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New organometallic single-source precursors for $CuGaS_2$ – polytypism in gallite nanocrystals obtained by thermolysis[†]

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The complex $[({}^{i}Pr_{3}PCu)_{2}(Me_{2}Ga)_{2}(SCH_{2}CH_{2}S)_{2}]$ (4) was synthesized from trimethylgallium, $[({}^{i}Pr_{3}PCu)_{4}(SCH_{2}CH_{2}S)_{2}]$ (1) and ethanedithiol by elimination of methane. The related monomethyl compound $[({}^{i}Pr_{3}PCu)_{2}(MeGaSPh)_{2}(SCH_{2}CH_{2}S)_{2}]$ (5) has been prepared from $[({}^{i}Pr_{3}PCuSPh)_{3}]$ (2) and $[(MeGaSCH_{2}CH_{2}S)_{2}]$ (3) by a ligand exchange reaction in tetrahydrofuran solution. The molecular structures of 1 and 3–5 were determined by single crystal X-ray diffraction. Thermolysis of 4 and 5 results in the formation of the ternary semiconductor CuGaS_{2}, gallite. The residue of 5 was characterized using X-ray powder diffraction, energy dispersive X-ray spectroscopy and transmission electron microscopy. The CuGaS_{2} crystals obtained are mainly hexagonal plates of around 200 to 300 nm diameter and 10 to 30 nm thickness, exhibiting an unusual metastable hexagonal crystal structure, related to wurtzite. Partially, the usual tetragonal chalcopyrite structure or its disordered cubic zinc-blende analogue is realized by stacking faults, resulting in an overall similarity to the zinc-blende–wurtzite polytypism in ZnS and related compounds.

Introduction

The ternary compound semiconductors CuME_2 (M = Ga, In; E = S, Se) have attracted considerable attention due to their applicability as light absorbing materials in high efficiency thin film solar cells. In the industrial fabrication process, the thin films are usually deposited by co-evaporation of the elements or by sulfurization/selenization of thin metal films.¹ Efforts have been made to synthesize molecular single-source precursors (SSPs) for these semiconductors,² because a solvent-assisted spray pyrolysis process could simplify and improve the thin film processing in view of the deposition parameters requested, *e.g.* lower temperature, atmospheric pressure and reliable stoichiometry control.³ Here we report on the synthesis, characterization and thermolysis of new organometallic SSPs for CuGaS₂.

The crystal structure of CuGaS₂ has first been investigated in a systematic study of 20 compounds with the general formula $M^{I}M^{III}E_2$ ($M^{I} = Cu$, Ag; $M^{III} = Al$, Ga, In, Tl; E = S, Se, Te); all of these "Harry Hahn phases" were found to crystallize in the tetragonal chalcopyrite structure (space group $I\bar{4}2d$, Fig. 1a).⁴ If the metal ions are statistically disordered in this tetragonal

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Fig. 1 Four structures of $CuGaS_2$: (a) tetragonal chalcopyrite structure, (b) cation-disordered cubic zinc-blende modification, (c) hypothetical ordered orthorhombic phase and (d) cation-disordered hexagonal wurt-zite-CuGaS₂. The different anion layer stacking is indicated; the unit cells are marked.

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structure, the *c*-axis is halved, leading to the cubic zinc-blende structure (space group $F\bar{4}3m$, Fig. 1b). Both structures exhibit a repeated ABC-stacking of identical anion layers. Similar to hexagonal ZnS, wurtzite (space group $P6_3mc$), a cation-disordered phase with AB-stacking of identical layers can be constructed for CuGaS₂ (Fig. 1d). Ordering of the cations in this wurtzite-CuGaS₂ may result in an orthorhombic modification (space group $Pna2_1$, Fig. 1c), which is known to exist as the high-temperature phase of AgInS₂.⁵ The tetrahedral coordination of the atoms is retained in all cases, therefore they are energetically nearly equivalent.

