DALTON
FULL PAPER

Syntheses and structures of new copper(I)–indium(III)–selenide clusters †

Andreas Eichhöfer *[a] **and Dieter Fenske** [b]

[a] *Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany*
[b] *Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstraße Geb. Nr. 30.45, D-76128 Karlsruhe, Germany*

Received 10th December 1999, Accepted 27th January 2000

The reaction of $Se(SiMe_3)_2$ with mixtures of copper(I) chloride and indium(III) chloride in the presence of phosphine ligands PR_3 (R = organic group) yielded the new clusters $[Cu_6In_8Se_{13}Cl_4(PPh_3)_6(C_4H_8O)]$ **1**, $[Cu_6In_8Se_{13}Cl_4(P^nPr_2Ph)_{12}]$ **2** and $[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$ **3**. The molecular structures of **1**, **2** and **3** have been characterised by X-ray crystallography and compared with the chalcopyrite structure of bulk $CuInSe_2$. UV-VIS Solid state absorption spectra have been measured for **1** and **3**.

Introduction

The compound $CuInSe_2$ is together with CdTe one of the most promising materials for thin film technology in solar cells. Conversion efficiencies close to 18% have been achieved under laboratory conditions.[1] Devices with the highest efficiencies were fabricated using coevaporation of the elements or selenisation of metal layers. Unfortunately, the prepared films often have high defect densities and it is difficult to maintain the stoichiometry during the deposition, both factors limiting the efficiency of the cells. Hence, a reliable low temperature method for producing high-quality $CuInSe_2$ is highly desirable. There are only a few examples of those for ternary or multinary compounds in contrast to the existence of many single-source precursors for binary materials. The compound $[(Ph_3P)_2CuIn(SeEt)_4]$ described by Kanatzidis and co-workers[2] is the only structurally characterised example of a single-source precursor to the ternary semiconductor $CuInSe_2$. Cluster compounds similar to the known copper selenide clusters such as $[Cu_{32}Se_{16}(PPh_3)_{12}]$, $[Cu_{52}Se_{26}(PPh_3)_{16}]$, $[Cu_{72}Se_{36}(PPh_3)_{20}]$ and $[Cu_{146}Se_{72}(PPh_3)_{30}]$[3a] or silver selenide clusters such as $[Ag_{30}Se_8(Se^tBu)_{14}(P^nPr_3)_8]$, $[Ag_{90}Se_{38}(Se^tBu)_{14}(PEt_3)_{22}]$, $[Ag_{114}Se_{34}(Se^nBu)_{46}(PtBu_3)_{14}]$, $[Ag_{112}Se_{32}(Se^nBu)_{48}(P^tBu_3)_{12}]$, and $[Ag_{172}Se_{40}(Se^nBu)_{92}(dppp)_4]$[3b] [dppe = $Ph_2P(CH_2)_3PPh_2$] with a $CuInSe_2$ cluster core and an organic ligand shell would be particularly interesting candidates for the fabrication of thin films because of their solubility in organic solvents. Spanhel and co-workers[4] have shown in a recent publication that reaction of CuI, $InCl_3$ and $S(SiMe_3)_2$ in the presence of a tertiary phosphine leads to the formation of $CuInS_2$ nanoparticles. We now report that it is also possible to crystallise and isolate cluster compounds from similar reactions with $Se(SiMe_3)_2$ and have investigated their molecular structures by single crystal X-ray diffraction (XRD).

Experimental

Standard Schlenk techniques were employed throughout the syntheses using a double manifold vacuum line with high purity dry nitrogen. The solvent tetrahydrofuran was dried over sodium–benzophenone and distilled under nitrogen and heptane was collected after refluxing over $LiAlH_4$. Anhydrous CuCl and $InCl_3$ were obtained from Aldrich. $Se(SiMe_3)_2$[5] was prepared according to standard literature procedures.

