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Solution state fluxionality and thermolysis reactions of bimetallic single source precursors for I-III-VI chalcopyrite materials

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ABSTRACT

Complexes of the type $(PPh_3)_2M(\mu\text{-}SEt)_2E(SEt)_2$ (M = Cu, Ag; E = Al, Ga, In) are effective and versatile molecular precursors for bimetallic and mixed MES_2 chalcopyrite nanomaterials. In solution at room temperature, these compounds exhibit spectroscopic characteristics inconsistent with their cyclic solid state structures, and variable temperature NMR investigations in this report show that this discrepancy is a result of rapid exchange of thiolate groups between bridging and terminal positions. These experiments show that the exchange is unimolecular and does not involve phosphine dissociation or free thiol. Exchange rates are not strongly affected by thiolate electronic properties or the identity of E, but are significantly slower for more sterically demanding phosphine and thiolate ligands. Data are consistent with a simple turnstyle exchange mechanism involving dissociation of one bridging thiolate ligand from M, although crossover studies suggest that full ionic dissociation (into $[(PPh_3)_2M][E(SEt)_4]$) is also facile, and that dissociation into neutral fragments $(PPh_3)_2MSEt + E(SEt)_3$ may proceed at higher temperatures. Additional investigation of the solution state thermolyses of the same complexes demonstrates that the processes above do not correlate to their decomposition behavior, as thermal sensitivity is most strongly effected by thiolate electronic properties, and likely depends most strongly on cleavage of C—S bonds.

1. Introduction

The preparation of ternary and more complex semiconductor materials requires researchers to untangle a knot of interwoven selectivity challenges, as numerous parameters including composition, phase, and particle size must be simultaneously controlled to deliver materials with the desired optoelectronic properties. The use of molecular single source precursors (SSPs) has proven to be a useful strategy for overcoming these challenges in some cases, as delivery of all constituent elements from a single starting material helps establish the stoichiometry of a target, affording chemists greater freedom to manipulate reaction conditions in search of desirable outcomes in other dimensions [1–8]. One set of synthetic targets appropriate to these techniques are I-III-VI materials closely related to $Cu(In/Ga)Se_2$ [9–11], and we and others have built on initial reports [12] of bimetallic thiolate complexes to prepare a variety of potential SSPs for these materials on this model [13–24]. Some of these SSPs have been shown to deliver outstanding size and phase control in the preparation of promising chalcopyrite nanomaterials [25], and to provide tools for building more complex quaternary materials [26]. The benefits of this approach are typically attributed to the defined nature of the precursor molecules as compared to the more complicated speciation under traditional multisource conditions, making the structure and behavior of molecular precursors critical to their useful deployment in the preparation of materials.

Most recently we reported the synthesis and characterization of an extended series of analogous SSPs of the general form $(PPh_3)_2ME(SEt)_4$ incorporating Cu or Ag as the 1+ metal M, and Al, Ga, or In as the 3+ metal or metalloid E (M/E = Cu/Al: **1**; Cu/Ga: **2**, Cu/In: **3**, Ag/Al: **4**, Ag/Ga: **5**, Ag/In: **6**) (Fig. 1) [27]. All of these complexes were determined by X-ray diffraction crystallography to have very similar $(PPh_3)_2M(\mu\text{-}SEt)_2E(SEt)_2$ solid-state structures featuring four-membered MES_2 rings, and to decompose upon thermolysis to yield MES_2 materials. The behavior of these complexes in solution, however, remains comparatively obscure. Basic spectroscopic data suggest that solution state structures may not match those adopted in the solid state, and the process by which these precursors decompose to inorganic materials has not been investigated. Herein we describe further studies of complexes **1**–**6** and analogues, undertaken with the goal of drawing comparisons that might inform efforts to optimize them for materials synthesis. Three varieties of investigations were pursued: variable temperature NMR analysis of individual SSP complexes and analogues, related studies of crossover reactions among bimetallic complexes and

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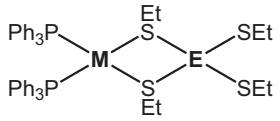

M =		Cu	Ag
E =	Al	1	4
	Ga	2	5
	In	3	6

Fig. 1. Biomelcular complexes **1–6**.

monometallic fragments, and comparative monitoring of the solution-phase decomposition reactions of the SSP complexes.

