The Crystal Structure of Bis(thiourea)silver(I) Chloride. A New Type of Bridge Bond

Sir:

From the results of a systematic investigation of metal–sulfur bonds in thiourea complexes, we wish to report a structure that reveals the first known example of a bridging three-center delocalized system involving a pπ sulfur–carbon MO.

$Ag[SC(NH_2)_2]_2Cl$ ($Ag(tu)_2Cl$) was prepared by the method of Nardelli,[1] and single crystals were grown by slow evaporation of the reaction mixture. The crystals were found to be monoclinic, $P2_1/a$, with cell constants $a = 36.70 \pm 0.04$, $b = 8.24 \pm 0.01$, $c = 5.87 \pm 0.01$ A, and $\beta = 92° 50' \pm 15'$. The calculated density with eight formula entities per unit cell is 2.22 g cm^{-3}, compared to the observed density of 2.18 g cm^{-3}. A crystal 0.02 × 0.04 × 0.1 mm was mounted about the needle axis and used to measure 1679 independent *hkl* intensities on a Picker diffractometer equipped with a GE single crystal orienter by a scanning technique with nickel-filtered Cu Kα radiation. The linear absorption coefficient (μ) was calculated to be 32 cm^{-1}. No corrections were made for absorption nor anomalous dispersion.

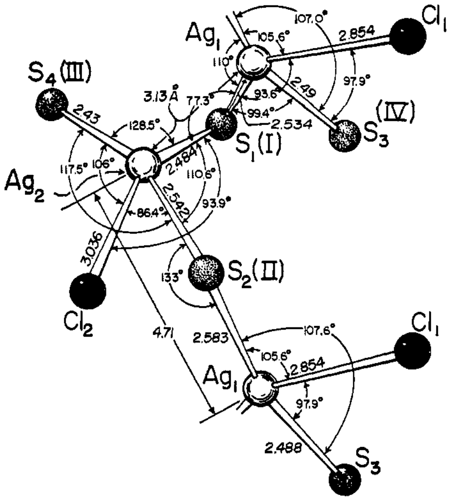

Figure 1. Details of the $-Ag_1-S_2-Ag_2-S_1-Ag_1-$ chain. The thiourea groups are not shown for the sake of simplicity. Roman numerals refer to the four different types of metal–sulfur bonds

The silver, sulfur, and chlorine atom positions were located from the three-dimensional Patterson function,[2] and the carbon and nitrogen atom positions were found by standard three-dimensional electron density techniques. Refinement was performed by complete matrix least squares,[3] including anisotropic temperature factors, minimizing the function $\Sigma_i w_i(F_o - F_c)^2$. The observations were weighted as the inverse of their variances: $\sigma^2(F^2) = S(1/Lp)^2[N + 2B + (0.04N)^2]$.[4] The final disagreement index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was found to be 0.067.

The structure may be described as made up of distorted tetrahedra sharing two apices with neighboring tetrahedra to form an infinite spiralling chain in the *c* direction. The tetrahedra are in turn made up of a central silver and its coordinated chlorine and sulfur atoms. However, the chain is not uniformly repeating, but the Ag–Ag distances alternate between a short 3.134 A and a long 4.710 A, both ±0.002 A. The Ag atoms with the short Ag–Ag distance are connected by sulfur bridges with $Ag_2-S_1-Ag_1$ angles of 77.3°, and the long Ag–Ag distance corresponds to a $Ag_1-S_2-Ag_2$ bridge angle of 133°, both ±0.1°. The distorted tetrahedron about each Ag is then completed by a terminal Ag–S bond and a long Ag–Cl linkage (Figure 1). The Ag–S distances all fall between 2.48 and 2.59 A and are indicative of relatively strong covalent bonding. The sum of single bond covalent radii[5] would be 2.56 A. This is in contrast to the Cd–S distance in, *e.g.*, $Cd(tu)_4Cl_2$[6] (tu = thiourea), which was found to be 2.72 A on the average. The bridged and terminal thiourea groups are all planar and not significantly different from one another, nor from free thiourea[7] itself.

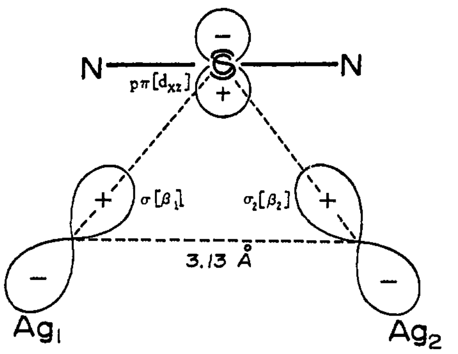

Figure 2. View, normal to the bridge plane, of the orbitals used to make the $Ag_1-S_1-Ag_2$ bridge. Considering the orbitals all in the plane and neglecting the negative lobes of the Ag orbitals, the electron-deficient MO would be $\psi_{ED} = \sigma_1 + \sigma_2 + p\pi$. Considering the orbitals shown as d orbitals with a nodal plane in the plane of the bridge, then we can construct $\psi_\pi = \beta_1 + \beta_2 + 3d_{xz}$ and $\psi_{nb} = \beta_1 - \beta_2$.