Shifting of the layers, and thereby the zinc-blende–wurtzite phase transition requires an intermediate trigonal planar coordination sphere.⁵ The zinc-blende–wurtzite polytypism is well known from binary semiconductors, for which it was shown that the zinc-blende structure is monotonically stabilized over the wurtzite structure as the anion size increases (except for first-row cations).⁶

Recent attempts to produce ternary semiconductor nanoparticles led to the formation of hexagonal CuInS2,7 CuInSe28 and $\operatorname{CuIn}_{1-x}\operatorname{Ga}_{x}\operatorname{S}_{2}$ ($0 \le x \le 1$).⁹ In the latter case, wurtzite-CuGaS₂ (x = 1) was obtained as 'tadpole'-shaped crystals with typical lengths of about 30 to 50 nm.9 To our knowledge, this recent work is the only report about hexagonal wurtzite-CuGaS₂ so far. The motivation for the synthesis of these semiconductor nanoparticles is that their colloidal dispersions may serve as inks for high-throughput printing techniques applicable for thin film deposition. Usually, the synthesis of the nanoparticles is achieved by mixing metal salts with a chalcogen source in high boiling coordinating solvents, and heating this mixture to elevated temperatures of 100 to 350 °C. A SSP has been used to produce CuInS2 nanoparticles in a mixture of dodecanethiol and trioctylphosphine.^{7e} The ratio of these surfactants as well as the reaction temperature were found to influence the crystal structure (wurtzite or zinc-blende) of the product.^{7e} Stacking faults in the nanocrystals were reported for CuInS2 obtained from metal chlorides and thiourea in oleylamine,^{7d} and from



Fig. 2 Molecular structures of (a) $[({}^{1}Pr_{3}PCu)_{4}(SCH_{2}CH_{2}S)_{2}]$ (1) and (b) $[(MeGaSCH_{2}CH_{2}S)_{2}]$ (3). Thermal ellipsoids of C, Cu, Ga, P and S are drawn at 50% probability level. Selected bond lengths [pm] and angles [°] for 1: Cu1–S1 225.78(4), Cu1–S2 227.31(4), Cu2–S1 225.97 (4), Cu2–S2' 229.65(4), Cu1–P1 219.46(4), Cu2–P2 224.74(4), P1– Cu1–S1 138.89(1), P1–Cu1–S2 122.90(2), S1–Cu1–S2 97.05(1), P2– Cu2–S1 117.29(2), P2–Cu2–S2' 120.95(2), S1–Cu2–S2' 121.51(1), Cu1–S1–Cu2 105.05(2), Cu1–S2–Cu2' 113.19(2).

 $[Cu(SON(CN^{i}Pr_{2})_{2})_{2}]$ and $[In(SON(CN^{i}Pr_{2})_{2})_{3}]$ in a mixture of dodecanethiol and oleylamine.^{7g}

As it turned out, the bulk thermolysis of the new SSPs presented herein produces $CuGaS_2$ nanocrystals with hexagonal domains, which were thoroughly characterized by X-ray powder diffraction, energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM).

Results and discussion

Synthesis and molecular structures of 1-5

The copper complex $[({}^{i}Pr_{3}PCu)_{4}(SCH_{2}CH_{2}S)_{2}]$ (1) can be prepared from triisopropylphosphine, copper(1)-oxide and ethanedithiol in toluene by elimination of water. The complex is tetranuclear and contains an eight-membered Cu₄S₄-ring (Fig. 2a), as revealed by single crystal X-ray structure determination (space group $P2_1/c$).[‡] The molecule is centrosymmetric, the two independent copper atoms are coordinated in a trigonal planar fashion by two sulphur atoms and one phosphine ligand, each. Atom Cu1 is chelated by the ethanedithiolate ligand, whereas Cu2 connects the ethanedithiolate ligand and its symmetry equivalent. The Cu-S bond lengths range from 225 to 230 pm, which are typical values for threefold coordinated copper. Because of the relatively rigid bite angle of the ethanedithiolate ligand, the angle S1-Cu1-S2 (97°) is much smaller than S1-Cu2-S2' (122°). The resulting difference in the steric strain at the two independent copper atoms manifests in two different Cu-P bond lengths (219 and 225 pm).

The compounds [(¹Pr₃PCuSPh)₃] (2)and $[(MeGaSCH_2CH_2S)_2]$ (3) have been described in the literature already.^{10,11} For 2 the synthesis as well as the crystal structure were reported. The complex can be obtained from copper(1)acetate, triisopropylphosphine and Me₃SiSPh. The crystal structure is built up from nearly planar six-membered Cu₃S₃-rings, with one phosphine ligand bound to each copper atom and a rarely observed planar environment for some of the sulfur atoms.¹⁰ Compound **3** was synthesized from Me₃Ga and ethanedithiol, and characterized spectroscopically. Its low solubility in common organic solvents was attributed to association in the solid state, and from mass spectra it was concluded that it might be trimeric.¹¹ According to the structural determination by single crystal X-ray diffraction reported herein, the compound is

