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Stepwise Introduction of Thiolates in Copper−Indium Binuclear Complexes

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We report the synthesis and characterization of copper−indium binuclear I−III complexes composing the series $(Ph_3P)_2CuIn(SEt)_xCl_{4-x}$ (**1**−**5**; $0 \leq x \leq 4$). Members of the series, which are prepared by variations in the stoichiometry, are compared in terms of their solid-state structures, spectroscopic features, and suitability as precursors for $CuInS_2$ materials. The regiochemistry of thiolate substitution, the preference for monomeric versus dimeric (eight-membered ring) structures, and new synthetic strategies informed by this series are all discussed.

Many binuclear inorganic systems have attracted interest for their unique magnetic,[1] optical,[2] and semiconducting properties.[3] We and others have been exploring the use of copper−indium I−III complexes as molecular precursors for $CuInS_2$ nanoparticles.[4,5] Although species of the form $(Ph_3P)_2Cu(\mu\text{-}SR)_2In(SR)_2$ show great promise for this application, our own efforts to scale-up their preparation using reported procedures encountered irreproducibility. This challenge led us to revisit these syntheses, and in the course of investigating new procedures, we have prepared several novel species. Herein, we report the preparation and characterization of complexes $(Ph_3P)_2CuIn(SEt)_xCl_{4-x}$, where x varies from 0 to 4 as chlorides are replaced by thiolates across the series. These complexes presented a unique opportunity to study regiochemical selectivity and structural changes through a sequence of substitution reactions at a binuclear center, and their identification has informed the optimization of an improved synthetic procedure for the tetrathiolate complex.

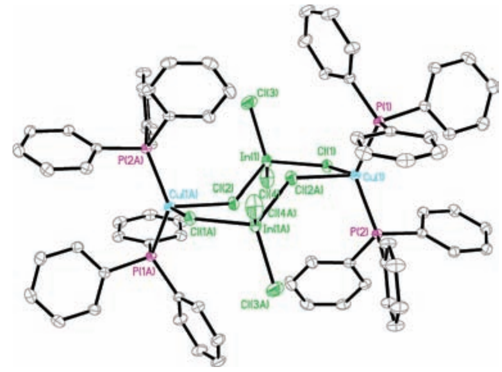

Figure 1. X-ray crystal structure of **1** with 30% probability thermal ellipsoids depicted (H atoms are omitted for clarity). Selected bond lengths are given in Table 1.

Reports by Hepp et al.[5] and Hirpo et al.[6] describe the synthesis of $(Ph_3P)_2Cu(\mu\text{-}SEt)_2In(SEt)_2$ by the addition of copper complexes in CH_3CN to methanolic $Na[In(SEt)_4]$ generated in situ. Experiments with less polar solvents, motivated by the hope that these might overcome limitations in the generality and reproducibility of the original method, revealed that the addition of $(PPh_3)_2CuCl$ to $InCl_3$ in benzene at 80 °C results in dissolution of these independently insoluble materials. A soluble adduct was crystallized by slow cooling and characterized, and analysis by X-ray crystallography indicates that this complex exists in the solid state as $\{(Ph_3P)_2Cu(\mu\text{-}Cl)_2InCl_2\}_2$ (**1**), a dimer of the anticipated $(Ph_3P)_2CuInCl_4$ formula featuring an eight-membered ring of alternating Cu and In ions interspaced with chloride ligands in a chairlike conformation (Figure 1).

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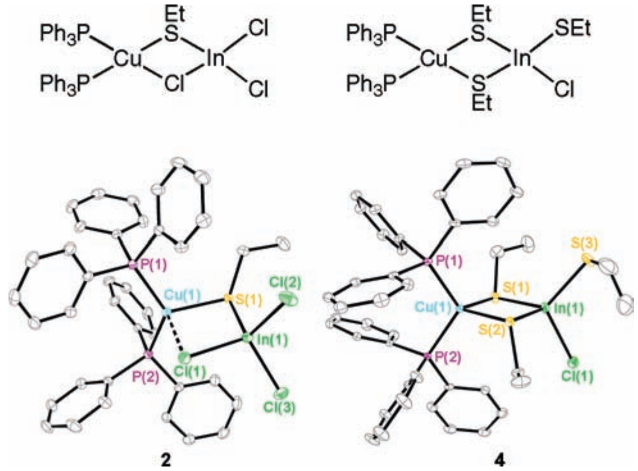
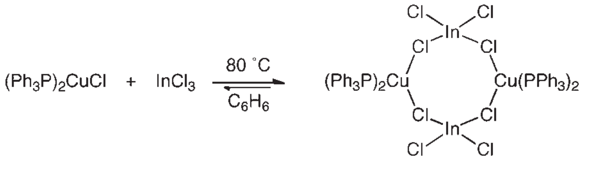


