[Cu$_{40}$Se$_{16}$($\text{S-C}_6\text{H}_4\text{-CN}$)$_8$(dppm)$_8$]: A Disc-like Copper Cluster with a Nitrile-functionalized Ligand Shell

Robert Langer$^{a,b}$, Dieter Fenske$^{b,c,d}$ and Olaf Fuhr$^{b,c,d}$

$^a$ Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

$^b$ Lehn Institute of Functional Materials, Sun Yat-Sen University, 135 Xingang Road, 510275 Guangzhou, China

$^c$ Institut für Anorganische Chemie and DFG-Centrum für funktionelle Nanostrukturen (CFN), Karlsruher Institut für Technologie, Engesserstraße 15, 76133 Karlsruhe, Germany

$^d$ Institut für Nanotechnologie, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Reprint requests to Dr. Olaf Fuhr. Fax: +49 721 608 26368. E-mail: olaf.fuhr@kit.edu


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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The new copper chalcogenide cluster [Cu$_{40}$Se$_{16}$($\text{S-C}_6\text{H}_4\text{-CN}$)$_8$(dppm)$_8$] (I) with nitrile groups in the organic ligand shell has been synthesized and characterized by single-crystal X-ray diffraction and IR spectroscopy. The arrangement of the chalcogen atoms in I is similar to a close packing and is best described as two parallel layers with an $ab$ stacking sequence. The resulting structure is a rare example of a disc-like cluster molecule.

Key words: Copper, Chalcogens, Cluster Compounds, X-Ray Diffraction, IR Spectroscopy

Introduction

Nanosscopic particles of semiconductor materials produced by size- and shape-selective synthetic approaches are of significant importance, due to their tunable electronic and optical properties [1, 2]. Especially, ligand-stabilized cluster compounds with an exact stoichiometry allow for the determination of size-dependent physical properties [3 – 8]. The selective functionalization of the organic shell in such clusters can potentially increase the solubility, help to understand the influence of the functional groups on the structural motif and allow the construction of networks or the immobilization on surfaces. Previously, we reported on the synthesis, physical properties and reactivity of coinage metal clusters with different functional groups in the ligand shell, including methylthioether-functionalized phosphanes [9, 10] as well as bromo-[11], nitro- [12], ether- [13] and amino-functionalized thiolates [14].

Metal complexes containing nitrile ligands are well examined systems in coordination chemistry and known for most transition metals [15 – 17]. With regard to the coordinative properties of nitrile groups, the synthesis of transition metal clusters with such functional groups would be desirable, and 4-mercaptobenzonitrile seems to be a promising candidate for achieving this goal. Several complexes with different cyanobenzenealthioketates have been reported, ranging from perfluorinated cyanobenzenealthioketate to dicyanobenzenealthioketate ligands [18 – 24], whereas in most cases the nitrile groups remained uncoordinated.

Recently, we investigated the synthesis, physical properties and reactivity of phosphane-stabilized silver clusters with 4-cyanobenzenealthioketate as a ligand [25]. Depending on the reaction conditions, silver thiolate clusters react either under loss of the phosphane ligand, decompose under formation of the phosphane-stabilized silver halides or undergo complete rearrangement. Herein we present our attempts to synthesize the corresponding copper clusters.

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Results and Discussion

Synthesis of \([\text{Cu}_{40}\text{Se}_{16}(\text{S-C}_6\text{H}_4\text{-CN})_8(\text{dppm})_8]\) (I)

Initially, the synthesis of small nitrile-functionalized copper thiolate clusters was intended by the reaction of CuOAc with 4-mercaptobenzonitrile in the presence of tertiary phosphanes. In contrast to the results obtained with silver [25], the variation of the stoichiometry, the tertiary phosphate, the solvent and other reaction parameters such as temperature, in these reactions usually resulted in the quantitative formation of insoluble yellow precipitates, which are assumed to be oligomeric or even polymeric copper thiolates. The low solubility in common organic solvents and the yellow color, which did not change as a function of time, allowed for slow crystallization of the reaction products. Thus, brown crystals of \([\text{Cu}_{40}\text{Se}_{16}(\text{S-C}_6\text{H}_4\text{-CN})_8(\text{dppm})_8]\) (I), suitable for single-crystal X-ray diffraction, could be isolated when a 1:1 mixture of \(p\)-NC-C\(_6\)H\(_4\)-SH and Se(SiMe\(_3\))\(_2\) was added to a suspension of CuOAc and dppm at \(-30^\circ\text{C}\) (Scheme 1, dppm = bis(diphenylphosphino)methane). The IR spectrum of I, measured from a KBr pellet, exhibits a strong band at 2218 cm\(^{-1}\), assignable to the free nitrile group of the coordinated phenyl thiolate ligand.

Crystal structure of \([\text{Cu}_{40}\text{Se}_{16}(\text{S-C}_6\text{H}_4\text{-CN})_8(\text{dppm})_8]\) (I)

The centrosymmetric cluster I (Fig. 1) which contains 40 copper atoms crystallizes in the monoclinic space group \(P2_1/n\) with two molecules per unit cell and half a molecule in the asymmetric unit. Furthermore six THF molecules have been refined [26]. Crystallographic data and refinement details are summarized in Table 1; Table 2 lists selected bond lengths and angles.