[‡] Crystallographic data: 1 (C₄₀H₉₂Cu₄P₄S₄), *M* = 1079.42, monoclinic, *a* = 11.4153(6), *b* = 21.140(1), *c* = 11.0770(6) Å, *β* = 100.105(5)°, *V* = 2631.6(2) Å³, *T* = 180(2) K, space group *P*2₁/*c* (no. 14), *Z* = 2, 15748 reflections measured, 5733 unique (*R*_{int} = 0.0235), *R*₁ = 0.0197 (*I* > $2\sigma(I)$), w*R*₂ = 0.0439 (all data). 3 (C₆H₁₄Ga₂S₄), *M* = 353.85, triclinic, *a* = 6.603(1), *b* = 6.761(1), *c* = 7.116(1) Å, *α* = 73.93(1)°, *β* = 80.80(1)°, *γ* = 83.69(1)°, *γ* = 80.057(8) Å³, *T* = 180(2) K, space group *P*Ī (no. 2), *Z* = 1, 3134 reflections measured, 1452 unique (*R*_{int} = 0.0288), *R*₁ = 0.0161 (*I* > $2\sigma(I)$), w*R*₂ = 0.0397 (all data). 4 (C₂₆H₆₂Cu₂Ga₂P₂S₄), *M* = 831.46, monoclinic, *a* = 17.437(1), *b* = 15.7295(7), *c* = 15.365(1) Å, *β* = 116.444(5)°, *V* = 3773.3(4) Å³, *T* = 105(2) K, space group *C*2/*c* (no. 15), *Z* = 4, 12 527 reflections measured, 4106 unique (*R*_{int} = 0.0339), *R*₁ = 0.0188 (*I* > $2\sigma(I)$), w*R*₂ = 0.0464 (all data). 5 • 2 THF (C₄₄H₈₂Cu₂Ga₂O₂P₂S₆), *M* = 1163.92, triclinic, *a* = 10.600(1), *b* = 11.507(1), *c* = 13.693(2) Å, *α* = 67.290(7)°, *β* = 72.432(8)°, *γ* = 65.161(7)°, *V* = 1378.6(2) Å³, *T* = 180(2) K, space group *P*I (no. 2), *Z* = 1, 11622 reflections measured, 5374 unique (*R*_{int} = 0.0796), *R*₁ = 0.0535 (*I* > $2\sigma(I)$), w*R*₂ = 0.1409 (all data).

dimeric in the solid state, but this may be different in solution and the gas phase, as it is well known that organometallic chalcogenolates of group 13 metals undergo exchange reactions involving different aggregates, when dissolved.¹² The molecular structure in the crystal is shown in Fig. 2b. The central Ga₂S₂ring and the chair-like structure is generated out of the asymmetric MeGaSCH₂CH₂S-unit by the crystallographic inversion centre (space group $P\overline{1}$). The Ga–S bond lengths in this ring are 237.18(5) pm for Ga1-S2 and 239.69(5) pm for Ga1-S2', which are typical values for Ga...Ga-µ2-bridging thiolate ligands. The terminal bond Ga1-S1 is relatively short (222.93(5) pm). The Ga-C bond length is 194.5(2) pm. As can be expected from the different covalent vs. dative character of Ga-C and Ga-S bonds,¹³ the angles C-Ga-S (112° to 125°) are larger than the angles S-Ga-S (93° to 106°). The smallest bond angle of 86.02 (2)° is Ga1-S2-Ga1'.

The ternary complex $[({}^{i}Pr_{3}PCu)_{2}(Me_{2}Ga)_{2}(SCH_{2}CH_{2}S)_{2}]$ (4) can be obtained from the binary complex 1, trimethylgallium and ethanedithiol in toluene solution (Scheme 1). The molecular structure (Fig. 3) in the crystal (space group C2/c) is related to that of 1, again with a crystallographic inversion center in the molecule. The two chelated copper units are retained, but the other copper atoms in 1 are replaced by gallium atoms. Therefore, the eight-membered Cu₄S₄-ring system in 1 changes into an eight-membered Cu₂Ga₂S₄-ring system in 4. The bond lengths and angles in the (${}^{i}Pr_{3}PCuSCH_{2}CH_{2}S$)⁻-units containing the chelated copper atoms are nearly the same as in 1. One of the ${}^{i}Pr$ -groups in the phosphine ligand is slightly disordered; the disorder could be resolved by measuring the crystal at lower temperature (105 K). The Ga–S bond lengths are around 235 pm. As expected, ¹³ the largest bond angle at the gallium atom is



Scheme 1 Synthesis of 4 and 5 from 1–3.



