# Catenation of 2,2'-Bis(ethylthiomethyl)biphenyl with Copper(I) Bromide

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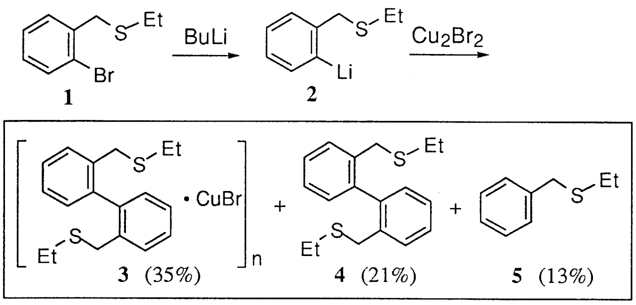
Treatment of 2-(ethylthiomethyl)phenyllithium with copper(I) bromide afforded a polymeric coordination compound in which 2,2'-bis(ethylthiomethyl)biphenyl molecules were linked by copper(I) bromide cores. This polymeric complex dissociates on dissolution in organic solvents and reforms on recrystallization from the solution. Other copper(I) salts also gave similar compounds, when reacted with the lithium compound.

Organocopper(I) compounds, which are generally prepared by reactions of an organolithium or a Grignard reagent with a copper salt,[1,2] are known to be stabilized by an amino ligand which can coordinate to the copper(I) center intramolecularly.[3,4] Interestingly, however, examples of organocopper(I) compounds which are stabilized by a thioether ligand within the same molecule are few,[5] in spite of the fact that copper–sulfur interactions are known to be strong.

We have been interested in measuring the rates of dissociation of coordination compounds as well as others with use of the dynamic NMR technique. These interests as well as the scarce examples of the copper(I) compounds that are stabilized by a thioether ligand prompted us to examine preparation of this type of compounds in general. However, a reaction of 2-(ethylthiomethyl)phenyllithium with copper(I) bromide did not give an expected copper compound but 2,2-bis(ethylehiomethyl)biphenyl and a complex which was composed of the biphenyl and copper(I) bromide. We wish to report and discuss the results in this paper.

The organolithium compound (**2**), prepared from 2-bromobenzyl ethyl sulfide (**1**) and butyllithium, was mixed with one equivalent of copper(I) bromide in ether at –30 °C. This mixture was warmed up to 0 °C and stirred for 3 h at the temperature. Three major compounds were isolated from the reaction mixture; colorless crystals, an oil, and benzyl ethyl sulfide (**5**) in 35, 21, and 13% yields, respectively (Scheme 1). The oily product was easily assigned to 2,2'-bis(ethylthiomethyl)biphenyl (**4**),[6] which was an expected coupling product of the Ullmann reaction.

The crystalline product[7] was stable under ambient conditions and soluble in ordinary organic solvents. X-Ray crystallography afforded a structure for the compound **3** as shown in Fig. 1.[8] This structure has a repeating unit composed of two molecules of compound **4** with a dinuclear copper cluster with two bridging bromide ions to form a polymeric structure.



**Scheme 1.**

The $Cu_2Br_2$ unit takes a planar parallelogram. The two copper atoms, Cu and Cu', which are located at apexes that form obtuse angles of the parallelogram, take two sulfide ligands each, thus forming tetrahedral structures about them. The two bromines, Br and Br', are placed at apexes that form acute angles of the parallelogram. The bond lengths, Cu–Br and Cu–Br', are 2.537(1) and 2.499(1) Å, respectively. The Cu–S bond lengths of 2.30 Å are typical for that in a copper(I) complex with terminal sulfide ligands.[9]

The polymeric structure is formed by copper atoms that take one sulfur of a 2,2'-bis(ethylthiomethyl)biphenyl molecule and another sulfur from another molecule of the biphenyl as cramp ligands. The Cu' atom takes another pair of compound **4** as ligands to form a kind of two strands. The biphenyl molecule, in which the two benzene rings are almost orthogonal with each other, can in principle take two enantiomeric forms, *P* or *M* helix about the pivot bond. In Fig. 1, one can see *P*- and *M*-ligands are arranged regularly along lower and upper rows, respectively, and are ligating to Cu and Cu', respectively.

On being dissolved in an organic solvent, the complex should dissociate into smaller species from the polymeric structure. The molecular weight of **3** was determined to be 437±20 for a chloroform solution by the vapor pressure osmometric method. The value is almost equal to the total weight of one bidentate ligand, one copper atom, and one bromine atom (429.6), this suggesting that molecules exist as a monomeric form in a solution (**3**, n=1). On recrystallization from the solution, the polymeric form was reproduced.

$^1H$ NMR signals due to benzylic methylene protons and the ethyl-methylene protons in **3** are observed at room temperature as AB and AB of $ABX_3$ patterns, respectively, at lower fields than those in the metal free ligand **4**. These signals exhibited no line shape change up to 75 °C in toluene-$d_8$, where the complex began to decompose with broadenings of the signals that drifted. Because biphenyls that carry a methyl or an equivalent substituent at 2 and 2' positions show barrier to rotation of about 20 kcal mol$^{-1}$,[10,11] these data are in conformity with those reported and further indicate that the sulfur inversion is slow up to 75 °C on the NMR time scale as are other similar compounds.[12,13]

Although the mechanism of the formation of **3** is not clear from available data, 2-(ethylthiomethyl)phenylcopper(I) must be a key intermediate in the reaction. Reductive elimination of copper atoms from this species or a related organocopper complex forms a biphenyl structure as was observed in thermal decomposition of a similar organocopper compound.[14] Simultaneous or subsequent complex formation of the bidentate ligand with CuBr produces copper complex **3**. This postulate was supported by the fact that mixing the ligand (**4**) and copper(I) bromide in ether gave the complex (**3**).