Syntheses

$[Cu_6In_8Se_{13}Cl_4(PPh_3)_6(C_4H_8O)]\cdot 0.5C_4H_8O$ 1. Copper(I) chloride (0.09 g, 0.9 mmol) was dissolved along with $InCl_3$ (0.20 g, 0.9 mmol) and PPh_3 (0.48 g, 1.8 mmol) in THF (25 ml). Upon addition of $Se(SiMe_3)_2$ (0.31 ml, 1.37 mmol) an orange solution was formed. Layering with heptane or careful evaporation of the solvent yielded yellow needles of **1**. Yield: 70% (Found: C, 33.37; H, 2.61. $C_{114}H_{90}Cl_4Cu_6In_8O_{1.5}P_6Se_{13}$ requires C, 33.09; H, 2.19%).

$[Cu_6In_8Se_{13}Cl_4(P^nPr_2Ph)_{12}]$ 2. Indium trichloride (0.39 g, 1.76 mmol) was dissolved along with P^nPr_2Ph (0.37 ml, 3.52 mmol) in THF (20 ml). Addition of $Se(SiMe_3)_2$ (0.69 ml, 3.08 mmol) led to the formation of a yellow precipitate. To this suspension was added a solution of CuCl (0.17 g, 1.76 mmol) and P^nPr_2Ph (0.74 ml, 3.52 mmol) in THF (20 ml). After three days the solution turned orange. Careful evaporation of the solvent yielded yellow crystals of **2**. Yield: 73% (Found: C, 35.93; H, 4.54. $C_{144}H_{228}Cl_4Cu_6In_8P_{12}Se_{13}$ requires C, 36.04; H, 4.79%).

$[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$ 3. Copper(I) chloride (0.11 g, 1.1 mmol) was dissolved along with $InCl_3$ (0.25 g, 1.1 mmol) and PPh_3 (0.29 g, 1.1 mmol) in THF (25 ml). Upon addition of $PhSeSiMe_3$ (0.51 ml, 2.2 mmol) and $Se(SiMe_3)_2$ (0.25 ml, 1.1 mmol) the reaction solution turned red. After three days small red cubic crystals of **3** grew in the flask. Careful evaporation of the solvent did not result in further crystallisation. Yield: 10% (Found: C, 31.06; H, 3.33. $C_{216}H_{180}In_{15}Cu_{11}P_4Se_{40}$ requires C, 30.67; H, 2.15%).

Crystal structural analyses

Single crystal structural analyses of compounds **1**–**3** were performed using a Stoe-IPDS diffractometer (Mo-Kα radiation) equipped with an imaging plate area detector and a rotating anode. Structure solution and refinement were carried out using SHELXS 86[6] and SHELXL 97[7] software and direct methods techniques. All calculations were performed on a

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† Dedicated to Professor Dr G. Becker on the occasion of his 60th birthday.

DOI: 10.1039/a909737f

Silicon Graphics INDY computer. Molecular diagrams were prepared using the SCHAKAL 97 program.[8]

Compound 1. *Crystal data.* $C_{112}H_{86}Cl_4Cu_6In_8OP_6Se_{13}\cdot 0.5C_4H_8O$, $M = 4137.76$, orthorhombic, space group $P2_12_12_1$, $a = 22.228(4)$, $b = 22.989(5)$, $c = 28.829(6)$ Å, $V = 14732(5)$ Å^3, at 200 K, $Z = 4$, $D_c = 1.866$ g cm^{-3}, μ(Mo-Kα) = 5.461 mm^{-1}, $2\theta_{max} = 50°$, 25505 independent reflections measured ($R_{int} = 0.0941$) and 21812 with $I > 2\sigma(I)$.

The structure was refined on F^2. All Se, Cu, P and C atoms were refined anisotropically except those C atoms of THF which were refined isotropically. Positions for H atoms except those of THF were calculated to yield $R = 0.0605$, $wR = 0.1555$. Absolute structure parameter 0.026(10).