Fig. 3 Molecular structure of $[({}^{i}Pr_{3}PCu)_{2}(Me_{2}Ga)_{2}(SCH_{2}CH_{2}S)_{2}]$ (4). Thermal ellipsoids of C, Cu, Ga, P and S are drawn at 50% probability level. Selected bond lengths [pm] and angles [°]: Cu1–S1 227.01(4), Cu1–S2 226.04(4), Cu1–P1 220.24(4), Ga1–S1 235.65(4), Ga1–S2' 234.49(4), Ga1–C1 197.2(2), Ga1–C2 197.4(2), P1–Cu1–S1 126.88(2), P1–Cu1–S2 134.76(2), S1–Cu1–S2 94.42(2), Cu1–S1–Ga1 118.68(2), Cu1–S2–Ga1' 116.04(2), S1–Ga1–S2' 109.42(1), C1–Ga1–C2 123.84 (9).

C1–Ga1–C2 (124°), whereas the angle S1–Ga1–S2' is nearly ideal for tetrahedral coordination.

The ternary complex $[(^{i}Pr_{3}PCu)_{2}(MeGaSPh)_{2}(SCH_{2}CH_{2}S)_{2}]$ (5) can be obtained by mixing 2 and 3 in tetrahydrofuran (Scheme 1). The complex co-crystallizes with solvent molecules in space group $P\overline{1}$, but these can be easily removed in vacuum, resulting in a solvent-free powder of 5. Obviously, ligand exchange reactions take place in solution, since the SPh⁻-ligand initially bound only to copper atoms in 2 is found as a terminal ligand at the gallium atom in 5 (Fig. 4). It is noteworthy that attempts to synthesize 5 from 4 and HSPh were not successful. In 4, the methyl groups at the gallium atom do not show any reactivity towards thiols. Although synthesized in a different manner, it is useful to compare the structures of 4 and 5 by assuming a substitution of one of the methyl groups at the gallium atom by a phenylthiolate ligand. The molecule of 5 again contains a crystallographic inversion centre. The bond lengths and angles in the (¹Pr₃PCuSCH₂CH₂S)⁻-units containing the chelated copper atoms are similar to those in 1 and 4. The Ga-S bonds in the Cu₂Ga₂S₄-ring system are around 232 pm, and are therefore somewhat shorter than in 4, which is the expected effect of the substitution of the more covalently bound methyl group by a partially datively bound thiolate ligand.¹³ As expected, the terminal bond Ga1-S3 (227 pm) is shorter than the bridging Ga-S bonds in the ring.

Thermolysis of 4 and 5

The thermolysis of **4** and **5** was investigated by thermogravimetry (TG), differential scanning calorimetry (DSC) and simultaneous mass spectrometry. The curves recorded are shown in Fig. 5. According to the TG curve of compound **4**, the thermolysis starts at a temperature of 201 °C and ends at 320 °C. The first derivative of this TG curve (DTG) shows two distinct minima,



Fig. 4 Molecular structure of $[({}^{i}Pr_{3}PCu)_{2}(MeGaSPh)_{2}(SCH_{2}CH_{2}S)_{2}]$ (5). Thermal ellipsoids of C, Cu, Ga, P and S are drawn at 50% probability level. Selected bond lengths [pm] and angles [°]: Cu1–S1 227.6 (1), Cu1–S2 229.0(1), Cu1–P1 221.4(1), Ga1–S1 231.6(1), Ga1–S2' 233.3(1), Ga1–S3 226.7(1), Ga1–C1 196.8(5), P1–Cu1–S1 131.97(5), P1–Cu1–S2 133.36(5), S1–Cu1–S2 93.06(4), Cu1–S1–Ga1 120.23(6), Cu1–S2–Ga1' 116.35(6), S1–Ga1–S2' 112.04(5), S3–Ga1–S1 98.90(5), S3–Ga1–S2' 107.89(5), C1–Ga1–S3 117.7(2). corresponding to a two-step decomposition process. The first step involves the release of the phosphine ligands, as can be seen from the m/z curves (ⁱPr₃P⁺, m/z = 160). This first step is completed at 255 °C and corresponds to the partial mass change of 38.4%, in good agreement with the mass proportion of ⁱPr₃P in 4 (38.5%). The mass loss proceeds slower in the second step, and some *n*-butane (C₄H₁₀⁺, m/z = 58) is detected, which may be a recombination product from methyl groups at the gallium atom and the ethylene bridges of the ethanedithiolate ligand. The m/z curve for methyl fragments (CH₃⁺, m/z = 15) shows a maximum for each decomposition step. The overall mass loss of 60.7% is higher than expected (52.5%) for the formation of two formula units CuGaS₂ out of one molecule of **4**, indicating the loss of fragments which contain Cu, Ga and/or S atoms.

