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A chemically induced, room temperature, single source precursor to CuS (covellite) nanomaterials: synthesis and reactivity of $[\text{Cu}(\text{S}_2\text{CNHBz})]_n^\ddagger$

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Addition of two equivalents of NaS_2CNHBz to CuSO_4 affords the yellow diamagnetic coordination polymer $[\text{Cu}(\text{S}_2\text{CNHBz})]_n$ (1**), resulting from intramolecular electron-transfer and concomitant formation of the thiourea, $(\text{BzNH})_2\text{C}=\text{S}$. **1** reacts with PPh_3 and 1,1'-bis(diphenylphosphino)ferrocene (dppf) in CH_2Cl_2 to give monomeric $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHBz})(\text{PPh}_3)_2]$ (**2**) and $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHBz})(\kappa^2\text{-dppf})]$ (**3**), respectively, both of which have been crystallographically characterised. While **1** is thermally stable in dimethylsulfoxide (DMSO) up to ca. 70 °C, addition of $n\text{BuNH}_2$ to **1** leads to its rapid decomposition to afford CuS (covellite) nanomaterials; indeed in neat $n\text{BuNH}_2$, covellite formation is rapid at room temperature. Thus, **1** serves as an effective low-temperature base-induced single source precursor to covellite nanomaterials.**

The single source precursor (SSP) approach to nanoscale materials has been extensively developed over the past two decades^{1–3} with dithiocarbamate complexes⁴ being widely utilised as SSPs for the synthesis of metal-sulfide nanomaterials.⁵ Nanoscale copper chalcogenides are of particular interest due to their novel physical properties.⁶ A variety of stoichiometric phases are accessible, ranging for the sulfides from copper-rich (Cu_2S) to sulfur-rich (CuS). Importantly, these materials have phase-dependent direct/indirect bandgaps in the range of 1.1–2.0 eV and consequently are utilised for applications such as optical filters, solar cells, photovoltaics, optical imaging devices and super-ionic materials.⁶

Copper-dithiocarbamate chemistry has been extensively developed with Cu(I), Cu(II) and Cu(III) complexes being accessible.⁷ Most prevalent are Cu(II) dialkyl-dithiocarbamate complexes, $[\text{Cu}(\kappa^2\text{-S}_2\text{CNR}_2)_2]$, which are air and moisture stable

dark brown solids, easily prepared upon addition of Cu(II) salts to NaS_2CNR_2 in water or MeOH.⁷ Both Cu(I) and Cu(II) dialkyl-dithiocarbamate complexes have been effectively utilised as SSPs, both towards copper sulfides and also copper-containing ternary and quaternary sulfides.^{5,7} The former is exemplified by the work of Alivisatos and co-workers, who utilised the thermal decomposition of $[\text{Cu}(\kappa^2\text{-S}_2\text{CNET}_2)_2]$ to prepare copper-rich djurleite ($\text{Cu}_{1.94}\text{S}$) quantum dots (QDs) with tuneable localized surface plasmon resonances (LSPRs).^{8,9} Recent studies have identified the so-called Cu(II) sulfide, covellite (CuS), as the material of choice for QD applications.^{10–12} It has a relatively small window of thermal stability, losing sulfur above ca. 130 °C (ref. 13) and consequently, dialkyl-dithiocarbamate SSPs with their relatively high decomposition temperatures are barely suitable for its formation.⁵ Consequently, the design of low-temperature SSPs to covellite, and indeed other ternary and quaternary metal sulfide nanomaterials, is of significant interest.

We have recently reported that the carboxylic-acid derivative $[\text{Cu}\{\kappa^2\text{-S}_2\text{CN}(\text{CH}_2\text{CO}_2\text{H})_2\}_2]$ decomposes at ca. 90 °C (in water) to afford CuS (covellite) nanomaterials, the relatively low decomposition temperature being associated with a non-C–N cleavage pathway.¹⁴ A second strategy for the synthesis of low temperature SSPs towards metal-sulfides is to utilise primary amine-derived dithiocarbamates, $[\text{M}(\kappa^2\text{-S}_2\text{CNHR})_2]$, and this approach has been successfully applied for the formation of nanoscale nickel,¹⁵ zinc^{16,17} and cadmium^{17–19} sulfides. Such species, which also form *in situ via* amine-exchange when $[\text{M}(\kappa^2\text{-S}_2\text{CNR}_2)_2]$ are decomposed in long chain amines such as oleylamine,^{14,20–22} eliminate RNCS (under basic conditions), a process initiated by deprotonation with concomitant formation of the dithiocarbamate complexes $[\text{M}(\kappa^2\text{-S}_2\text{CNR})_2]^{2-}$.²³ For copper, however, despite contrary reports,^{24–32} complexes of the type $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHR})_2]$ or $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHAr})_2]$ have not been established. Indeed, a well-developed synthesis of organic isothiocyanates (RNCS) utilises the *in situ* formation of $\text{M}(\kappa^2\text{-S}_2\text{CNHR}/\text{Ar})$ (M = alkali metal), which eliminate organic isothiocyanate,³³ a process that can be accelerated upon addition of copper salts.³⁴ Interestingly, the unwanted by-