Compound 2. *Crystal data.* $C_{144}H_{228}Cl_4Cu_6In_8P_{12}Se_{13}$, $M = 4798.98$, monoclinic, space group $P2_1/c$, $a = 19.609(4)$, $b = 31.841(6)$, $c = 34.232(7)$ Å, $\beta = 91.72(3)°$, $V = 21364(6)$ Å^3, at 200 K, $Z = 4$, $D_c = 1.492$ g cm^{-3}, μ(Mo-Kα) = 3.819 mm^{-1}, $2\theta_{max} = 48°$, 26186 independent reflections measured ($R_{int} = 0.0923$) and 14452 with $I > 2\sigma(I)$.

The structure was refined on F^2. All Se, Cu and P atoms were refined anisotropically, all C atoms isotropically and positions for H atoms were calculated to yield $R = 0.0854$, $wR = 0.2148$.

Compound 3. $C_{216}H_{180}In_{15}Cu_{11}P_4Se_{40}$, $M = 8456.29$, cubic, space group $I\bar{4}3m$, $a = b = c = 25.431(3)$ Å, $V = 16447(3)$ Å^3, at 200 K, $Z = 2$, $D_c = 1.676$ g cm^{-3}, μ(Mo-Kα) = 6.201 mm^{-1}, $2\theta_{max} = 50°$, 2670 independent reflections measured ($R_{int} = 0.071$) and 2539 with $I > 2\sigma(I)$.

The structure was refined on F^2. All Se, Cu and P atoms were refined anisotropically and C atoms isotropically to yield $R = 0.0439$, $wR = 0.1429$. Absolute structure parameter 0.05(2). Atoms In1 and Cu1 were statistically disordered about the six equivalent positions.

CCDC reference number 186/1824.

See http://www.rsc.org/suppdata/dt/a9/a909737f/ for crystallographic files in .cif format.

Results and discussion

The compounds **1**, **2** and **3** have been prepared according to eqns. (1)–(3) as yellow, yellow and red crystals respectively.

$$\mathrm{CuCl + InCl_3 + 2PPh_3 \xrightarrow[THF]{+2Se(SiMe_3)_2} [Cu_6In_8Se_{13}Cl_4(PPh_3)_6(C_4H_8O)]\ \mathbf{1} + 2Se(SiMe_3)_2} \quad (1)$$

$$\mathrm{CuCl + InCl_3 + 2P^nPr_2Ph \xrightarrow[THF/Et_2O]{Se(SiMe_3)_2} [Cu_6In_8Se_{13}Cl_4(P^nPr_2Ph)_{12}]\ \mathbf{2}} \quad (2)$$

$$\mathrm{CuCl + InCl_3 + PPh_3 \xrightarrow[THF]{+PhSeSiMe_3/Se(SiMe_3)_2} [Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]\ \mathbf{3}} \quad (3)$$

All three compounds have had their structures determined by X-ray crystallography.

Fig. 1 shows the molecular structure of compound **1** which crystallises in the space group $P2_12_12_1$. A central selenium atom (Se1) is tetrahedrally surrounded by four inner indium atoms (In1–In4) (In–Se: 263.1–291.5(2) pm). Each of these four inner indium atoms are bound through three μ_3-Se^{2-} ligands (Se2–Se13) to four outer indium atoms (In5–In8) (In–Se: 255.9–258.5(2) pm), which also form a tetrahedron. In addition each of the four outer indium atoms is bound to a terminal chlorine ligand (Cl1–Cl4) (In–Cl: 238.8–240.6(3) pm). Atom In3 is additionally co-ordinated by an THF molecule (In3–O1: 241.4(10) pm). Therefore In3 has a trigonal bipyramidal surrounding with a distance In3–Se1 of 291.5(2) pm which is significantly longer than the other In–Se1 distances which have values between 263.1(1) and 265.3(1) pm. Each of the other seven indium atoms has a distorted tetrahedral coordination sphere (Se–In–Se 102.90–120.58(5)°; Cl–In–Se 99.51–108.47(11)°). This part of the structure $[In_8Cl_4Se_{13}]^{6-}$ is therefore isostructural to known IIb–VI cluster complexes of the type $[M_8Cl_4Se(SePh)_{12}]^{2-}$ (M = Zn or Cd).[9] Each of the six remaining CuPPh$_3$ units (Cu1–Cu6, P1–P6) (Cu–P: 224.1–225.6(4) pm) is co-ordinated by two of the twelve outer selenium atoms which adopt a distorted trigonal co-ordination for the copper atoms (Cu–Se 236.2–241.5(2) pm; Se–Cu–P 109.66–122.64(12)°; Se–Cu–Se 126.76–129.72(8)°). Twelve of the selenium atoms (Se2–Se13) form a distorted icosahedron centred on Se1. The eight indium atoms cap the triangular faces of the icosahedron, whereby four of the indium atoms (In1–In4) lie within and four (In5–In8) outside of the icosahedron. In addition six CuPPh$_3$ units bridge six edges of the icosahedron.