For compound **5** a distinct endothermic signal is observed in the DSC curve at 107 °C, which can be assigned to the melting of the compound. The mass change and thereby the decomposition starts at 216 °C (extrapolated from the TG curve). The first derivative of the TG curve displays three minima, corresponding to a three-step decomposition process. From the m/z curves it can be concluded that the first step involves the release of phosphine ligands (${}^{i}Pr_{3}P^{+}$, m/z = 160), and in the second step *n*-butane (C₄H₁₀⁺, m/z = 58) is detected. In the third step the phenyl groups (C₆H₆⁺, m/z = 78) are released, presumably as SPh₂. The end temperature extrapolated from the TG curve is 395 °C. The overall mass change of 58.9% is in reasonable



Fig. 5 Thermolysis of compounds (a) 4 and (b) 5. The TG curve, its first derivative (DTG), the DSC curve and selected ion current curves are shown. (a) m/z = 58 multiplied by factor 20, m/z = 160 multiplied by factor 2000; (b) m/z = 78 multiplied by factor 10, m/z = 58 multiplied by factor 10, m/z = 58 multiplied by factor 500.

agreement with the calculated value (61.3%) for two formula units $CuGaS_2$ out of one molecule of **5**.

The greenish brown residues of several thermolysis experiments at different temperatures were investigated by X-ray powder diffraction (XRPD). The determination of the unit cell constants and an estimation of the fractions of the phases present were achieved by Rietveld refinement (see Fig. 6 and ESI[†]). The powder patterns obtained from residues of 4 always display the reflection peaks expected for tetragonal CuGaS₂. Additionally, peaks corresponding to hexagonal CuGaS₂ and Cu_{2-x}S, digenite, are observed. The presence of digenite indicates that some Me₃Ga is released during the thermolysis. The phase fraction of the cation-disordered hexagonal modification of CuGaS₂ is higher when the maximum temperature of the thermolysis is lower, and the respective reflections completely vanish when the maximum temperature is 900 °C. Depending on thermolysis conditions, the phase fraction of digenite ranges from 9% to 24%.

In contrast, no binary copper sulfides are observed in powder patterns obtained from residues of **5**. The reflection peaks are generally broader, indicating smaller crystal sizes. The reflections expected for the usual ordered tetragonal phase of CuGaS₂ do not show the required tetragonal splitting, which can be assigned to cation disorder, *i.e.* cubic CuGaS₂. When a sample of **5** is heated slightly above the end temperature of the thermal decomposition process, the residue consists of approximately 61% hexagonal and 39% cubic CuGaS₂ (Fig. 6). The hexagonal unit cell axes were determined to be a = 374.28(5) pm and c = 621.6(2) pm, the cubic unit cell axis was determined to be a = 531.67(5) pm. The resulting volume of the hexagonal unit cell is 75.41(3) Å³ (Z = 1), and compares well with the volume of the cubic unit cell, which is 150.29(5) Å³ (Z = 2).

In order to characterize the unusual hexagonal modification of $CuGaS_2$ in more detail, the residue of **5** obtained at a maximum temperature of 400 °C was investigated by temperature dependent XRPD, TEM and EDX. From temperature dependent XRPD (Fig. 7) it can be seen that the metastable cation-



Fig. 6 Rietveld refinement (w $R_p = 0.0946$, $R_p = 0.0734$, $R(F^2) = 0.0387$) of the powder pattern obtained from the residue of **5** heated in a quartz tube to 400 °C. Observed (+) and calculated intensities, reflection positions of cubic (first row) and hexagonal (second row) CuGaS₂ and the difference curve are displayed.



Fig. 7 Temperature dependent XRPD patterns of the residue of 5. The 112, 220 and 024 reflections from the tetragonal phase are indexed at T = 700 °C.

disordered hexagonal phase transforms slowly into the usual tetragonal phase at temperatures above approximately 600 °C, where the relative intensities start to shift, respectively. The phase transition is accompanied by ordering of the metal ions; the tetragonal reflection splitting is well resolved at 700 °C, but the peaks of the hexagonal phase are still present at this temperature, because completion of the phase transition takes several hours of time. Similar results have been obtained for thermally treated samples of hexagonal CuInS₂, although there were significant intensity shifts at 500 °C. Four hours at 600 °C resulted in complete transformation.^{7b} Therefore, the gallium homologue seems to be somewhat more stable, kinetically.