The short Ag–Ag distance and the accompanying sharp bridge angle are strikingly similar to the electron-deficient bridges in polymeric dimethylberyllium[8] and dimeric trimethylaluminum,[9,10] where the metal–metal distances are approximately equal to the sum of the covalent radii; the bridge angles are 66 and 74.3°, respectively. Furthermore, in the sharp-angled bridge in $Ag(tu)_2Cl$, not only is the angle between the Ag_1-Ag_2 midpoint and the bridging sulfur–carbon bond approximately 90° (104°), but also the lines defined by Ag_1-Ag_2 and the nitrogen atoms of this thiourea group are essentially parallel. This strongly suggests (in the absence of d orbitals) that we have a three-center electron-deficient bridge bond ($\psi_{ED} = \sigma_1 + \sigma_2 + p\pi$) with σ (*e.g.*, sp^3 hybrids) orbitals from each silver and a pπ MO and its electron pair from the bridging thiourea (Figure 2). However, this cannot be entirely correct for such a bridge would demand not only an elongated Ag–S bridge distance compared to the other bridge bond, but also an elongated distance compared to the

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terminal Ag–S bonds. Such an elongation is not observed. Even more important is the fact that the thiourea group involved in the sharp bridge bond does not have an elongated S–C distance. In fact, all the S–C distances are within less than a standard deviation (±0.016 A) of the S–C distance found in free thiourea.

The additional use of empty sulfur 3d orbitals without the use of filled Ag 4d orbitals does not alleviate this problem. A possible explanation for the invariance of the thiourea S–C bond length on complex formation can be seen by referring to Figure 2. In addition to the electron-deficient three-center bond previously described, a three-center bonding MO can be constructed from the sulfur $3d_{xz}$ and appropriately oriented Ag 4d (β) orbitals. These would lead to a bonding π three-center MO, $\psi_\pi = \beta_1 + \beta_2 + d_{xz}$, and a nonbonding MO, $\psi_{nb} = \beta_1 - \beta_2$. The four electrons, two from each Ag 4d orbital, would then be accommodated in these orbitals. ψ_π would be able to return much of the charge withdrawn from the S–C pπ MO by the three-center σ–pπ–σ electron-deficient MO. It is to be noted that ψ_{nb} is antibonding with respect to metal–metal bonding, and there is little to be gained by forming metal–metal bonds from any of the other filled metal orbitals. The other sulfur 3d orbitals would not interact with the silver 4d orbitals in such a way as to return charge to the S–C pπ MO. For comparison, a Ag–Ag distance of 3.03 A has been observed in $AgP(CH_3)_3 \cdot C_2H$;[11] and the Ag–Ag distance in metallic silver is 2.889 A.[5]

On the other hand, for the Ag_2–S_2–Ag_1 wide angle bridge (133°) the angle between the Ag_1–Ag_2 midpoint and the S_2–C bond is 154°; but the lines defined by Ag_2–Ag_1 and the nitrogen atoms of this thiourea group are also parallel. This bridging is most easily understood in terms of two filled sp^2 sulfur orbitals forming two electron-pair donor–acceptor bonds. These orbitals are nonbonding in thiourea itself and use of these orbitals would not elongate the S–C bond distance. Hence, the use of S 3d or Ag 4d orbitals is not demanded in this bridge.

The geometry of the nonbridged Ag_2–S_4 and Ag_1–S_3 bonds is easily understood in terms of a sp^2 sulfur donor orbital.

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On the Interpretation of Nuclear Magnetic Resonance Spectra of Stereoregular Polymers

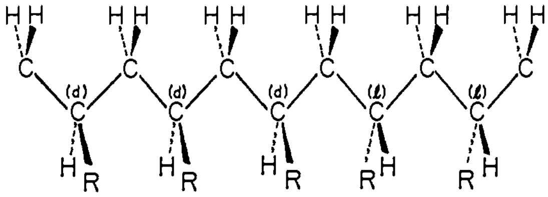
Sir:

In a paper published recently,[1] one of the present authors and his collaborators concluded that typical isotactic polymer chains are stereoirregular to an appreciable degree. This conclusion was reached on the grounds that the chain dimensions (*i.e.*, the unperturbed mean square end-to-end length $\langle r^2 \rangle_0$) and their temperature coefficients, as found by experiment for those isotactic polymers which have been investigated,[2–5] are irreconcilable with a perfect stereoregular structure. Syndiotactic units were cited[1] as seemingly the most likely source of stereoirregularity. The presence of 5–10% of such units would bring theoretical calculations[1] into agreement with experiments[2] on isotactic poly(*n*-butene-1) and poly(*n*-pentene-1). Results for other isotactic chains, including especially polypropylene[3] and poly(isopropyl acrylate),[5] though perhaps less complete, point to a similar degree of departure from perfect stereoregularity.

The postulation of so large a proportion of syndiotactic units (*i.e.*, dyads) would appear to be at variance with the nmr spectra of typical isotactic polymers, notably polypropylene[6,7] and poly(isopropyl acrylate).[8] Their β-proton (CH_2) spectra give no evidence whatever of a discernible peak at the location of the singlet which characterizes the predominantly syndiotactic polymer. From 100-Mc nmr spectra of carefully extracted isotactic polypropylene published recently by Natta and co-workers,[7] the absence of a syndiotactic peak would seem to imply a level not exceeding 2% for such dyads.[9]

It is the burden of this communication to point out that *the nmr peak for an isolated syndiotactic unit in a preponderantly isotactic chain should occur at a location differing, perhaps markedly, from that for such a unit in an all-syndiotactic chain.* The peak for the isolated syndiotactic dyad may well be obscured by one of the quartet of peaks for methylene groups of the isotactic units. Certainly, these protons should not appear at the same location as found for the syndiotactic chain, and their shift could conceivably be as large as the 0.39-ppm shift[7] between the nonequivalent protons in the isotactic chain.

This result follows directly from analysis of the conformation of the predominantly isotactic chain in the neighborhood of a syndiotactic dyad. Consider for example the portion of a vinyl polymer chain which is represented in its planar conformation by



The letters *d* and *l* serve to differentiate the two sets of asymmetric centers.[1] Let the rotational states for a given bond be designated *t*, g^+, and g^- for *trans*, *gauche*$^+$, and *gauche*$^-$, respectively. Then the ster-

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