is about as volatile as hexaborane(10) but is highly unstable at room temperature. It is to be noted that $C_3B_3H_7$ is related to known molecules in the isoelectronic series: B_6H_{10} (four bridge protons), CB_5H_9 (three bridges),[2] $C_2B_4H_8$ (two bridges),[3] $C_3B_3H_7$ (one bridge), and the hypothetical molecule[4] $C_4B_2H_6$ (no bridges).

The mechanisms operating in this reaction system are at present a matter for speculation, but it seems likely that hydroboration reactions are involved at early stages.[5] The observed formation of methylated species fits the pattern noted in other recent studies of borane–acetylene reactions,[2,5,6] but its occurrence at ambient temperature is novel. A detailed investigation of the B_4H_{10}–C_2H_2 reaction and the chemistry of the tricarbahexaborane(7) derivatives is in progress.

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Electron-Deficient Bonding Involving Sulfur Atoms. II. The Crystal Structure of $Cu_4[SC(NH_2)_2]_9(NO_3)_4$

Sir:

In a previous communication[1] we described a new type of bridge bond in the structure of bis(thiourea)-silver(I) chloride in which a thiourea S–C $p\pi$ molecular orbital was used to form a three-center bridge bond with $\sigma(sp^3)$ Ag(I) orbitals. During the course of structure investigations of a number of metal–thiourea complexes we prepared a complex of thiourea with cuprous ion with the unusual formula of $Cu_4[SC(NH_2)_2]_9(NO_3)_4$, hereafter referred to as $Cu_4(tu)_9(NO_3)_4$. The crystal structure revealed no less than five different types of metal–sulfur bonds, at least one of which is a completely new type of three-center electron-deficient bridge bond involving a sulfur sp^2 nonbonding orbital.

Stoichiometric amounts of cupric nitrate and thiourea were caused to react in aqueous solution and the solution was allowed to cool and evaporate to grow single crystals of $Cu_4(tu)_9(NO_3)_4$. The crystals were found to be orthorhombic; with Cu K(α_1 = 1.505, α_2 = 1.544 A), the cell constants are a = 14.94, b = 21.76, and c = 14.63 A, all ±0.01 A. Four $Cu_4(tu)_9(NO_3)_4$ entities per cell gave a calculated density of 1.71 g cm^{-3} in good agreement with the 1.75 g cm^{-3} observed. Systematic absences indicated the possible space groups to be $Pbc2_1$ or Pbcm; the structure analysis confirmed the latter (*vide infra*). A single crystal 0.1 × 0.2 × 0.3 mm was mounted with the long dimension vertical on a G.E. single-crystal orienter seated on a Picker diffractometer for the collection of 1099 independent *hkl* intensity data by a scanning technique.

The structure was solved by conventional three-dimensional Patterson and Fourier techniques.[2] Refinement was carried out by complete matrix least squares including anisotropic temperature factors[3] with observations weighted as the inverse of their variances.[4] The final disagreement index, R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$), was found to be 0.108. A final three-dimensional difference map did not indicate any unusual features.

The structure may be described as made up of a rectangle of Cu atoms (Cu_1,Cu_2,Cu_1',Cu_2'; Figures 1 and 2) which are connected by bridging sulfur atoms of thiourea groups. These rectangles are, in turn, interconnected by other sulfur bridges to form an infinite polymer of sulfur-bridged Cu atoms propagating in the c direction. By this means each Cu is surrounded by four S atoms to give Cu(I) its most common tetrahedral coordination. The only functions of the nitrate groups, other than that of perhaps participation in some hydrogen bonding, are to fill "holes" left by the polymer and balance charge.

There exist in the structure no less than five distinctly different types of metal–sulfur bonds (see roman numerals in Figure 1). Of course, molecular packing may well be important in such a complex structure, and it is difficult to determine its magnitude. However, we wish to describe and discuss each of these types of metal–sulfur bonds in turn.