According to several scanning TEM images in combination with EDX mapping, the residue consists of hexagonal crystal plates with 200 to 300 nm diameter and 10 to 30 nm thickness, with Cu, Ga and S homogeneously present (various images are included in the ESI†). Nano-probe EDX measurements of the three crystals shown in Fig. 8 give, in agreement with the formula CuGaS₂, an average of 24.7 at% Cu, 25.0 at% Ga and 50.3 at% S. The selected area electron diffraction (SAED) patterns of these crystals show sixfold symmetry (Fig. 8), consistent with the hexagonal crystal system. It should be noted here that a tetragonal or cubic CuGaS₂ crystal would also display sixfold symmetry along the zone axis [221] or [111], respectively.

A high resolution TEM (HRTEM) image of a hexagonal CuGaS₂ crystal with beam direction parallel to the [0001] zone axis is shown in Fig. 9. The d(100) spacing is in agreement with the value $a/2 \times \sqrt{3} = 324$ pm, which has to be expected from the hexagonal unit cell determined by Rietveld refinement. The indexing of the fast Fourier transform (FFT) of the HRTEM image is consistent with a hexagonal modification of CuGaS₂; in the tetragonal and cubic phases these reflections would be extinguished.

TEM images with beam direction perpendicular to the [0001] zone axis of the nanocrystals are shown in Fig. 10 and 11. It can be seen that the crystals are friable along the *c*-axis, the smeared reflections (streaks) in the SAED pattern indicate the presence of stacking faults. The AB-stacking of the layers in the hexagonal domains and the ABC-stacking in the cubic domains are clearly distinguishable in the HRTEM image shown in Fig. 11, and are consistent with simulated HRTEM images (see ESI[†]). The cubic domains are preferably located in the surface region, while the



Fig. 8 TEM bright-field image of $CuGaS_2$ nanocrystals sedimented by drop-casting. Crystals 1, 2 and 3 in (0001) orientation, where in 3 two crystals overlap. Inset: electron diffraction pattern of crystal 1.



Fig. 9 HRTEM lattice image of a $CuGaS_2$ crystal. Beam direction parallel to [0001]. The inset represents the FFT of the image shown.

hexagonal domains build up most of the bulk of the nanocrystals.

Experimental section

All reactions were carried out in an atmosphere of dry nitrogen by standard Schlenk line and dry box techniques. THF and toluene were dried over sodium–benzophenone and *n*-heptane was dried over CaH₂. All solvents were distilled under a nitrogen atmosphere prior to use. Ethanedithiol and Cu₂O were purchased commercially. Me₃Ga–OEt₂ and ⁱPr₃P were prepared according to the literature.^{14,15} Elemental analyses were carried out with a Vario EL-Heraeus microanalyzer. ¹H (400 MHz) and ³¹P (161.9 MHz) NMR spectra were recorded with C₆D₆ as the solvent on a Bruker Avance DRX-400 instrument using SiMe₄ as the internal standard and H₃PO₄ as the external standard,



Fig. 10 TEM bright-field image of CuGaS₂ nanocrystals embedded in epoxy. Inset: electron diffraction pattern of the crystal encircled.



Fig. 11 HRTEM lattice image of a $CuGaS_2$ crystal. Beam direction perpendicular to [0001], in particular parallel to [11–20] of the hexagonal phase. Insets: FFT and Bragg-filtered portion of the crystal.

respectively. Chemical shifts are given in ppm, coupling constants are denoted in Hz.

Synthesis of $[({}^{i}Pr_{3}PCu)_{4}(SCH_{2}CH_{2}S)_{2}]$ (1). To a suspension of 0.70 g (4.9 mmol) Cu₂O in 10 ml toluene, 0.45 ml (5.4 mmol) ethanedithiol and 3.80 ml (19.9 mmol) ${}^{i}Pr_{3}P$ were added. The reaction mixture was refluxed for 1 hour, resulting in a clear yellow solution. Storage of this solution for three days at -20 °C yields colourless crystals of 1 (2.64 g, 100%). Excess of ${}^{i}Pr_{3}P$ is necessary, but can be recovered by distillation. Elemental analysis found: C 44.3, H 8.6, S 12.2; calc. for 1: C 44.5, H 8.6, S 11.9. 1 H NMR: 3.10 (br s, 8H_{CH2}), 1.84 (m, 12H_{CH-iPr}), 1.17 (dd, ${}^{3}J_{HH} = 7$, ${}^{3}J_{PH} = 14$, 72H_{CH3-iPr}). ${}^{31}P{}^{1}$ H} NMR: 30.6 (br s), 19.5 (br s).

