Crystal and Molecular Structure of the Polymeric Complex Chloro(2,5-dithiahexane)copper(I)

By **Edward N. Baker** * and **Peter M. Garrick**, Department of Chemistry, Biochemistry, and Biophysics, Massey University, Palmerston North, New Zealand

The crystal and molecular structure of the title complex has been determined by single-crystal *X*-ray diffraction techniques, from diffractometer data. The crystals are monoclinic, with a = 7.673(2), b = 6.727(2), c = 15.700(5) Å, β = 104.8°, Z = 4, and space group $P2_1/c$. The structure has been refined by full-matrix least-squares methods to a final R factor of 0.035 for 1 710 independent reflections. The complex is polymeric, with adjacent molecules in the crystal joined by a bond between the copper atom of one molecule and one of the sulphur atoms of the dithiahexane ligand of a neighbouring molecule. Each copper atom has a distorted-tetrahedral geometry, with two bonds to the sulphur atoms of the dithiahexane ligand [Cu–S 2.336(1) and 2.342(1) Å], one to a terminal chlorine atom [Cu–Cl 2.239(1) Å], and one to one sulphur atom of a neighbouring molecule [Cu–S 2.315(1) Å].

RECENT interest in copper complexes of thioether ligands has arisen for several reasons. Preparative and spectroscopic studies [1] have shown that stable complexes of both Cu^{I} and Cu^{II} can be prepared, allowing the possibility of a detailed comparison of the bonding of copper(I) and copper(II) atoms in similar environments. Furthermore, the copper(I) complexes display a variety of stoicheiometries, with some simple four-co-ordinate tetrahedral species and others which are apparently three-co-ordinate or polynuclear. A third point of interest lies in the possible relevance of such complexes as bonding models for biological molecules. The thioether ligands resemble the side chain of the amino-acid methionine, a ligand for iron in cytochrome C, and a potential metal ligand in other proteins. In the ' blue ' copper redox proteins, for example, some of the copper atoms, either singly (Type I) or in pairs (Type III) apparently co-ordinate to one or more sulphur ligands.[2–5]

We have undertaken *X*-ray structure analyses of several of these copper–thioether complexes in order to examine the influence of the metal oxidation state and the co-ordination environment on the Cu–S bonding.[6] The structure analysis of chloro(2,5-dithiahexane)-copper(I), [{Cu(dth)Cl}$_n$] was undertaken because spectroscopic studies [1] indicated a terminal Cu–Cl bond, and suggested a three-co-ordinate trigonal-planar complex different in structure from the other complexes investigated. The crystal structure reported here shows that the complex is, in fact, four-co-ordinate, distorted tetrahedral, with a terminal Cu–Cl bond, as predicted, but with rather unusual bridging through one sulphur atom of the dth ligand to give a polymeric structure.

EXPERIMENTAL

The complex [{Cu(dth)Cl}$_n$], prepared as described previously,[1] was crystallised from methanol as clear needle-shaped crystals. The space group and approximate cell dimensions were obtained from oscillation and Weissenberg photographs. More accurate cell dimensions were obtained from a least-squares analysis of the positions of 12 general reflections on a four-circle *X*-ray diffractometer.

Crystal Data.—$C_4H_{10}ClCuS_2$, M = 221, Monoclinic, a = 7.672(2), b = 6.727(2), c = 15.700(5) Å, β = 104.8°, U = 784 Å^3, $F(000)$ = 448, D_m = 1.89(1) g cm^{-3} (by flotation), Z = 4, D_c = 1.88 g cm^{-3}, Mo-K_α radiation, μ(Mo-K_α) = 37.0 cm^{-1}, space group $P2_1/c$ from systematic absences.

Data Collection and Reduction.—Intensity measurements were made with a computer-controlled Hilger and Watts four-circle *X*-ray diffractometer, using zirconium-filtered Mo-K_α *X*-radiation, on a crystal of dimensions *ca.* 0.04 × 0.02 × 0.02 cm mounted along the longest dimension. The orientation of the crystal was defined by a least-squares treatment of the positions of 12 general reflections. Intensities were measured by means of a θ—2θ scan, consisting of 35 steps of 0.02°, through each reflection, with a count lasting 1.4 s at each step and a background count of 7 s at the beginning and end of each scan. Three standard reflections, chosen from different regions of

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reciprocal space, were monitored every 100 general reflections as a check against possible crystal deterioration or misalignment. No significant intensity reduction was noted during data collection. Reflections hkl, $\bar{h}kl$, $hk\bar{l}$, and $\bar{h}k\bar{l}$ were measured, up to θ 27°. Equivalent reflections were merged, to give a total of 1 524 observed [for which $I_{hkl} > \sigma(I_{hkl})$] and 186 unobserved reflections. The usual Lorentz and polarisation corrections were applied, but no correction was made for absorption.

