. This is also the first well documented case in which a nitrogen atom of a thiourea,[6] dithiobiuret[7] or related molecule is used in bond formation to a metal. It is suggested that the compound is formed by the following process, either concerted or stepwise and not necessarily in the order given: (1) electron transfer to two Cu^{II} species from S to affect ring closure, (2) loss of a proton from the ring in a non-aqueous medium leaving an approximate sp^2 N orbital and a lone pair and reducing the charge on the ring from 2+ to 1+, (3) formation of the Cu–N bond with the sp^2 N orbital from (2) with either one of the Cu^{I} ions reduced by this ligand or other Cu^{I} ions in solution.

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