2. Experimental

2.1. Materials and methods

Anhydrous metal salts CuCl, AgCl, $InCl_3$, as well as Na metal, PPh_3, and tri-*tert*-butylphosphine (P(*t*-Bu)$_3$) were purchased from commercial suppliers and used as received. $GaCl_3$ and $AlCl_3$ were purchased from commercial suppliers and sublimed under vacuum prior to use. Ethanethiol, (EtSH), 2-methyl-2-propanethiol (*t*-BuSH,), α-toluenethiol (BnSH), *p*-methylthiophenol, ((*p*-Tol)SH), and 2-propanethiol ((*i*-Pr)SH) were purchased from commercial suppliers, degassed under vacuum, and dried over 4 Å molecular sieves prior to use. All solvents were degassed with bubbling N_2 and stored under N_2 over 4 Å molecular sieves prior to use. NaSEt was prepared by the reaction of HSEt with Na^0 in diethyl ether [17]. NMR solvents were degassed under vacuum, stored over molecular sieves, and filtered through activated alumina immediately prior use. Complexes **1–6** were prepared according to literature methods by thiolate substitution of the corresponding bimetallic chlorides [27]. Complexes **2-S(Bn)** and **3-S(Bn)** were prepared by previously described thiolate exchange of complexes **2** and **3**. [18] Complexes **3-P(*t*-Bu)** and **6-P(*t*-Bu)** were prepared according to a published method involving in the treatment of the respective phosphino-metal chlorides with tetrathiolato indate salts [13,20].

All SSPs preparations and manipulations were carried out with oven-dried glassware under inert nitrogen atmosphere using a glovebox or standard Schlenk techniques. (All aluminum and gallium complexes described are strongly prone to hydrolysis, and indium complexes **3** and **6** also degrade over time in ambient conditions.) NMR spectra were obtained using a Varian JEOL ECX 300 spectrometer. Chemical shifts (δ) are listed as parts per million (ppm) downfield from tetramethylsilane, and coupling constants are listed in Hz. ^{1}H NMR and ^{13}C NMR spectra were referenced at measurement temperatures to uncorrected chemical shifts of residual solvent peaks (C_6D_6 δ 7.16; CD_2Cl_2 δ 5.32) and ^{13}P NMR spectra were referenced to an external 85% H_3PO_4 standard at room temperature. Metal analyses were performed using a Varian 715-ES ICP Optical Emission Spectrometer.

2.2. Synthesis of $(PPh_3)_2Cu(\mu\text{-}S(i\text{-}Pr))_2In(S(i\text{-}Pr))_2$ (3-S(i-Pr))

Ethanethiolate complex **3** (234 mg, 0.246 mmol) was dissolved in 10 mL toluene, and a small excess of 2-propanethiol (76 mg, 1.0 mmol) was added. The resulting solution was slowly evaporated to dryness under vacuum, removing ethanethiol (bp 35 °C) and driving the thiol exchange equilibrium toward the product. Additional toluene (5 mL) and 2-propanethiol (20 mg, 0.26 mmol) were added, then evaporated to dryness to ensure complete substitution. The resulting solid was recrystallized from benzene layered with pentane at room temperature to yield **3-S(*i*-Pr)** as an off-white solid (215 mg, 87% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.38–7.21 (m, 30H, Ar), 3.24, (m, 4H, $J_{H\text{-}H}$ = 7.0 Hz, SC*H*,), 1.21 (t, 24H, $J_{H\text{-}H}$ = 7.2 Hz, C*H*$_3$).^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 133.3 (d, $J_{P\text{-}C}$ = 19.6 Hz), 132.7, 130.9, 128.7, 26.84, 20.52. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 1.64. Analysis calculated for $C_{48}H_{58}CuInP_2S_4$: C, 57.45; H, 5.83; S, 12.78. Found: C, 57.26; H, 5.85; S, 12.69.