The four-membered ring defined by Cu_1,Cu_2,S_1,S_2 contains sulfur bridges of type I and has a particularly interesting geometry: (1) the Cu_1–Cu_2 distance is only 2.707 ± 0.005 A; (2) the Cu–S–Cu angles are only 69°; (3) the dihedral angle between normals of the planes defined by Cu_1–$S_1(S_2)$–Cu_2 and the $S_1(S_2)$ thiourea plane is 86°; (4) the angle between a line formed by the intersection of the plane defined by the $S_1(S_2)$ thiourea group and the Cu_1–$S_1(S_2)$–Cu_2 plane with the S_1–C_1(S_2–C_2) bond is 110°.[5] Further, individually, each thiourea group is planar within experimental error.

This short metal–metal distance and the accompanying sharp bridge angle are strikingly similar to the electron-deficient bridges in polymeric dimethylberyllium[6] and dimeric trimethylaluminum[7,8] where the metal–metal distances are approximately equal to the sum of the covalent radii and the bridge angles are 66 and 74.3°, respectively. If the reasonable assumption is made that the sulfur atom in thiourea is sp^2 hybridized

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(2) Sly–Shoemaker–Van den Hende Fourier program for the IBM 7090.

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(5) The notation Cu_1–$S_1(S_2)$–Cu_2 refers to either the Cu_1–S_1–Cu_2 plane or the Cu_1–S_2–Cu_2 plane and, in similar fashion, $S_1(S_2)$ refers to S_1 or S_2. Items 2, 3, and 4 are average values, but the differences are at most three standard deviations. However, the four-membered ring (Cu_1,Cu_2,S_1,S_2) has two sets of distinctly different Cu–S distances: Cu–S_1, 2.469; Cu_2–S_1, 2.291; Cu_1–S_2, 2.326; Cu_2–S_2, 2.472 A (all ±0.008 A). The Cu_1,S_1,Cu_2,S_2 unit is also not quite planar with Cu_1,Cu_2,S_1,S_2 displaced +0.042, + 0.043, −0.155, and −0.134 A, respectively, from the best least-squares plane through the four atoms. These details can be understood in terms of refinements of the postulated model, but space limits the discussion.

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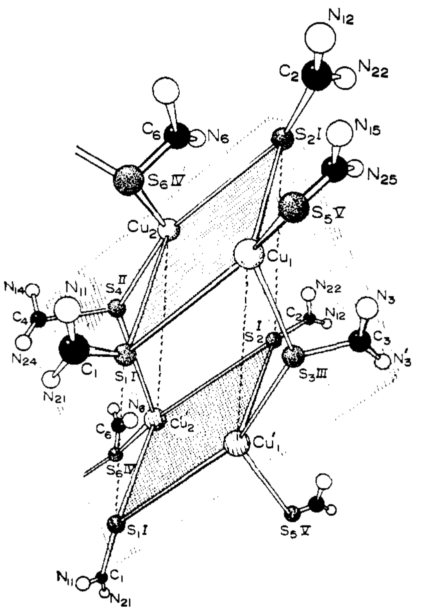

Figure 1. Perspective view of the $Cu_4(tu)_9(NO_3)_4$ polymer. S_6 at the top left bridges this "tetramer" to an adjacent "tetramer" to complete the polymer; see also S_6 at lower right. Dotted area indicates the approximate plane defined by Cu_1,Cu_2,S_1,S_2.

with a C–S σ and π bond and the nonbonding electron pairs in sp^2 orbitals in the molecular plane, then the above analogies, items 3 and 4, are all understandable by considering the four-membered ring as two sets of three-center electron-deficient bonds. Each Cu contributes a $\sigma(sp^3)$ orbital and each S one sp^2 orbital with its electron pair to this three-center bridge.[9] This is equivalent to a four-center, four-electron, electron-deficient description. The average S–C distance, 1.75 A, is only slightly greater than one standard deviation (±0.03 A) of the 1.71 ± 0.01 A observed in free thiourea.[10] In contrast to the Ag–S–Ag bridge in $Ag(tu)_2Cl$, this type of electron-deficient bridge does not require a lengthening of the S–C bond. Hence, there is no demand for the use of the Cu 3d orbitals as was true of the 4d orbitals in $Ag(tu)_2Cl$.