The chalcogen substructure is built up of 16 selenium and eight sulfur atoms forming two parallel hexagonal layers. These are stacked in an \(ab\) sequence representing a small cutout of a close packed structure. (Fig. 1, c and d). A similar arrangement of chalcogen atoms was observed in \([\text{Cu}_{30}\text{Se}_{24}(\text{S-thiaz})_2(\text{dppm})_{10}]\) and \([\text{Cu}_{38}\text{Se}_{24}(\text{S-thiaz})_2(\text{dppm})_{10}]\) (HS-thiaz = 2-mercaptothiazoline) [27]. In these two compounds the chalcogen substructure consists of 24 selenium atoms, which are arranged in an analogous way like the 16 selenium and 8 sulfur atoms in I. Since the thiolate ligands in I contribute one negative charge and the selenide ligands two, only 40 copper(I) ions are required for the charge balance to result in a neutral cluster.

Of the 40 copper atoms in I, 24 occupy either linear (Cu1, Cu2), trigonal-planar or tetrahedral sites inside the chalcogen substructure. However, it is not possible to give unequivocal coordination numbers in all cases, as most of the copper atoms do not occupy the ideal positions of their coordination polyhedra. In general, the linearly coordinated atoms show a shift towards a third chalcogen atom (e.g. Cu1 is shifted towards Se5′, 3.161 Å); the trigonal-planar coordinated atoms either have a tendency to a linear coordination with two short and one long Cu–E bond, or they are shifted out of the trigonal plane in direction of a fourth selenium atom; for tetrahedral coordination there is a tendency towards a trigonal prismatic surrounding. Cu3–Cu8 and their symmetry equivalents have distorted trigonal-planar environments by three selenium atoms and one phosphorus atom (Cu16–Cu20 and symmetry equivalents; Cu–Se: 2.199 – 2.393 Å). Cu12 and Cu12’ are tetrahedrally coordinated by one selenium atom and three sulfur atoms (Cu–Se: 2.579 Å, Cu–S: 2.310 – 2.540 Å). The remaining copper atoms have either a distorted trigonal-planar environment of two chalcogen atoms and one phosphorus atom (Cu13–Cu15 and symmetry equivalents; Cu–Se: 2.430 – 2.503 Å, Cu–S: 2.366 Å) or a distorted tetrahedral environment of three chalcogen atoms and one phosphorus atom (Cu16–Cu20 and
symmetry equivalents; Cu–Se: 2.458 – 2.942 Å, Cu–S: 2.376 – 2.411 Å). The copper-phosphorus distances are with 2.215 – 2.262 Å in the expected range. The selenide ligands in 1 are either acting as $\mu_5$-bridges (Se2, Se5, Se6, Se7 and symmetry equivalents) or $\mu_6$-bridges to the copper atoms (Se1, Se3, Se4, Se8 and symmetry equivalents), while the coordination mode of the sulfur atoms of the thiolate ligands is ranging from $\mu_2$- (S2 and S2') to $\mu_3$- (S1, S1', S4 and S4') and $\mu_4$-bridging (S3 and S3'). In accordance with the observations made for nitrile-functionalized silver chalcogenide clusters, the nitrile groups in compound 1 remain uncoordinated (Fig. 1b) [25]. However, the observed yellow insoluble
precipitates obtained from reactions with various other phosphines and different ratios of the starting materials suggest that mainly polymeric copper thiolates are formed in which the S-C\textsubscript{6}H\textsubscript{4}-CN ligands likely act as bridging ligands.

**Conclusion**

In conclusion, we describe an unusual copper chalcogenide cluster with nitrile groups in the ligand shell. In contrast to the reactivity observed for silver(I) salts with p-NC-C\textsubscript{6}H\textsubscript{4}-SH, the isolation of a phosphane-stabilized copper thiolate with this ligand alone was not possible. Small amounts of the thiol and of Se(SiMe\textsubscript{3})\textsubscript{2} had to be employed in the described synthesis. I exhibits a disc-like structure of the heavy atom framework. The arrangement of the chalcogen atoms in I is similar to a close packing and can be described as two parallel layers with an ab stacking sequence. The nitrile groups of the thiolate groups remain uncoordinated.

**Experimental Section**

**Materials and methods**

Due to the high oxygen and moisture sensitivity of the compounds used, all reactions were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. THF was dried with sodium benzophenone. Copper(I) acetate [28], Se(SiMe\textsubscript{3})\textsubscript{2} [29, 30], dpmp [31] and 4-cyanothiophenol [32] were prepared according to literature procedures. IR spectra were obtained from KBr pellets with a Brucker IFS instrument. Elemental analyses were performed on an Elementar VarioEL V2.10 Elemental Analyzer.