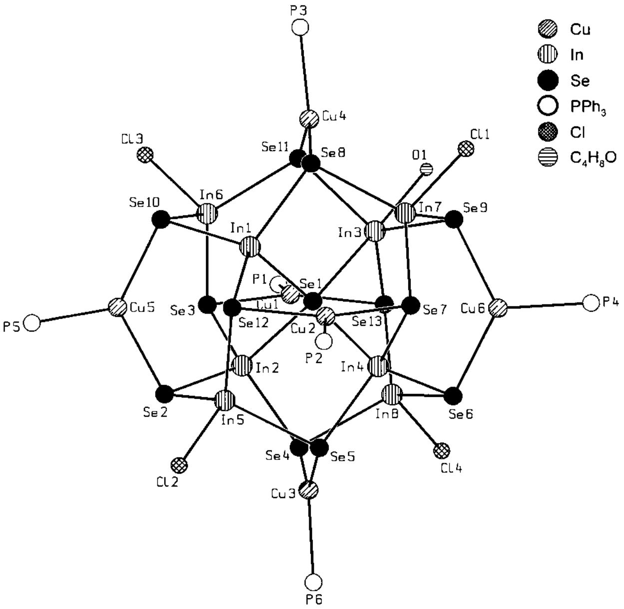

Fig. 1 Molecular structure of $[Cu_6In_8Se_{13}Cl_4(PPh_3)_6(C_4H_8O)]$ **1**. Carbon and hydrogen atoms are omitted for clarity. Selected bond lengths/pm and angles/°: μ_4-Se1–In, Se1–In2 263.1(1) to Se1–In3 291.5(2); μ_3-Se–In, Se4–In8 258.5(2) to Se5–In5 255.9(2); μ_3-Se–Cu, Se8–Cu4 236.2(2) to Se12–Cu2 241.5(2); In–Cl, In5–Cl2 238.8(3) to In6–Cl3 240.6(3); Cu–P, Cu6–P4 224.1(4) to Cu5–P5 225.6(4); Se–In–Se, Se3–In2–Se1 102.90(5) to Se11–In7–Se13 120.58(5); Se–In–Cl, Se9–In3–Cl1 99.51(10) to Se12–In1–Cl2 108.47(11); Se–Cu–Se, Se7–Cu2–Se12 126.76(8) to Se8–Cu4–Se11 129.72(8); Se–Cu–P, Se2–Cu7–P5 109.66(12) to Se7–Cu2–P2 122.64(12).

Compound **2** crystallises as yellow needles in the monoclinic space group $P2_1/c$. The molecular structure of **2** is similar to that of **1** despite the fact that each copper atom is co-ordinated by two P^{n}Pr$_2$Ph ligands to give a tetrahedral environment for the copper atoms. Bond lengths and angles are comparable to those of **1**.

