Trigonal Planar Copper(I) and Electron Deficient Bridge Bonds in Bis(thiourea)copper(I) Chloride

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DURING a systematic study of thiourea complexes of the transition metals, we have found a complex of Cu(I) with trigonal planar geometry as well as containing a three-centre delocalized bridge bond. This is both novel geometry and bonding for Cu(I).

Bis(thiourea)copper(I) chloride, $Cu[SC(NH_2)_2]_2Cl$, was prepared from cuprous chloride and thiourea in aqueous solution[1] and single crystals were grown by slow evaporation of the reaction mixture: M, 175, monoclinic, $P2_1/a$. With Cu-$K(\alpha_1\alpha_2$ λ = 1·5405, 1·5443 Å), a = 35·81 ± 0·04, b = 8·24, c = 5·81 both ±0·01 Å, β = 92·5 ± 0·2°, D_m = 1·94 ± 0·02 g.cm.$^{-3}$, Z = 8, D_c = 1·98 g.cm.$^{-3}$, 1558 independent *hkl* intensity data were collected by standard multiple film equi-inclination Weissenberg methods. The structure was solved by standard techniques[2] and refined by complete matrix least-squares with anisotropic temperature factors to a final conventional R of 0·106.

The structure may be described as made up of almost trigonal planar Cu(I) triangles sharing vertices with adjacent triangles to form a chain,

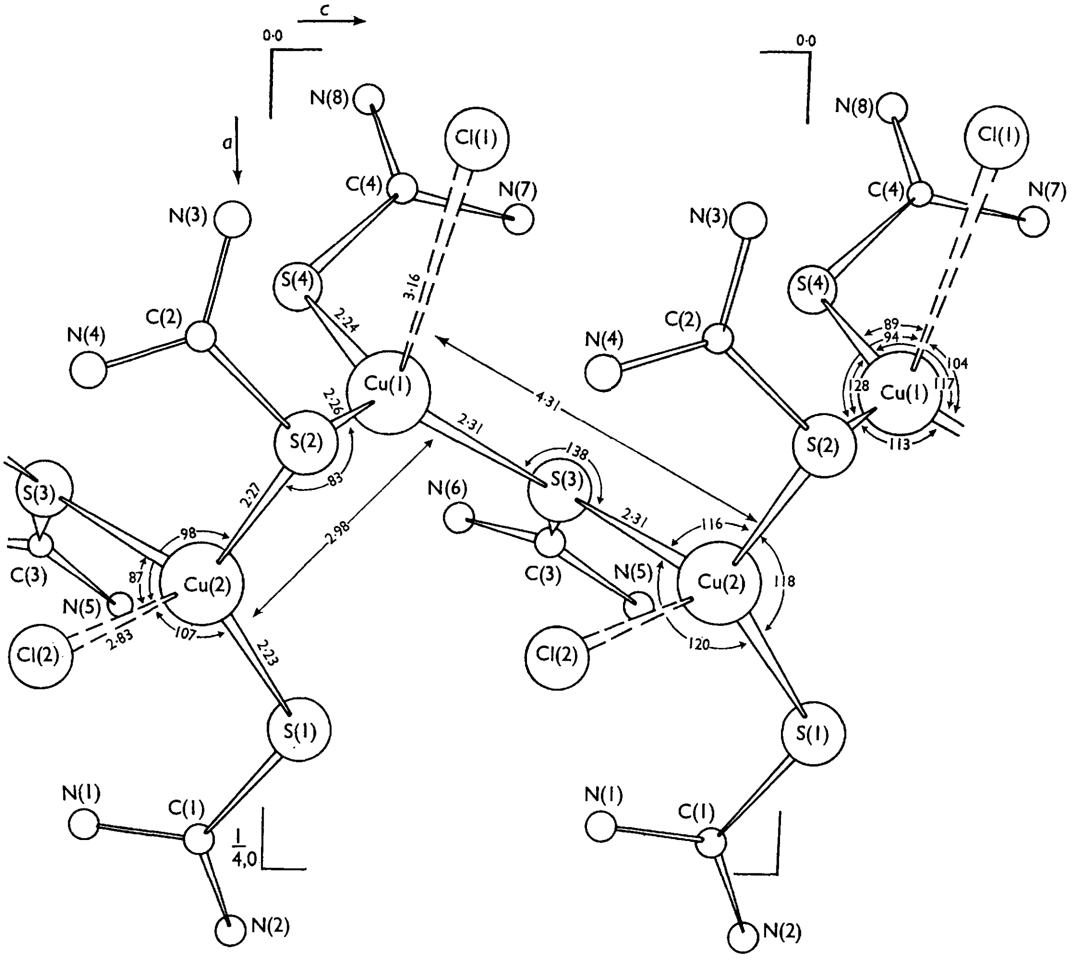

FIGURE 1. *View of the* $Cu[SC(NH_2)_2]_2Cl$ *chain down the* b *axis showing the important distances and angles. The chain runs approximately left to right. Standard deviations in* Å *are*: Cu–Cu ± 0·004; Cu–S, Cu–Cl ± 0·005. *The angles are* ±0·2° *or less.*