Reaction of the lithium compound (**2**) with other copper(I) halides, $Cu_2Cl_2$ and $Cu_2I_2$, gave also similar compounds as judged from the NMR spectra. Further study is in progress.

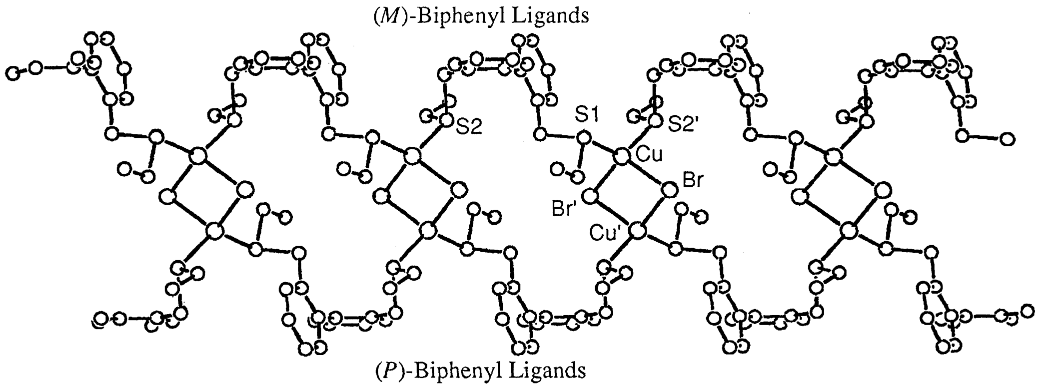


**Figure 1.** X-Ray structure of complex **3** (Hydrogen atoms are omitted). Selected structural parameters, Cu–Br 2.537(1), Cu–Br' 2.499(1), Cu–S1 2.304(2), Cu–S2' 2.295(2) Å. Br–Cu–Br' 109.17(4), Cu–Br'–Cu' 70.83(4), Br–Cu–S1 105.31(6), Br–Cu–S2' 100.49(6), Br'–Cu–S1 109.14(6), Br'–Cu–S2' 106.82(6), S1–Cu–S2' 124.91(8)°.

Recently, aggregation of ligands by complex formation with metal ions has been reported in supramolecular chemistry.[15] Our results, catenation of the biphenyl ligands, add another case of aggregation of molecules by ligation and expand the horizon of this type of aggregation.

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6 Spectroscopic data for compound **4**: bp 195—200 °C / 1mm Hg. $^1$H NMR (CDCl$_3$) $\delta$=1.08 (3H, t, $J$=7.4 Hz), 2.35 (2H, q, $J$=7.4 Hz), 3.44 and 3.54 (2H, ABq, $J$=13.2 Hz), 7.21 (1H, dd, $J$=7.4 and 1.7 Hz), 7.26 (1H, dt, $J$=1.5 and 7.4 Hz), 7.33 (1H, dt, $J$=1.7 and 7.4 Hz), 7.48 (1H, dd, $J$=1.4 and 7.4 Hz). $^{13}$C NMR (CDCl$_3$) $\delta$=14.4, 25.9, 33.6, 126.4, 127.6, 129.4, 130.2, 136.5, 140.1.

7 Analytical and spectroscopic data for compound **3**: mp 147—148 °C. Found: C, 48.57; H, 4.94%. Calcd for $C_{18}H_{22}S_2CuBr$: C, 48.48; H, 4.97% $^1$H NMR (CDCl$_3$) $\delta$=1.27 (3H, t, X of ABX$_3$, $J$=7.5 Hz), 2.71 and 2.76 (2H, AB of ABX$_3$, $J_{AB}$=13.3, $J_{AX}$=$J_{BX}$=7.5 Hz), 3.69 and 3.86 (2H, ABq, $J$=11.8 Hz), 7.13 (1H, dd, $J$=1.4 and 7.5 Hz), 7.32 (1H, dt, $J$=1.4 and 7.4 Hz), 7.38 (1H, dt, $J$=1.4 and 7.5 Hz), 7.53 (1H, dd, $J$=1.4 and 7.5 Hz). $^{13}$C NMR (CDCl$_3$) $\delta$=13.9, 30.1, 35.3, 127.2, 128.1, 130.5, 131.1, 134.6, 139.8.

8 Crystal data for compounds **3**: $C_{18}H_{22}S_2CuBr$, FW= 429.60, monoclinic, space group $P2_1/n$, $a$=11.610(4), $b$= 20.735(7), $c$=8.171(3) Å, $\beta$=103.10(3)°, $V$=1915(1) Å$^3$, $Z$=4, $D_c$=1.546 g cm$^{-3}$, $\mu$(Mo $K_\alpha$)=24.30 cm$^{-1}$, $R$=0.047, $R_w$=0.032 for 2266 observed reflections.

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