Compound **3** crystallises in a cubic body centred lattice. The solution of the structure is possible in the space group $I\bar{4}3m$ but symmetric disorder of the organic ligands gives rise to the presumption of twinning of the crystals. Hence the description of the structure and the given bond lengths and angles have to be interpreted in light of this. Fig. 2 shows the molecular structure of **3** without carbon and hydrogen atoms in two different orientations. The highly symmetric cluster core with the four phosphorus atoms (P1, P1A, P1B, P1C) at each corner has a tetrahedral shape. By analogy to similar tetrahedral molecules of IIb–VI compounds the building units of the cluster are adamantane and barrelane cages of indium, copper and selenium atoms. At each corner of the cluster there is an adamantane cage formed of, for example, one copper atom

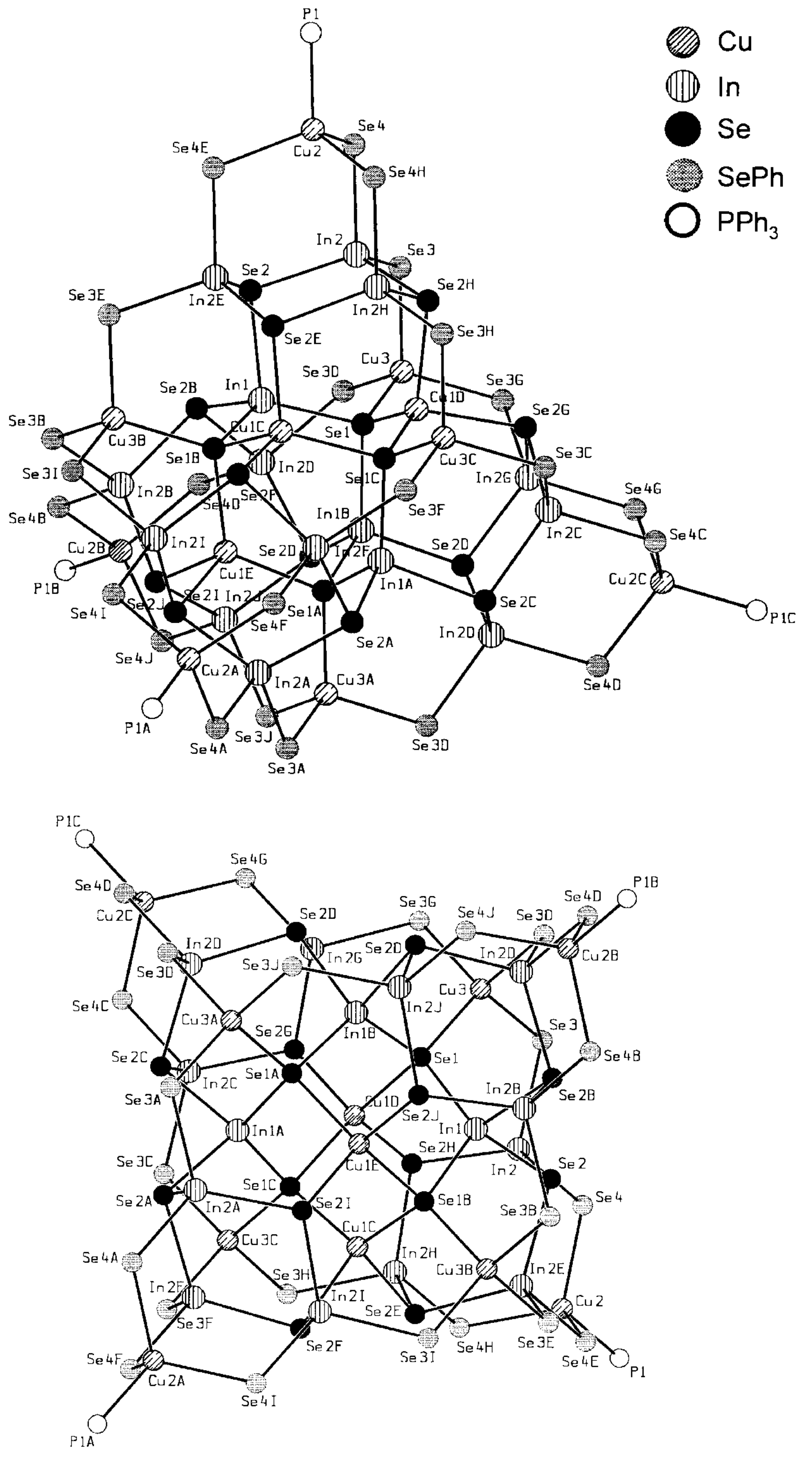

Fig. 2 Molecular structure of [$Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4$] **3** in two different orientations. Carbon and hydrogen atoms are omitted for clarity. Atoms Cu1 and In1 are statistically distributed over the six symmetry equivalent sites of this position. Selected bond lengths/pm and angles/°: μ_4-Se–In, Se1–In1 245.8(1); μ_4-Se–Cu, Se1–Cu3 244.2(3); μ_3-Se–In, Se2–In1 256.6(1); Se2–In1 256.8(1); μ-PhSe–In, Se3–In2 259.1(1); Se4–In2 258.6(1); μ-PhSe–Cu, Se3–Cu3 245.1(1); Se4–Cu2 245.0(1); Cu–P, Cu2–P1 229.5(5); Se–Cu2–Se, Se4–Cu2–Se4F 110.00(5); Se–Cu2–P, Se4–Cu2–P1 108.94(5); Se–Cu3–Se, Se1–Cu3–Se3 110.45(5); Se3–Cu3–Se3D 108.48(5); Se–In1–Se, Se1–In1–Se2 109.76(2); Se1–In1–Se1B 119.91(9); Se2–In1–Se2B 95.04(6); Se–In2–Se, Se2–In2–Se2I 119.96(5); Se4–In2–Se3 107.40(4); Se4–In2–Se2 107.43(3); Se2–In2–Se3 107.51(3).