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product in this transformation is copper sulfide. We thus set out to investigate whether primary amine-derived dithiocarbamate salts of copper had any significant stability, and if so to harness them as low-temperature SSPs for the synthesis of covalent nanomaterials.

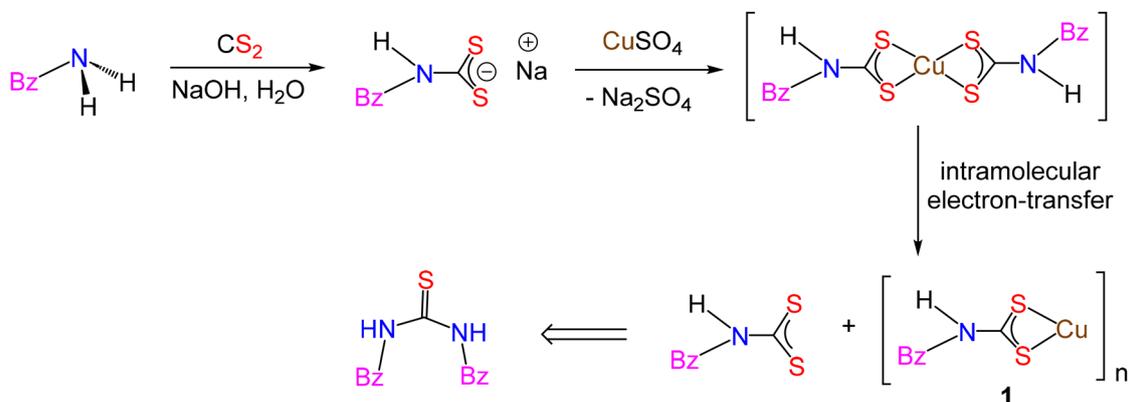
We initially screened a range of primary alkyl and aryl amine-derived dithiocarbamate salts with Cu(II) salts. There are some differences in the outcomes of these reactions depending upon the primary amine used, but there is a group of primary alkylamines that behave in a similar manner, and in this contribution, we focus on BzNH₂. Dropwise addition of an aqueous solution of CuSO₄·5H₂O to a well-stirred aqueous solution of two equivalents of NaS₂CNHBz in air results in the formation of a heavy bright yellow precipitate. After complete addition, filtration followed by sequential washing with water, MeOH and THF and drying at *ca.* 60 °C afforded [Cu(S₂CNHBz)]_n (**1**) as a bright yellow solid in *ca.* 70–80% yield. A pertinent experimental observation was the immediate formation of a dark brown color upon addition of each drop of CuSO₄·5H₂O to the pale-yellow NaS₂CNHBz solution, which dissipated rapidly (over *ca.* 1–2 s). We interpret this observation as resulting from the initial formation of [Cu(κ²-S₂CNHBz)₂], which rapidly converts *via* an intramolecular electron-transfer to the isolated product. The fate of the oxidised dithiocarbamate was established as the thiourea (BzNH)₂C=S (see below and the ESI[†]), thus allowing a reaction pathway to be established (Scheme 1).

The bright yellow colour of **1** immediately suggested a Cu(I) complex, and its diamagnetic nature was confirmed by a magnetic susceptibility measurement, while elemental analysis is consistent with a copper–dithiocarbamate ratio of 1 : 1. The IR spectrum shows a strong sharp absorption at 3221 cm⁻¹ consistent with the presence of a non-hydrogen bonded N–H moiety. Unfortunately, it is insoluble in non-coordinating solvents but slowly dissolves with stirring in DMSO, the lemon-yellow solid dissolving to give an orange-brown solution. Both ¹H and ¹³C{¹H} NMR spectra in d⁶-DMSO are consistent with the Cu(I) assignment, with sharp resonances being seen. Notable features are the presence of a resonance at δ 10.90