Figure 2. ORTEP diagrams for **2** and **4** are given with 30% probability thermal ellipsoids (H atoms are omitted for clarity). Compound **2** cocrystallized with C_6H_6, which is omitted for clarity. Selected bond lengths are given in Table 1. For **2**: P(1)−Cu(1)−P(2) 129.48(3)°; Cu(1)−S(1)−In(1) 87.20(2)°; Cl(2)−In(1)−Cl(3) 108.47(3)°; Cl(1)−In(1)−Cl(2) 113.96(3)°. For **4**: P(1)−Cu(1)−P(2) 115.30(4)°; Cu(1)−S(1)−In(1) 82.42(4)°; S(1)−In(1)−S(2) 97.18(4)°; S(1)−Cu(1)−S(2) 99.54(4)°; Cl(1)−In(1)−S(3) 111.65(5)°.

Complex **1** is stable up to 239 °C with a melting point range of 205.0−209.9 °C, and while it is sensitive to water, it can be stored for several months in an inert dry atmosphere. Complex **1** dissociates to starting materials upon stirring for several days in benzene at room temperature, but reheating the resulting mixture to 80 °C for 1 h regenerates **1**. We attribute this behavior to the establishment of an equilibrium between adduct **1** and trace starting materials, from which $InCl_3$ precipitates over time at low temperature (eq 1).



(1)

1

The chlorides in **1** may be replaced by thiolates via the addition of sodium thiolate salts to the adduct in a benzene solution, and the extent of substitution may be controlled by the temperature and stoichiometry. Complexes **2**−**4** (Figure 2) have thus been synthesized by the addition of NaSEt to **1** in appropriate ratios (eq 2).

Substitution occurs significantly faster with heating, and to achieve complete replacement of the chlorides in the preparation of $(Ph_3P)_2Cu(\mu\text{-}SEt)_2In(SEt)_2$ (**5**), the reaction must be heated to reflux for 12 h.

$$\{(Ph_3P)_2Cu(\mu\text{-}Cl)_2InCl_2\}_2 \xrightarrow[C_6H_6]{2x\ NaSEt} 2(Ph_3P)_2CuIn(SEt)_xCl_{4-x} \qquad (2)$$

1

2, $x = 1$
3, $x = 2$
4, $x = 3$
5, $x = 4$

Complexes **2**−**5** may also be prepared from $(Ph_3P)_2CuSEt$ (**6**), in which one substitution has already taken place.

Table 1. Overview of the Bond Lengths (Å) across the CuIn Series Wherein the Longest Bond Length of the Class Is Reported

	1	2	4	5[6]
In−Cl (Cu)	2.3886(5)	2.3964(7)		
In−Cl	2.3350(6)	2.3472(8)	2.4150(13)	
Cu−P	2.2519(5)	2.2699(8)	2.2662(11)	2.277(2)
Cu−S (In)		2.3315(7)	2.4586(11)	2.418(2)
In−S (Cu)		2.4434(7)	2.4909(11)	2.494(2)
Cu−Cl	2.5134(6)	2.8892(5)		

The reaction between **6**, $InCl_3$, and 3 equiv of NaSEt (eq 3) affords the same final product of **5** after 12 h at 80 °C.

$$(Ph_3P)_2CuSEt \xrightarrow[C_6H_6]{1.\ InCl_3\quad 2.\ (x\text{-}1)\ NaSEt} (Ph_3P)_2CuIn(SEt)_xCl_{4-x} \qquad (3)$$

6

2, $x = 1$
3, $x = 2$
4, $x = 3$
5, $x = 4$

With the exception of complex **3**, each species in the substitution pathway was characterized by X-ray diffraction crystallography. The eight-membered ring of **1** does not appear to be typical of I−III bimetallic systems.[7] However, there are few published I−III structures available for comparison.[7,8] The planar rings observed in **2** and **4** alleviate steric strain that would be generated by thiolate incorporation into the bridging positions of **1**.

The solid-state structures of complexes **2** and **4** (Figure 2) indicate that substitutions of chlorides by ethyl thiolates occur first at the bridging positions. The initial exchange at this position is contrary to obvious steric arguments, suggesting that these are overcome by the electronic preference for locating the more electron-donating S atom in this position. The trend also runs opposite to that observed in a related silver(I)−indium(III) system featuring terminal thiocarboxylate ligands, but this difference is consistent with the preference for locating relatively electron-rich ethyl thiolate ligands in the bridging positions and the electron-poor thiocarboxylate in terminal locations.[8a]

Across the series **1**−**5**, several trends in the bond length may be observed as the Cl ions are replaced by ethyl thiolate groups (Table 1). The average Cu−P distance lengthens from 2.252(1) Å in **1** to 2.277(2) Å in **5**. Additionally, In−Cl bonds at both the terminal and bridging positions are observed to lengthen as more electron-rich thiolates replace the relatively electron-poor chloride ligands. Similarly, In−S and Cu−S, average bond lengths for both bridging and terminal positions, increase with additional thiolate incorporation. These changes in bond lengths may be attributed to the increased basicity of the thiolate groups relative to the chloride ligands. This donation may also explain the remarkably long Cu−Cl contact in **2** as compared to **1**, although there are no analogous structures available for direct comparison.