(Cu2), three selenium atoms of $SePh^-$ ligands (Se4, Se4E, Se4H), three indium atoms (In2, In2E, In2H) and three Se^{2-} ligands (Se2, Se2E, Se2H). In the next layer three barrelane cages are condensed to the lower face of the adamantane with three additionally bridging $SePh^-$ groups (Se3, Se3E, Se3H), *e.g.* the cage formed by In2E, Se2, Se2E, Se3E, In1, Cu1C, Cu3B and Se1B. Four of these building units consisting of one adamantane cage and three basal barrelane cages are linked together around a central adamantane cage (In1, Se1, Cu1D, Se1C, Cu1C, Se1B, Cu1E, Se1A, In1A, In1B). All copper and indium atoms possess distorted tetrahedral geometry. Atom Cu1 and its symmetry equivalents are each bonded to four Se^{2-} ligands (Cu1–Se1 245.9(1); Cu1–Se2 256.7(1) pm), Cu2 and its symmetry equivalents by one phosphorus atom (P1) from a triphenylphosphine ligand (Cu2–P1 229.5(5) pm) and three selenium atoms (Se4, Se4E, Se4H) from the selenolate ligands (Se4–Cu2 244.8(1) pm). On the other hand Cu3 and its symmetry equivalents exhibit co-ordination by three selenium atoms from $SePh^-$ ligands (Se3, Se3D, Se3G) (Cu3–Se3 245.1(1) pm) and one Se^{2-} ligand (Se1) (Cu3–Se1 244.2(3) pm). Atom In1 and its symmetry equivalents are each bonded to four Se^{2-} ligands (Se2, Se2B, Se1, Se1B) (In1–Se2: 256.6(1) pm; In1–

Table 1 Relative elemental weights of Cu : In : Se in clusters **1** and **3** from TRFA

Compound	Relative elemental weight Cu : Se : In Theory	 Experiment
$[Cu_6In_8Se_{13}Cl_4(PPh_3)_6(C_4H_8O)]$	1 : 2.69 : 2.41	1 : 2.71 : 2.38
$[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$	1 : 4.52 : 2.46	1 : 4.60 : 2.66
$[Cu_8In_{18}Se_{16}(SePh)_{24}(PPh_3)_4]^{6+}$	1 : 6.21 : 4.07	
$[Cu_{14}In_{12}Se_{16}(SePh)_{24}(PPh_3)_4]^{6-}$	1 : 3.55 : 1.55	

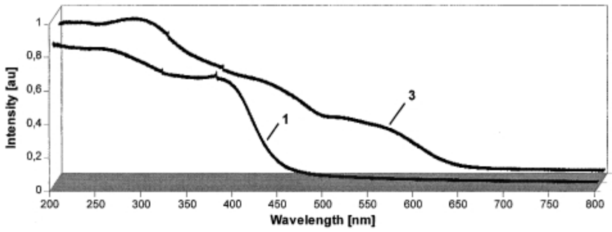

Fig. 3 The UV-VIS solid state absorption spectra (mull in mineral oil) of clusters **1** and **3**.