assigned to the NH group in the ¹H NMR spectrum, and a singlet at 204.3 ppm in the ¹³C{¹H} spectrum associated with the quaternary backbone carbon. The insolubility of **1** in non-coordinating solvents suggests that it is a coordination polymer, dissolving to form a DMSO solvate. Copper(I) dithiocarbamate clusters [Cu(μ³-S₂CNR₂)₄] are normally tetrahedral clusters^{7,35–37} with good solubility in organic solvents. Liu and co-workers have recently reported the molecular structure of a xanthate analogue, namely [Cu(S₂COPrⁱ)_∞], which is a 1D coordination polymer with the xanthate spanning four different copper centres in a κ⁴-μ¹, μ³-fashion,³⁸ while [Cu(S₂COMe)_∞] is a 2D coordination polymer with the xanthate bound in a κ⁴-μ², μ²-fashion.³⁹ While preparing this manuscript, Jung and co-workers reported the molecular structure of [Cu{μ³-S₂CNH(CH₂CH₂OH)}₄], which adopts a tetrahedral geometry.⁴⁰ No yields were given, nor characterising data or solubility information, the authors simply stating that the complex was separated from the THF washing of the insoluble yellow precipitate initially formed from the reaction. Thus, the precise structure of **1** remains undetermined and we are continuing our efforts to obtain crystals of **1** suitable for X-ray crystallography.

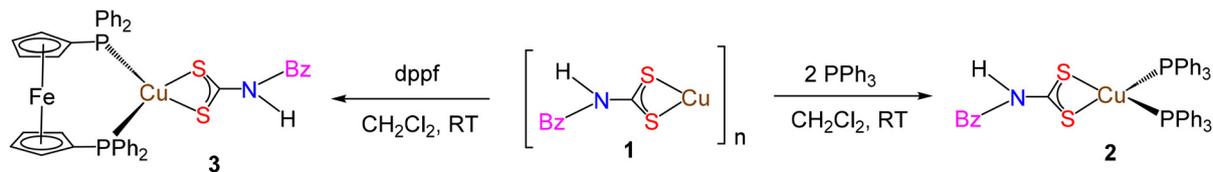
Formation of **1** occurs *via* an intramolecular electron transfer from the dithiocarbamate to the Cu(II) centre (Scheme 1), likely following initial coordination, hence the observation of an initially formed brown bis(dithiocarbamate) intermediate. While dithiocarbamate radicals generated from secondary amines dimerise to afford thiuram disulfides,⁴¹ oxidation of primary amine dithiocarbamate salts is known to result in mixtures of the corresponding isothiocyanates, RNCS, and thioureas (RNH)₂C=S, with the latter being favoured at high pH.⁴² We thus worked-up the MeOH wash and NMR spectroscopy and X-ray diffraction showed that (BzNH)₂C=S was generated (see ESI[†]) in full accordance with the proposed intramolecular electron-transfer and subsequent reactivity of the BzNHCS₂ radical (Scheme 1).

Complex **1** is converted into soluble mononuclear species upon addition of phosphines. For example, addition of *ca.* 2 equivalents of PPh₃ to a CH₂Cl₂ suspension in air results in



Scheme 1 Proposed formation of [Cu(S₂CNHBz)]_n (**1**) and (BzNH)₂C=S.





Scheme 2 Reactivity of **1** towards PPh_3 and dppf.

rapid dissolution and discoloration to afford clear solutions from which $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHBz})(\text{PPh}_3)_2]$ (**2**) is isolated in high yield. Similar reactivity was observed with diphosphines, and the addition of CH_2Cl_2 to a mixture of **1** and 1,1'-bis(diphenylphosphino)ferrocene (dppf) resulted in the rapid formation of $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHBz})(\kappa^2\text{-dppf})]$ (**3**) (Scheme 2). Both **2** and **3** were characterised by X-ray crystallography (Fig. 1) proving the stoichiometry of **1**. The structure of **2** is similar to that of $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHPh})(\text{PPh}_3)_2]$, formed upon the reaction of $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{PPh}_3)_2]$ with PhNCS ,^{43,44} and the structure of **3** is similar to that of $[\text{Cu}\{\kappa^2\text{-S}_2\text{CNBz}(\text{CH}_2\text{py})\}(\kappa^2\text{-dppf})]$ formed upon addition of the secondary amine-dithiocarbamate salt to $[\text{Cu}(\kappa^2\text{-dppf})(\mu\text{-Br})_2]$.⁴⁵ Spectroscopic data are in full accordance with the solid-state structures. In the ^1H NMR spectra, the NH proton is observed at *ca.* δ 7.50 and in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra each shows a singlet associated with phosphine coordination.