Structure Determination.—The position of the copper atom was determined from a three-dimensional Patterson synthesis, and a subsequent electron-density map phased by the copper atom led to the identification of the positions of the remaining non-hydrogen atoms. The structure was seen, unexpectedly, to be polymeric, and the connectivity of the atoms established that the bridging atoms were sulphur rather than chlorine. The structure was refined by full-matrix least-squares methods, using a local version of the program ORFLS[7] adapted for the Burroughs B6700 computer by the University of Canterbury. The quantity minimised was $\Sigma w(\Delta F)^2$, where $\Delta F = k|F_o| - |F_c|$ and the weighting $w = 4F_o^2/[\sigma(F_o)^2]^2$. Four cycles of least-squares refinement with isotropic temperature factors for all the atoms reduced the conventional R factor to 0.082. Two further cycles, with anisotropic temperature factors, reduced R to 0.046, and a difference electron-density map then revealed the positions of all the hydrogen atoms. For the two final refinement cycles, hydrogen atoms were included in the structure-factor calculation (with temperature factors *ca.* 1.2 times those of their carbon atoms) but were not refined. This reduced the R factor from 0.038 to convergence at R 0.035 (for all the 1 710 independent reflections, observed and unobserved); R' was 0.039. A subsequent difference electron-density map contained no feature higher than 0.5 e Å^{-3} or lower than -0.5 e Å^{-3}.

Final atomic co-ordinates are listed in Table 1 and bond lengths and angles in Table 2. The numbering system for non-hydrogen atoms is shown in the Figure, hydrogen atoms being numbered according to the carbon atoms to which they are attached. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22195 (6 pp.).*

TABLE 1

Final atomic co-ordinates, with standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu	0.131 5(1)	0.116 3(1)	0.240 5(1)
Cl	0.222 4(1)	0.064 6(1)	0.117 6(1)
S(1)	0.141 1(1)	0.453 3(1)	0.277 3(1)
S(2)	0.313 2(1)	0.033 2(1)	0.379 8(1)
C(1)	0.310 4(5)	0.562 6(5)	0.229 5(2)
C(2)	0.255 6(5)	0.443 4(5)	0.393 5(2)
C(3)	0.394 7(4)	0.279 9(5)	0.417 1(2)
C(4)	0.161 4(5)	−0.010 6(6)	0.448 2(2)
H(1a)	0.435	0.530	0.278
H(1b)	0.270	0.530	0.164
H(1c)	0.300	0.710	0.220
H(2a)	0.150	0.435	0.423
H(2b)	0.300	0.580	0.414
H(3a)	0.438	0.295	0.481
H(3b)	0.505	0.310	0.390
H(4a)	0.058	0.070	0.442
H(4b)	0.207	−0.035	0.508
H(4c)	0.100	−0.130	0.430

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) Lengths *

Cu–Cl	2.239(1)	S(1)–C(1)	1.814(3)
Cu–S(1)	2.336(1)	S(1)–C(2)	1.813(3)
Cu–S(1^{I})	2.315(1)	S(2)–C(3)	1.817(3)
Cu–S(2)	2.342(2)	S(2)–C(4)	1.799(3)
		C(2)–C(3)	1.511(5)

C–H bonds range from 0.93 to 1.08 Å (mean 1.00 Å)

(*b*) Angles

S(1)–Cu–S(2)	91.54(3)	Cu^{II}–S(1)–C(1)	118.6(1)
S(1)–Cu–Cl	111.53(3)	Cu^{II}–S(1)–C(2)	109.3(1)
S(1)–Cu–S(1^{I})	117.37(2)	C(1)–S(1)–C(2)	102.5(2)
S(2)–Cu–Cl	121.70(3)	Cu–S(2)–C(3)	99.1(1)
S(2)–Cu–S(1^{I})	107.69(3)	Cu–S(2)–C(4)	106.0(1)
S(1^{I})–Cu–Cl	107.04(3)	C(3)–S(2)–C(4)	100.3(2)
Cu–S(1)–C(1)	105.8(1)	S(1)–C(2)–C(3)	113.8(2)
Cu–S(1)–C(2)	101.0(1)	S(2)–C(3)–C(2)	115.0(2)
Cu–S(1)–Cu^{II}	117.36(3)		

Bond angles at the carbon atoms, involving hydrogen atoms, all have approximately tetrahedral values

* Roman numeral superscripts refer to the following equivalent positions with respect to the reference molecule at (x, y, z):

I $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; II $-x, \frac{1}{2} + y, \frac{1}{2} - z$

