The Crystal and Molecular Structure of Dichlorobis(tetramethylthiourea)copper(II)

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Summary The crystal structure of dichlorobis(tetramethylthiourea)copper(II) has been solved and is made up of isolated molecules containing chlorine and sulphur-bonded copper(II) in a configuration intermediate between tetrahedral and square planar.

THIOUREA and its derivatives are readily oxidized in aqueous and non-aqueous solutions by many oxidizing agents including Cu^{2+}.[1] In this reaction thiourea is oxidized to formamidine disulphide while the Cu^{II} is reduced to Cu^{I}.[2,3] In the presence of an excess of thiourea (tu) the Cu^{I} ultimately forms a variety of stable complexes depending upon the anion as well as experimental conditions. The Cu^{I} complexes that have been characterized and their crystal structures determined are: [Cu(tu)$_3$Cl],[4] [Cu(tu)$_2$Cl],[5] [Cu$_2$(tu)$_6$$^{2+}$(BF$_4^-$)$_2$],[6] [Cu$_2(tu)_6$$^{2+}$(ClO$_4^-$)$_2$],[7] and [Cu$_4(tu)_9$(NO$_3$)$_4$].[8] Others have been reported,[9] but they have not yet been well-characterized. Zatko and Kratochvil[3] indicated that the oxidation of thiourea in acetonitrile by Cu^{II} proceeds *via* a red intermediate complex between Cu^{II} and thiourea. With thiourea as well as most substituted thioureas and various anions in a variety of solvents, this red intermediate is of a transitory nature and cannot be isolated. However, we have succeeded in isolating a ruby-red complex between Cu^{2+} and tetramethylthiourea (tmt) and have determined its crystal structure. This is the first well-characterized report of a thiourea–Cu^{II} complex. Complexes between Cu^{II} and ligands with the NC(S)N grouping are effective antitumour agents in certain animals.[10] Hence, the structure of the Cu^{II}–(tmt) complex may also be of biological significance.

Dichlorobis(tetramethylthiourea)copper(II), [Cu(tmt)$_2$Cl$_2$], was prepared from dilute aqueous solutions of copper(II) chloride dihydrate and tetramethylthiourea in a 1:4 molar ratio at 0°. A burgundy colour develops immediately and slowly fades. Upon slow evaporation of the solution, a red-brown oil develops from which ruby-red crystals are formed. These crystals are air-sensitive and were coated with Vaseline, then placed into thin-walled glass capillaries for diffraction studies. Crystal data: $a = 9{\cdot}464(4)$, $b = 8{\cdot}550(2)$, $c = 11{\cdot}532(4)$ Å, $\beta = 105{\cdot}6(1)°$, $D_m = 1{\cdot}46(2)$, $D_c = 1{\cdot}47$ g/cm^3, $U = 898{\cdot}9$ Å^3, $\mu = 14{\cdot}4$ cm^{-1}, $M = 398$, $P2_1$, $Z = 2$. The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares including anisotropic temperature factors to a final R of 0·077[11] from 1132 non-zero *hkl* planes collected with automated counter methods.

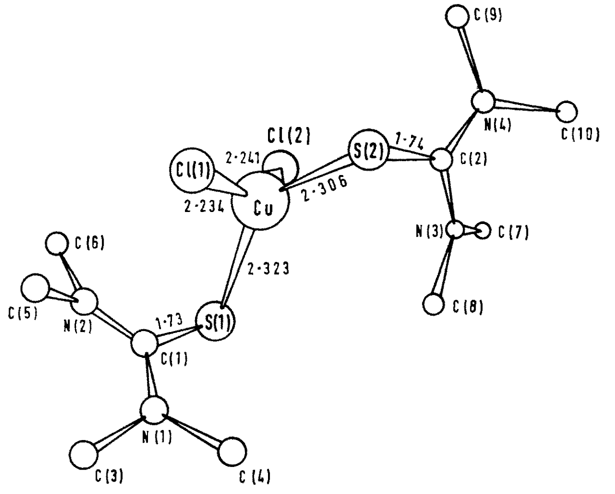

FIGURE. *Perspective view of the* [Cu(tmt)$_2$Cl$_2$] *molecule with most important distances and angles. The maximum e.s.d.'s are*: Cu–Cl = Cu–S = ± 0·006, S–C = ± 0·019, C–N = ± 0·03 Å. *The internal* C–N *distances are not significantly different from the average of* 1·33 Å *and the terminal* C–N *distances are not significantly different from the average of* 1·49 Å. *Relevant angles are*: Cl-Cu-Cl 145·1(2), S-Cu-S 140·1(3), Cu–S(1)–C(1) 108·7(7), Cu–S(2)–C(2) 108·9(7)°. *The angles with e.s.d.'s of* ±2° *about* C(1) *and* C(2) *are not significantly different from* 120°. *The terminal* C–N–C *angles are closed down to* 114° *average but the* C(1)–N–C *and* C(2)–N–C *angles are opened up to* 123° *average with both sets of e.s.d's at* ±2°.

The structure consists of isolated [Cu(tmt)$_2$Cl$_2$] molecules separated from their neighbours by ordinary van der Waals distances. The co-ordination polyhedron about the copper atom is best described as a considerably flattened tetrahedron retaining an approximate two-fold rotation axis of symmetry (Figure). This polyhedron is further distorted by a slight twist such that the dihedral angle between the planes Cl(1), Cu, Cl(2), and S(1), Cu, S(2) is 85·8 ± 0·5°. The Cu–Cl distances are shorter than the 2·31—2·43, all ±0·04 Å, observed in the distorted tetrahedron about copper in K_2CuCl_3[12] as well as the 2·316 ± 0·005 Å found for square-planar copper in $(NH_4)_2CuCl_4$.[1] However, the Cu–S distances can be compared to the 2·297—2·339,all ± 0·002 Å, found in bis(diethyldithiocarbamate)nickel(II).[14]

In each (tmt) group the sulphur, central carbon, and nitrogen atoms are coplanar, but the plane of the nitrogen and terminal carbon atoms are rotated out of this plane by *ca.* 20° in such a manner as to minimize steric interactions between methyl groups on the same (tmt) unit. Therefore, the delocalized π-orbital system that exists in thiourea is partially broken down and the S–C π-bond is more of a localized bond. The S–C distances in this complex seem somewhat longer than the 1·68(1) Å found in the free ligand.[15] All other bonded and non-bonded distances correspond to the expected values.

In some cases thiourea is exclusively a π-donor in forming transition-metal–sulphur bonds.[16] However, the dihedral angles between the planes defined by Cu–S–C and S–C–N are 64(2)° and 46(2)° for S(1) and S(2), respectively. Both the sulphur $p\pi$- and sp^2-orbitals are probably used to form the Cu–S bond in this case. Similar situations have been found in some substituted thiourea Ni^{II} complexes.[17]

In the past it has been assumed that an orange to red colour was characteristic of tetrahedral copper(II), yellow was characteristic of square planar $CuCl_4^{2-}$, and red was associated with distorted tetrahedral polymers, *e.g.*, K_2CuCl_3.[12] The present structure is essentially half-way between square planar and tetrahedral and is an isolated molecule.

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