As articulated in the introduction, a key aim of our research is to design and prepare low temperature single source precursors (SSPs) towards nanoscale metal sulfides.⁵ The decomposition of SSPs is normally thermally induced and thus we initially assessed the thermal stability of **1** in the solid-state *via* TGA-DSC measurements (Fig. 2). The most pertinent features are its stability until *ca.* 135 °C and then decomposition to CuS at *ca.* 300 °C in a two-stage process, the first of which involves a *ca.* 18% mass loss (*ca.* 44 amu) that is possibly due to the elimination of carbon monosulfide (CS).

In previous work, we have shown that secondary-amine derived dithiocarbamate complexes decompose at significantly lower temperatures in primary amine solutions than they do in the solid state, being associated with amine-exchange and the *in situ* generation of primary-amine derivatives.^{14,20–22} Complex **1** is stable in DMSO, up to *ca.* 70 °C, but heating at 90 °C for 3 h resulted in slow decomposition with concomitant formation of CuS (covellite). Decomposition was greatly accelerated upon addition of a small amount of $^n\text{BuNH}_2$ to a DMSO solution. Thus, at room temperature the solution initially darkens, possibly due to the formation of an amine adduct $[\text{Cu}(\text{S}_2\text{CNHBz})(\text{NH}_2^n\text{Bu})_n]$, and then slowly (*ca.* 12 h) becomes lighter with the concomitant deposition of a fine precipitate, indicative of the formation of CuS. The rate of decomposition is linked to the pH of the solution, indicating that the decomposition is base induced. Complex **1** dissolves in neat $^n\text{BuNH}_2$ (pH *ca.* 14) to initially (*ca.* 5 min) afford a brown solution, akin to that described above in DMSO, but over *ca.* 1 h this discolours with the deposition of a dark green precipitate, shown by PXRD to be nanoscale covellite (Fig. 3). As might be expected, diffraction peaks are very broad, indicative of the small particle size estimated at between 10 and 18 nm (av. 14.5 nm) by the Scherrer method. Thus, the decomposition of **1** is base-induced, likely being activated by the removal of the acidic N–H proton, with the formation of a dithiocarbamate complex⁴⁶ which decomposes *via* elimination of BzNCS.

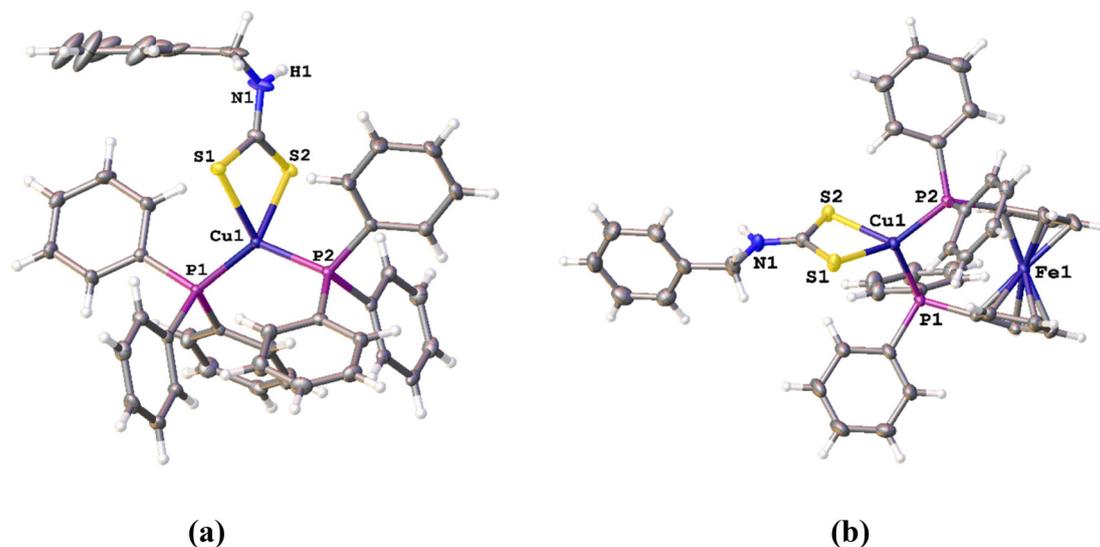


Fig. 1 Molecular structures of (a) $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHBz})(\text{PPh}_3)_2]$ (**2**) and (b) $[\text{Cu}(\kappa^2\text{-S}_2\text{CNHBz})(\kappa^2\text{-dppf})]$ (**3**).