Compounds 2 and 3 have been prepared according to the literature.^{10,11} For 3 a slightly modified method has been employed: toluene was used as the solvent instead of benzene, and the reaction mixture was heated up to 80 °C in order to

ensure completion of the reaction and to obtain single crystals of appropriate size for structure determination by X-ray diffraction.

Synthesis of $[({}^{i}Pr_{3}PCu)_{2}(Me_{2}Ga)_{2}(SCH_{2}CH_{2}S)_{2}]$ (4). In a mixture of 10 ml toluene and 1 ml THF, 0.65 g (0.6 mmol) of 1 were dissolved, and 0.45 ml (2.4 mmol) of Me₃Ga–OEt₂ and 1.2 ml of a 1 molar solution of ethanedithiol (1.2 mmol) in toluene were successively added *via* a syringe, resulting in a yellow solution. The solution was stirred for 6 h at ambient temperature, while methane gas evolution was observed, and the colour of the reaction mixture faded to colourless. The solution was layered with 10 ml of *n*-heptane, kept overnight at 2 °C and then for three days at -20 °C. Colourless crystals of 4 (0.75 g, 78%) formed, while *n*-heptane slowly diffused into the toluene solution. Elemental analysis found: C 37.6, H 7.8, S 15.4; calc. for 4: C 37.6, H 7.5, S 15.4. ¹H NMR: 3.30 (m, 4H_{CH2}), 2.80 (m, 4H_{CH2}), 1.73 (m, 6H_{CH-iPr}), 1.03 (dd, ³J_{HH} = 7, ³J_{PH} = 14, $36H_{CH3-iPr}$), 0.35 (s, $12H_{Me}$). ³¹P{¹H} NMR: 34.4 (br s).

Synthesis of [(ⁱPr₃PCu)₂(Me₂GaSPh)₂(SCH₂CH₂S)₂] (5). A total of 0.25 g (0.7 mmol; 1.4 mmol Ga) of 2 was dissolved in 20 ml THF and 0.48 g (0.5 mmol; 1.4 mmol Cu) of 1 were added, while stirring at room temperature. Half of the solvent was removed at reduced pressure and the colourless and clear solution was stored at -20 °C, resulting in crystallisation of 5.2 THF (0.43 g, 52%) as colourless plates. The yield may be increased by successive removal of solvent and/or further cooling of the reaction mixture. The crystal plates of 5.2 THF lose solvent when removed from the mother liquor, and thereby decompose to a colourless powder. The powder was dried in vacuum to give 5 nearly solvent free. Mp 107 °C. Elemental analysis found: C 42.8, H 6.9, S 18.6; calc. for 5: C 42.4, H 6.5, S 18.9; calc. for 5.2 THF: C 45.4, H 7.1, S 16.5. ¹H NMR: 7.83 (br s, $4H_{ortho-Ph}$), 7.06 (br s, $4H_{meta-Ph}$), 6.94 (t, ${}^{3}J_{HH} = 7$, $2H_{para-Ph}$ Ph), 3.21 (br s, 4H_{CH2}), 2.80 (br s, 4H_{CH2}), 1.72 (m, 6H_{CH-iPr}), 1.02 (dd, ${}^{3}J_{HH} = 7$, ${}^{3}J_{PH} = 14$, $36H_{CH3-iPr}$), 0.35 (br s, $6H_{Me}$). ³¹P{¹H} NMR: 33.3 (br s).

X-ray crystallographic data of single crystals were collected on a STOE IPDS 2T diffractometer. Data reduction and numerical absorption correction were performed with STOE X-RED.¹⁶ Structure solutions were carried out with direct methods (SIR 92)¹⁷ and refinement with SHELXL-97.¹⁸ Hydrogen atoms were calculated on idealized positions and all non-hydrogen atoms were refined with anisotropic thermal parameters. Figures were generated with Diamond 2.1b.¹⁹

The thermogravimetric measurements were performed with the thermobalance NETZSCH STA 409 CD in a stream of N₂ at a heat rate of 10 K min⁻¹. The DSC curve was measured with an empty Al_2O_3 crucible as the reference. Thermal analysis was carried out with the NETZSCH Proteus 5.0.1 software.²⁰