The Cu_2–S_4–Cu_2' bridge (type II) also appears to be electron deficient (using one sp^2 S orbital with its electron pair and two empty Cu orbitals), since the entire thiourea group must be in the mirror plane relating the Cu_2 to Cu_2' and the angle between S_4–(Cu_2–Cu_2' bisector) and the S_4–C_4 bond is 112°. However, since the Cu_2–Cu_2' distance is 4.192 ± 0.005 A and the Cu_2–S_4–Cu_2' angle is 122.0 ± 0.2°, this bridge must be much weaker and more complicated than the type I bridges.

The Cu_1–S_3–Cu_1' bridge (type III) is probably, in terms of bonding, the most complicated. In contrast to the Cu_2–S_4–Cu_2' bridge, only the S_3–C_3 bond of the thiourea group lies in the crystallographic mirror relating Cu_1 to Cu_1' and N_3 to N_3'. The distance between Cu_1 and Cu_1' is 4.161 ± 0.005 A, and the Cu_1–S_3–Cu_1' angle is 123.2 ± 0.2°. Further, the dihedral angle between the S_3 thiourea plane and the Cu_1–S_3–Cu_1' plane is 128°. This probably means that the sulfur $p\pi$MO as well as the sp^2 nonbonding orbitals both contribute electrons to this bridge, and even d orbitals may be involved.

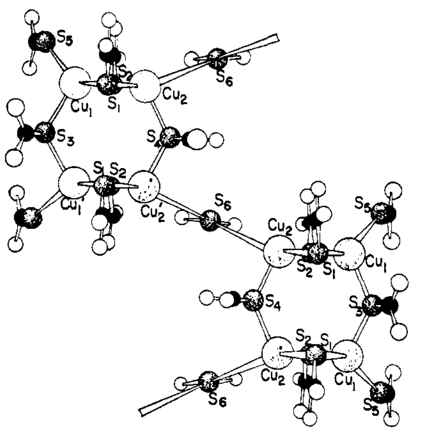

Figure 2. A side view of the $Cu_4(tu)_9(NO_3)_4$ polymer. A crystallographic mirror plane passes through S_4 and its thiourea group but only through S_3 and its associated carbon atom. The orientation of the S_1 and S_2 thiourea groups is noteworthy.

The S_6 bridging group connects two Cu atoms by more or less normal electron-pair bonds using both electron pairs in the sulfur sp^2 orbitals. S_5 is nonbridging and donates one electron pair from one of its sp^2 nonbonding orbitals to Cu_1. Hence we have five different types of metal–sulfur bonds, at least one of which is a completely new type of electron-deficient bond.

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[9] Diagramatically, this description is the same as ref 1, Figure 2, with $\psi ED = \sigma_1 + \sigma_2 + sp^2$. Other changes are obvious.

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[11] In partial fulfillment of the Ph.D. requirements, University of Pittsburgh, 1966.

[12] Address all correspondence to this author.

The Replacement of Phenolic Hydroxyl Groups by Hydrogen

Sir:

Up to the present time, no general method has been available for the removal of phenolic hydroxyl groups.[1] A method has recently been reported[2] for removing the phenolic hydroxyl group of various 3-methoxy-4-hydroxymorphine derivatives. This method involves a sodium and liquid ammonia cleavage of phenol ethers, whereas a similar, more generally applicable procedure[1] requires the preparation of a 2,4-dinitrophenyl ether of the phenol and catalytic reduction to the unstable diaminophenyl ether, followed by a sodium and liquid ammonia cleavage of the substituted ether to effect the desired replacement of phenolic hydroxyl group by hydrogen. Both of these procedures are based on the cleavage of diphenyl ethers by sodium in liquid ammonia,

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