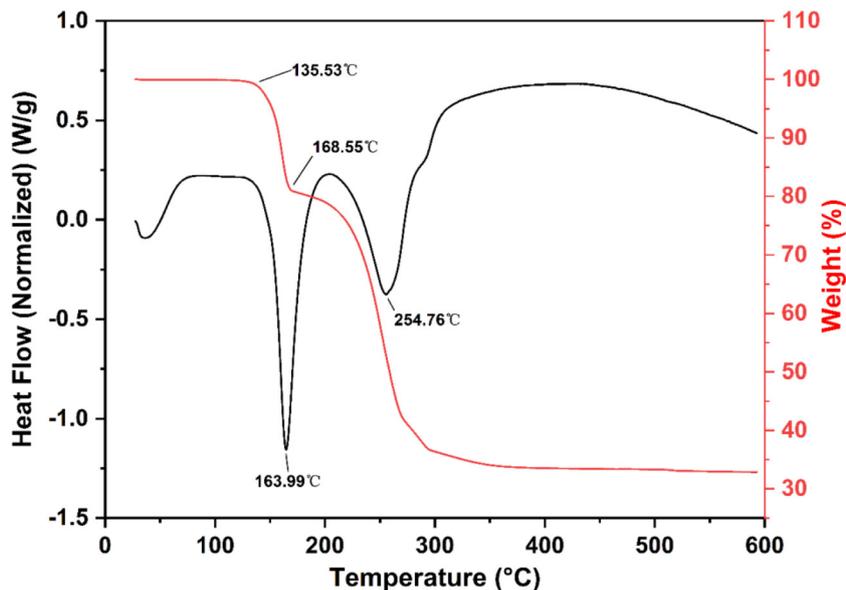


Fig. 2 TGA and DSC traces of the thermal decomposition of **1**.

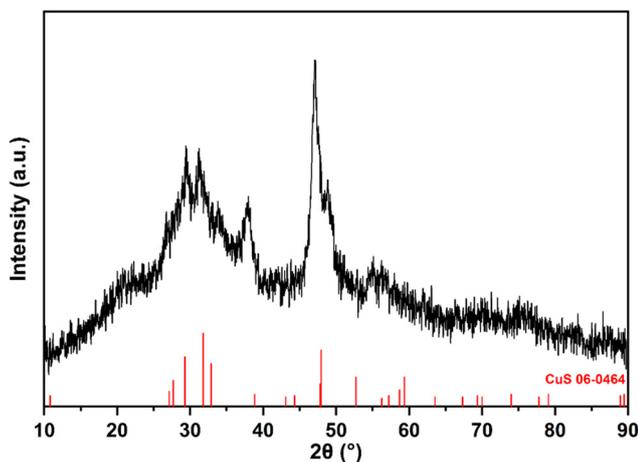


Fig. 3 Powder X-ray diffractogram of covellite (CuS) nanoparticles formed from the room temperature decomposition of **1** in n BuNH₂.

In this contribution we have unambiguously shown that the addition of the primary amine-dithiocarbamate NaS₂CNHBz to Cu(II) salts cleanly affords the Cu(I) dithiocarbamate [Cu(S₂CNHBz)]_n (**1**) as a result of a rapid intramolecular electron-transfer from the unstable Cu(II) complex [Cu(κ²-S₂CNHBz)₂]. Several older papers^{47–49} report a similar formation of Cu(I) complexes from dithiocarbamates derived from amino acids, but none was fully characterized. It has also been reported that ligand to metal charge transfer in [Cu(κ²-S₂CNEt₂)₂] is photochemically activated^{50,51} and a very recent article reports that, upon prolonged sitting in DMSO, [Cu{κ²-S₂CN(CH₂CO₂H)₂}₂] is reduced to afford the related Cu(I) complex.⁵² Indeed, this latter observation is fully consistent with our earlier findings on the low-temperature decompo-

sition of this Cu(II) complex, as amine solutions turn yellow upon warming.¹⁴ Thus, ligand to metal electron-transfer in Cu(II)-dithiocarbamate complexes may be widespread. We are in the process of screening the reactivity of a range of other primary amine-derived dithiocarbamates with Cu(II) salts. Preliminary results suggest that while the outcome of the reaction is dependent upon the nature of the substituents, there are a large group of primary amines that behave in the same way as that described here for benzylamine.

Author contributions

G. H. devised and supervised the project, the main conceptual ideas and proof outline. S. H., X. X. and G. H. performed synthesis, characterisation, and decomposition work. D. P. carried out single crystal X-ray diffraction studies. J. C. S. and X. X. supervised S. H. G. H. wrote the initial manuscript and all authors contributed to editing to generate the final version.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data for **2**, **3** and (BzNH)₂CS have been deposited at the CCDC under 2378475–2378477.†

Conflicts of interest

There are no conflicts to declare.



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