2.3. Synthesis of $(PPh_3)_2Cu(\mu\text{-}S(p\text{-}Tol))_2In(S(p\text{-}Tol))_2$ (3-S(p-Tol))

Ethanethiolate complex **3** (251 mg, 0.264 mmol) was dissolved in 10 mL toluene, and a small excess of *p*-tolylthiol (136 mg, 1.10 mol) was added. The resulting solution was slowly evacuated to dryness, removing ethanethiol (bp 35 °C) and driving the thiol exchange equilibrium toward the arylthiolate product. The resulting solid was recrystallized from benzene layered with pentane at room temperature to yield **3-S(p-Tol)** as an off-white solid (300 mg, 95% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 7.56 (d, $J_{H\text{-}H}$ = 7.4, Hz, 8H), 7.43 (m, 12H, P*Ph*$_3$), 6.99 (m, 18H, P*Ph*$_3$), 6.90 (d, $J_{H\text{-}H}$ = 7.4, Hz, 8H, S*Ar*CH$_3$), 2.37 (s, 12H, PhC*H*$_3$) ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 135.8, 134.3, 133.9, 132.9 (d, $J_{P\text{-}C}$ = 24.1 Hz), 130.4, 129.7, 128.5, 124.2, and 30.2. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 0.61. Analysis calculated for $C_{64}H_{58}CuInP_2S_4$: C, 64.29; H, 4.89; S, 10.73. Found: C, 64.25; H, 5.00; S, 10.46.

2.4. Synthesis of $Na[Ga(SEt)_4]$ (7)

Freshly sublimed $GaCl_3$ (1.01 g, 5.74 mmol) was dissolved in benzene (10 mL) in a 20 mL vial. Four equivalents of NaSEt (1.93 g, 22.9 mmol) were added to the solution, and the resulting suspension was stirred on a hot plate at 80 °C for 24 h, yielding a cloudy white solution. This mixture was filtered through Celite, and the filtrate was evacuated to dryness *in vacuo* yielding white solid. The crude product was recrystallized from benzene and pentane to yield **7** as white needles (1.72 g, 89% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 2.99 (q, $J_{H\text{-}H}$ = 7.2 Hz, 8H, SC*H*$_2$CH$_3$), 1.49 (t, $J_{H\text{-}H}$ = 7.2 Hz, 12H, SCH$_2$C*H*$_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.73 (q, $J_{H\text{-}H}$ = 7.2 Hz, 8H, SC*H*$_2$CH$_3$), 1.33 (t, $J_{H\text{-}H}$ = 7.2 Hz, 12H, SCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 25.2, 21.3. Analysis calculated for $C_8H_{20}GaNaS_4$: C, 28.49; H, 5.98; S, 38.03. Found: C, 28.69; H, 5.88; S, 37.70.

2.5. Variable temperature NMR experiments

NMR probe temperature measurements were calibrated against an external 4% CH_3OH/CD_3OD signal [28], and reported temperatures are corrected values. Samples were allowed to equilibrate at each temperature for at least 5 min, and spectra at all temperatures were referenced to the room temperature chemical shifts of residual solvent protons. Free energies of activation for terminal/bridging thiolate interconversion (ΔG, kcal/mol) were calculated using experimental temperatures (K) and the frequency differences between interconverting signals (ν_μ–ν_t, Hz) according to established equations [29]:

$$\Delta G = 4.574 \times T \times (\log(T/k) + 10.318) \quad (1)$$

In cases where decoalescence was observed (Table 1, entries 1–5 and 9–16) T is the coalescence temperature (K) and k in Eq. (1) is calculated according to Eq. (2):

$$k = \frac{\pi}{\sqrt{2}}(\nu_\mu - \nu_t) \quad (2)$$

where ν_μ–ν_t is the maximum chemical shift difference (Hz) between exchanging signals. Uncertainties in these exchange barriers are extrapolated from the ± 3 K precision of experimental T values for coalescence. In the cases where decoalescence was not observed, (Table 1, entries 6–8) T is 183 K, and k in Eq. (1) is estimated from line broadening using Eq. (3):

$$k = \frac{\pi(\nu_\mu - \nu_t)^2}{2(\nu - \nu_{std})} \quad (3)$$

where ν_μ–ν_t was taken as the average of the values observed for