X-ray powder diffraction patterns were measured on a STOE Stadi P diffractometer in Debye–Scherrer geometry with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.540598$ Å). Room temperature data were recorded with a linear PSD, high temperature measurements were performed with a STOE oven type 0.65.3 and a curved image plate detector. For an improved signal-to-noise ratio, several single measurements were added. Rietveld refinement was performed with GSAS.²¹ Simultaneously refined parameters included the diffractometer zero point, the fractions and cell constants of present phases, the background function (Chebyschev polynomial, GSAS background function 1) and profile

parameters (GSAS profile function 4). Asymmetry parameters for the reflections were taken from the actual diffractometer geometry.²² The cubic crystal structure of CuGaS₂ was modelled by substituting the Zn position in zinc-blende by half Ga and Cu, each. In the same manner, hexagonal CuGaS₂ was modelled by substituting the Zn position in wurtzite. Because of the crystal shape and polytypism of the CuGaS₂ nanocrystals, as confirmed by TEM, the micro-strain function of Stephens²³ was used to account for the obvious anisotropic reflection line broadening.

The TEM examinations have been carried out in a Philips CM 200 STEM equipped with a super twin objective lens ($U_0 = 200$ kV; point resolution 0.23 nm). Simulations of electron diffraction patterns and HRTEM images were done by the JEMS software package.²⁴ The chemical composition of samples was measured by a calibrated EDX system adapted to the STEM used (spot diameter in nano-probe mode 5–10 nm). Nanocrystalline CuGaS₂ samples for transmission electron microscopy (TEM) were prepared in two ways.

(1) $CuGaS_2$ powder was dispersed in ethanol by ultrasonic treatment followed by drop-casting onto carbon-coated molybdenum and/or nickel TEM grids. In this way the samples are ready for TEM inspection.

(2) The powder was mixed with M-Bond 610 glue. This mixture was fixed between two 400 μ m thick GaAs wafers acting as inert material. From this package some slices of 3 mm length and about 600 μ m thickness were cut by a diamond wire saw. These slices (cross-section technique) were mechanically thinned by grinding (40 μ m, 15 μ m, 5 μ m) and polished using a GATAN dimple grinder. To obtain electron transparency, finally, the so-prepared samples were thinned by Ar⁺ ions. Typical operation conditions employed during double-side ion milling are an accelerating voltage of 4 kV, beam currents of 0.5 mA and a beam incidence angle of 11° to 13°.

Conclusions

From Me₃Ga, ethanedithiol and the new copper complex [($^{i}Pr_{3}P-Cu$)₄(SCH₂CH₂S)₂] (1), the organometallic copper dimethyl gallium complex [($^{i}Pr_{3}PCu$)₂(Me₂Ga)₂(SCH₂CH₂S)₂] (4) has been prepared. The related copper monomethyl gallium complex [($^{i}Pr_{3}PCu$)₂(MeGaSPh)₂(SCH₂CH₂S)₂] (5) was obtained from [($^{i}Pr_{3}PCuSPh$)₃] (2) and [(MeGaSCH₂CH₂S)₂] (3) by a ligand exchange reaction. The molecular structures in the crystals of the two ternary compounds 4 and 5 are related to the structure of the copper complex 1, with a recurring central eight-membered M₄S₄-ring system (M = Cu, Ga) and two copper atoms chelated by ethanedithiolate ligands, each. Structural details and variations in the organometallic compounds 3–5 are in agreement with the predictions of the concept of the dative bond.¹³

Bulk thermolysis of the new organometallic single-source precursors 4 and 5 leads to the formation of $CuGaS_2$. It can be concluded from the thermogravimetric data that the substitution of methyl groups in 4 by phenylthiolate ligands in 5 results in an additional thermolysis step, and therefore a higher end temperature, but also in a lower mass change, which fits better to the calculated value for $CuGaS_2$ as the single residue of thermolysis. The observation of additional binary copper sulfide in the residue of 4, and its absence in the residue of 5, indicates that some Me₃Ga is released during the thermolysis of **4**, but not from **5**. In addition to the usual tetragonal or cation-disordered cubic modification of CuGaS₂, an unusual metastable hexagonal modification is observed in the residues of **4** and **5** by powder diffraction. As shown by electron microscopy, the residue of **5** consists of polytypic CuGaS₂ nanocrystals. To our knowledge, this is the first report on hexagonal CuGaS₂ obtained from single-source precursors, and also the first report on polytypism in CuGaS₂.

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