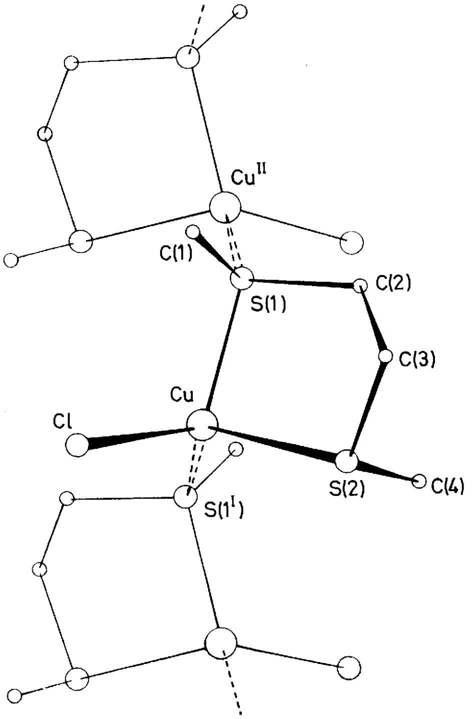

Diagram showing the polymeric structure of the complex. The Cu–S bond linking neighbouring Cu(dth)Cl entities is shown as a broken line

DISCUSSION

'Molecules' of Cu(dth)Cl (dth = 2,5-dithiahexane) form infinite chains in the crystal, as shown in the Figure. Each copper atom makes four bonds: two to

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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the sulphur atoms of the chelating dth ligand, one to the terminal chlorine atom, and one to one of the sulphur atoms of the dth ligand of a neighbouring molecule. The Cu(dth)Cl moieties are thus formed into polymeric chains through linking Cu–S bonds.

Such a structure, with bridging through sulphur in preference to chlorine atoms, was unexpected, since spectroscopic studies suggest that halide bridging occurs in other copper(I)–thioether complexes,[1] and the structures of many other halide-bridged copper(I) complexes have been reported (*e.g.* refs. 8 and 9). In contrast, although some complexes are known in which copper(I) atoms are bridged by the sulphur atoms of ligands such as substituted thioureas [10,11] and trimethylphosphine sulphide,[12] where the S atoms then become three-co-ordinate, to our knowledge only one example of bridging by a thioether ligand has previously been reported, *viz.* [$Cu_4I_4(SEt_2)_3$].[13]

Two features of interest in the bonding in [{Cu(dth)-Cl}$_n$] are the shortness of the bridging Cu–S bond [2.315(1) Å] compared with the two Cu–S bonds within the chelate ring [2.336(1) and 2.342(1) Å], and the equivalence of the latter two bonds. The usual trend in complexes where both bridging and terminal bonds exist is for the bridging to be longer than the terminal Cu–L bonds. For example, in [$Cu_4I_4(SEt_2)_3$] the bridging Cu–S bonds are 2.337(6) and 2.331(8) Å while the terminal Cu–S bonds are 2.297(10) and 2.298(9) Å. The longer Cu–S bonds in the chelate ring of [{Cu(dth)Cl}$_n$] probably do not arise because of strain in the ring, since shorter bonds [average 2.303(5) Å] are seen in the closely related complex [$Cu(dto)_2$][BF_4] (dto = 3,6-dithiaoctane).[6] Rather it is probable that the two ligands whose stereochemical arrangement about the copper atom is not restricted by the constraints of the chelate ring, *viz.* the terminal Cl atom and the S atom of the neighbouring molecule, can more easily be arranged to give maximum overlap with the copper orbitals. The Cu–Cl bond length does in fact lie at the lower end of the range (2.24—2.40 Å) observed for terminal Cu–Cl bonds in other tetrahedral copper(I) complexes,[14-16] and is close to that observed in three-co-ordinate complexes.[12,17] Thus a stronger interaction with Cl and S(1′) may allow weaker interaction with the chelating S atoms.

As a consequence of the sulphur bridging in the structure, the two sulphur atoms of each dth ligand are not equivalent, S(1) forming four bonds and S(2) only three. Despite this, the three 'intramolecular' bonds made by each, including the Cu–S bonds of the chelate ring, are closely similar in length, and the angles about S(1) and S(2) are also very similar. Thus the formation of an extra bond by S(1) apparently does not affect its stereochemistry or bonding to other ligands at all.

The stereochemistry of the copper atom is distorted tetrahedral. The chelate angle [91.54(3)°] is smaller than in [$Cu(dto)_2$][BF_4], where all four Cu ligands are in chelate rings and the chelate angle is expanded to an average of 94.8(2)°. The internal angles at the S atoms of [{Cu(dth)Cl}$_n$] [average 100.0(1)°] are correspondingly larger than those in [$Cu(dto)_2$][BF_4] [average 95.9(6)°].[6] Other bond lengths and angles are normal, and the S–C–C–S bridge has the usual asymmetric *gauche* configuration, with C(2) 0.22Å below the CuS_2 plane and C(3) 0.44Å above it.

Finally, the observation of bridging by a thioether ligand suggests that the side chain of methionine could act as a bridging ligand in metalloproteins. In the latter, metal atoms are thought often to occur as pairs or clusters (*e.g.* the e.s.r.-non-detectable, or Type III, copper atoms of copper proteins). Possible bridging ligands include cysteinyl sulphur atoms or disulphide groups, but the structure of [{Cu(dth)Cl}$_n$] suggests the methionine side chain as another possibility.

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