**X-Ray crystallography**

Crystals were removed from the reaction flask under a stream of nitrogen gas and immediately covered with perfluoropolyether oil (Riedel-de Haën). A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream. The data were collected with a Stoe IPDS II diffractometer using Mo\textsubscript{Kα} = 0.71073 Å radiation. Structure solution and refinement against F\textsuperscript{2} were carried out using SHELXS and SHELXL software [33]. Twelve uncoordinated THF molecules have been refined with a reasonable model. Thus the SQUEEZE algorithm of the program package PLATON [34] was applied to calculate the empty voids and to delete the diffuse diffraction. Crystallographic data of compound I are summarized in Table 1.

Table 2. Ranges of bond lengths (Å), and angles (deg) for I with estimated standard deviations in parentheses; Cu\textsubscript{dist}, Cu\textsubscript{tet}, Cu\textsubscript{tet}: copper atoms with a distorted linear (Cu1 and Cu2), trigonal-planar (Cu3–Cu11, Cu13–Cu15) or tetrahedral (Cu12, Cu16–Cu20) coordination sphere, respectively.

<table>
<thead>
<tr>
<th>Distances</th>
<th>Cu\textsubscript{dist}–Se</th>
<th>2.308(2) – 2.442(2)</th>
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<tbody>
<tr>
<td>Cu\textsubscript{tet}–Se</td>
<td>2.382(2) – 2.751(2)</td>
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<tr>
<td>Cu\textsubscript{tet}–S</td>
<td>2.199(3) – 2.393(3)</td>
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<tr>
<td>Cu\textsubscript{tet}–Se</td>
<td>2.458(2) – 2.942(2)</td>
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<tr>
<td>Cu\textsubscript{tet}–S</td>
<td>2.376(3) – 2.411(3)</td>
<td></td>
</tr>
<tr>
<td>Cu–μ1\textsubscript{4}–Se</td>
<td>2.308(2) – 2.630(2)</td>
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<tr>
<td>Cu–μ4–μ2–Se</td>
<td>2.374(2) – 2.751(2)</td>
<td></td>
</tr>
<tr>
<td>Cu–P</td>
<td>2.215(3) – 2.262(2)</td>
<td></td>
</tr>
<tr>
<td>Angles</td>
<td>Se–Cu\textsubscript{tet}–Se</td>
<td>122.03(6) – 166.53(7)</td>
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<tr>
<td></td>
<td>Se–Cu\textsubscript{dist}–Se</td>
<td>101.39(5) – 140.11(6)</td>
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<td></td>
<td>S–Cu\textsubscript{dist}–Se</td>
<td>98.81(7) – 133.34(9)</td>
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<tr>
<td></td>
<td>S–Cu\textsubscript{tet}–S</td>
<td>119.55(9) – 126.4(1)</td>
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<tr>
<td></td>
<td>Se–Cu\textsubscript{dist}–S</td>
<td>101.80(5) – 116.74(5)</td>
</tr>
<tr>
<td></td>
<td>S–Cu\textsubscript{dist}–S</td>
<td>95.89(7) – 124.36(8)</td>
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<td></td>
<td>S–Cu\textsubscript{tet}–S</td>
<td>97.27(9) – 116.3(1)</td>
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<td>P–Cu\textsubscript{dist}–S</td>
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<tr>
<td></td>
<td>P–Cu\textsubscript{dist}–S</td>
<td>111.9(1) – 118.8(1)</td>
</tr>
</tbody>
</table>

Crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Synthesis of \([\text{Cu}_4\text{Se}_{10}(\text{S-C}_6\text{H}_4\text{-CN})_6(\text{dppm})]_x\) (I)

\(p\)-NC-C\(_6\)H\(_4\)-SH (45 mg, 0.33 mmol) and Se(SiMe\(_3\))\(_2\) (0.08 mL, 0.33 mmol) were added to a suspension of CuOAc (125 mg, 1.00 mmol) and dppm (94 mg, 0.24 mmol) in 20 mL THF at \(-30^\circ\)C. The reaction mixture was allowed to reach ambient temperature within 16 h, and the resulting brown suspension was filtered. After two weeks brown crystals could be isolated from the filtrate, which were dried under vacuum. Yield: 23 mg (2.9 \times 10^{-3} \text{mmol}, 14\% based on the limiting reagent Se(SiMe\(_3\))\(_2\)). – Anal. for C\(_{35}\)H\(_{29}\)N\(_2\)P\(_4\)O\(_{16}\)Se\(_{16}\)Cu\(_{4}\) (7953.74 g mol\(^{-1}\)): calcd. C 38.66, H 2.64, N 1.41%; found C 38.33, H 2.58, N 1.15%. –

IR (KBr): \(\nu = 3047\) (m), 2925 (m), 2853 (m), 2536 (w), 2352 (w), 2218 (s, \(\nu_{\text{CN}}\)), 1955 (w), 1893 (w), 1809 (w), 1648 (w), 1582 (s), 1477 (s), 1435 (s), 1397 (m), 1362 (m), 1307 (m), 1246 (m), 1186 (w), 1174 (m), 1158 (m), 1098 (s), 1079 (s), 1026 (m), 1015 (m), 999 (m), 916 (w), 822 (w), 777 (m), 736 (s), 713 (m), 692 (s), 617 (w), 584 (w), 544 (m), 516 (s), 473 (m), 445 cm\(^{-1}\) (w).

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