To complement the crystal structures described above, the solution-state structures of these compounds in C_6D_6 were investigated by NMR spectroscopy. As ethyl thiolates replace chlorides, the ^1H NMR spectrum consistently exhibits only one set of ethyl resonances for all $MSCH_2CH_3$ species

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present. The methylene signal gradually shifts downfield from 2.63 ppm (at 1 equiv of thiolate) to 2.98 ppm (at 4 equiv), where equivalents are determined by the integration values of the bound methylene position (SCH_2CH_3) relative to the well-resolved *meta*-H atoms of the bound triphenylphosphine. The chemical shift is thus a very effective tool by which to gauge the degree of substitution in this system, and this shift does not appear to be affected by the temperature or concentration. The addition of **2** to **5** (in a 1:1 ratio) still results in the observation of a single methylene peak at 2.89 ppm, consistent with the averaging of all species present. The observation of only one set of ethyl resonances in **4**, **5**, and mixtures of **2** and **5**, as well as upon the addition of noninteger equivalents of thiolate, is consistent with rapid inter- and intramolecular exchange among thiolates, and the signals observed do not resolve even at −78 °C. The ^{13}C NMR spectra of **2**−**5** are consistent with the ^1H NMR spectra in the observation of a single resonance but appear less sensitive and show no significant shift with thiolate replacement.

A preliminary study into the reactivity of the chloride-containing complexes was also conducted. The addition of 2 equiv of sodium benzyl thiolate to **3** yielded a product of the general form $(Ph_3P)_2CuIn(SEt)_2(SBn)_2$ (**7**; eq 4). Analysis by ^1H NMR confirms bound ethyl and benzyl thiolates in a 2:2 substitution ratio, and experiments to assess the regioselectivity in this system are underway.

$$\underset{\mathbf{3}}{(Ph_3P)_2Cu(\mu\text{-}SEt)_2InCl_2} \xrightarrow[C_6H_6]{2\ NaSBn} \underset{\mathbf{7}}{(Ph_3P)_2CuIn(SEt)_2(SBn)_2} \qquad (4)$$

The results of nanoparticle syntheses using chloride-containing complexes **3** and **4** were inconsistent, in contrast to the successful production of chalcopyrite $CuInS_2$ nanoparticles from **5**.[4a] This reactivity of partially substituted species suggests that, although the thiolate occupies the bridging position in the solid-state structure, the solution phase likely allows rapid exchange between the terminal and bridging positions such that the $CuInS_2$ core, which must ultimately be generated in nanoparticle formation, is not always present. Such an exchange is also consistent with the lack of differentiation between the bridging and terminal positions in the NMR spectra of these compounds.

With identification of the partially substituted chlorides **2**−**4** came the recognition that these were frequently the prominent impurities in samples of tetrathiolate **5** and that the average degree of substitution could be easily determined from the chemical shift of the single ethyl resonance observed. Furthermore, the unexpected level of water sensitivity of these compounds suggested a need to conduct the reaction under rigorously anhydrous conditions. Taking this precaution and following the reaction by NMR spectroscopy, exploring a wide range of solvents, and varying the temperature, we determined that complex **5** could be prepared cleanly in 12 h by refluxing $(Ph_3P)_2CuCl$, $InCl_3$, and NaSEt in benzene and tetrahydrofuran, and this straightforward procedure has now been used to prepare **5** on the half-kilogram scale in 94% yield.

The future opportunities suggested by the syntheses of complexes **1**−**4** are similarly promising. The possibility of controlled, selective partial substitution offers a potential route to unsymmetrically substituted tetrathiolates such as the subject of the preliminary work described previously. The thiolate-bridged structures of **2**−**4** also offer a strong prediction as to how the regiochemistry of such targets might be controlled by electron demand, or perhaps the sequence of introduction. More generally, the move to a less polar solvent has enabled cleaner, more efficient isolation of targets from ionic byproducts and enhanced the level of precision possible in substitution. Application of this general approach to the synthesis of I−III binuclear compounds featuring chalcogenides and metals incompatible with the prior conditions is currently underway.

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Supporting Information Available: Crystallographic data in CIF format of **1**, **2**, and **4** and experimental procedures and additional characterization spectra for **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.