spiralling along the *c* direction. The triangles are made up in turn of a central Cu(I) with vertices of sulphur atoms from three different thiourea groups (Figure 1). An important feature of the structure is that the Cu–Cu separation alternates between a long and a short distance with an accompanying "broad" and a "sharp" Cu–S–Cu bridge angle. Each Cu atom has associated with it a "long" axial Cu–Cl distance. We view these as more or less ionic chlorine atoms, particularly since the analogous Ag–Cl distances[3] in $Ag[SC(NH_2)_2]_2Cl$ are somewhat shorter. The Cu–S distances fall in the range 2·23—2·31 Å and indicate substantial covalent bonding since a "normal" Cu–S single bond would be 2·39 Å.[4] Cu–S distances varying between 2·29 and 2·47 Å with individual standard deviations of ±0·008 Å were found in $Cu_4[SC(NH_2)_2]_9(NO_3)_4$.[5] The bridged and terminal thiourea groups are all planar and are not significantly different from one another or from free thiourea itself.[6]

This short metal–metal distance with its concommitant sharp bridge angle is very reminiscent of the short metal–metal distances and sharp bridge angles in polymeric dimethylberyllium[7] and dimeric trimethylaluminium,[8,9] which are generally accepted to be three-centre electron pair bridge bonds. It can be seen in Figure 1 that the S(2) thiourea group is perpendicular to the Cu(2)–S(2)–Cu(1) plane. Hence, the only orbitals and electrons this thiourea group can contribute to the bridge bond are from the S–C $p\pi$ molecular orbital. This means that we have a delocalized three-centre electron-pair bond (electron deficient) made up of (sp^2) orbitals from each Cu atom and the S–C $p\pi$ molecular orbital (Figure 2), which is analogous to the bonding in dimethylberyllium and trimethylaluminium, but involves sulphur instead of carbon. This interaction might be expected to elongate the C–S bond of thiourea from that of free thiourea, but this is not observed. Since free thiourea is planar[6] with non-bonding electron pairs on nitrogen it is unnecessary to invoke back-bonding to explain this invariance. This bridge bond could also be described as an ethylene-type linkage with one of the Cu sp^2 orbitals pointing toward the centre of the S–C bond. This would make the Cu atom more coplanar (*vide infra*) with the three sulphur neighbours, but it would make a larger distortion of the S–Cu–S angles from the idealized 120°. No doubt the true bonding picture is between these two extremes, and the maximum in the bonding electron density is probably not along the Cu(2)–S(2)–Cu(1) lines, but slightly displaced towards C(2), but not as far as the S(2)–C(2) mid-point. The displacement of Cu(1) is 0·2 Å from the S(2)S(3)S(4) plane and Cu(2) is 0·3 Å from the S(1)S(2)S(3) plane, both toward the respective C(1) atoms. This is a much more regular arrangement of ligands and Cu(I) to form a trigonal planar geometry than any previously reported.[10]

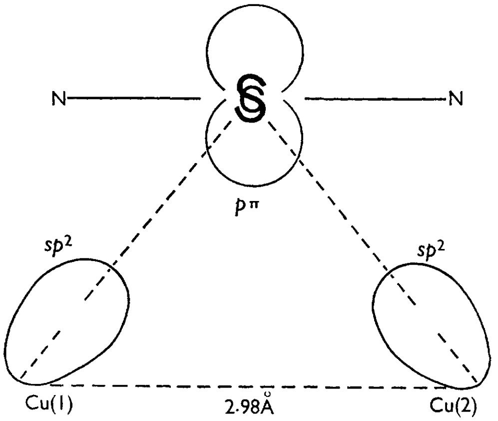

FIGURE 2. *View normal to* Cu(1)–S(2)–Cu(2) *plane of orbitals used to make the three-centre delocalized electron-pair bridge bond.*

The broad angled bridge is readily understandable in terms of normal two electron pair Cu–S bonds with electrons from the non-bonding sp^2 sulphur orbitals. Similarly the terminal Cu–S bonds involve one sp^2 sulphur non-bonding pair of electrons.

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[1] W. A. Spofford and E. L. Amma, to be published.

[2] For methods and computer programs see *e.g.* R. L. Girling and E. L. Amma, *Inorg. Chem.*, **1967**, **6**, 2009.

[3] E. A. Vizzini and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 2872.

[4] L. Pauling "Nature of the Chemical Bond" 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp. 246, 410.

[5] R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 4270.

[6] M. R. Truter, *Acta Cryst.*, 1967, **22**, 556.

[7] A. I. Snow and R. E. Rundle, *Acta Cryst.*, 1951, **4**, 348.

[8] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, 1953, **21**, 986.

[9] R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, 1967, **89**, 3121.

[10] N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, 1964, **3**, 1535.