Se1 245.8(1) pm), In2 and its symmetry equivalents by two Se^{2-} ligands (Se2, Se2H) (In2–Se2 256.9(1) pm) and two $SePh^{-}$ ligands (Se3, Se4) (In2–Se4 258.6(1); In2–Se3 259.1(1) pm). Each phenyl group of the selenolate ligands is split into two positions by a mirror plane passing through the appropriate selenium atom (Se3, Se4). The same is also true for the phenyl rings of the phosphine ligands. Atoms Cu1 and In1 are statistically distributed over the six symmetry equivalent sites of this position. This is shown by the thermal parameter which is too high for six indiums, and too low for six copper atoms, in comparison to the values for the other atoms. A further indication is that the two possible ordered structural compositions $[Cu_8In_{18}Se_{16}(SePh)_{24}(PPh_3)_4]^{6+}$ and $[Cu_{14}In_{12}Se_{16}(SePh)_{24}(PPh_3)_4]^{6-}$ would be ionic and there is no evidence for the existence of counter ions in the difference Fourier map. To obtain proof of the statistical distribution we determined relative elemental concentrations Cu : In : Se for **1** and **3** with TRFA (total reflection X-ray fluorescence analysis) using an Atomika Extra II: 50 kV, 38 mA (**3**); 50 kV, 12 mA (**1**); each 3000 s measuring time, W-Brems excitation (Table 1). Experimental values are in good agreement with the neutral disordered model giving a formula $[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$ for **3**.

From the UV-VIS solid state absorption spectra (Perkin-Elmer spectrometer Lambda 900 equipped with an integrating sphere, as mull in mineral oil between two quartz plates, in transmission mode) one can clearly see a red shift for the onset of the absorption maximum going from the smaller cluster **1** to the larger cluster **3** which is expected from the colour of the crystals (Fig. 3). Compound **1** displays two maxima at 250 and 380 nm. The spectrum of **3** shows in addition to one maximum at 280 nm several others shifted to higher wavelength. The absorption onset of **3** at 645 nm is significantly blue-shifted in respect of the value of 1240 nm (1.05 eV) for the bandgap of bulk $CuInSe_2$. Nonetheless one has to be careful in correlating the absorption maxima of **1** and **3** with bulk $CuInSe_2$ in terms of the quantum size effect since the co-ordination environment as well as the nature of the ligands are different.

Conclusion

The syntheses of the three copper indium selenide clusters **1**, **2** and **3** presented herein show that it is possible to synthesize and crystallise ternary cluster molecules *via* an organometallic approach by the reaction of the appropriate metal halides with silylated main group elements. Variation of the ligands and reaction conditions should lead to further possibly even larger molecules. However, the structures of the cluster cores show no analogy to the chalcopyrite structure of bulk $CuInSe_2$. Furthermore the low yield of **3** could give a hint for the difficulty of synthesizing and crystallising larger cluster molecules. This is almost certainly due to the problem of many clusters with different compositions but very similar energies existing for the same combination of metals and ligands. In the next step we aim to investigate the thermal properties of these materials and use them as precursor compounds for thin film fabrication of $CuInSe_2$.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft (SFB 195) and the German Israel foundation (GIF). We are grateful to Dr M. v. Wagner (Institut für Petrographie und Geochemie der Universität Karlsruhe, Professor Dr D. Stüben) for the measurement of the TRFA. Further we want to acknowledge E. Tröster for her invaluable assistance in the synthesis of the cluster molecules.

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Paper a909737f