



# Dual graphs realized in the compounds di- $\mu_3$ -4-mercaptopyridine catena-di- $\mu_2$ -iodo-di- $\mu_3$ -iodo- $\mu_4$ -iodo penta copper(I) and di- $\mu_3$ -4-mercaptopyridine-di-catena-iodo-di- $\mu_3$ -iodo tri copper(I)

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## ABSTRACT

Two compounds, [Cu<sub>5</sub>I<sub>5</sub>](SNC<sub>5</sub>H<sub>4</sub>)<sub>2</sub> [i] and [Cu<sub>3</sub>I<sub>3</sub>](SNC<sub>5</sub>H<sub>4</sub>)<sub>2</sub> [ii], were synthesized under hydrothermal conditions and the crystal structures were solved. Both compounds crystallized in space group I41/a. The iodide and the sulphur from mercaptopyridine are connected to copper atom, giving the copper atoms tetrahedral coordination geometry. The pyridine end of the organic moiety is non-bonding and fills the empty space around the tetrahedra formed from copper, sulphur and iodide.

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## 1. Introduction

Because divalent Cu(II) readily oxidizes iodide to iodine, Cu(II) occurs together with I<sup>-</sup> only when the two species are separated, like in catena-(bis(ethylenediamine)-copper(ii) tetrakis( $\mu_2$ -iodo)-di-copper(i)) [1]. Instead, the structural flexibility of Cu-I based systems is enabled by other factors: Cu accepts three and four coordination as well as intermediate solutions (as evidenced by disorder), the relative size that allows for the simultaneous occupancy of Cu in neighbouring, edge-sharing (and even face sharing) I<sub>4</sub> tetrahedra and the ability of I to act as a terminal or  $\mu_i$ -bridging ( $2 \leq i \leq 6$ ) ligand [2]. Further flexibility is offered by using soft donors such as N or S species that bond to Cu. Cu-I cluster compounds are well known for their prominent temperature dependent luminescence, and the title compounds are part of a larger study aimed at identifying new luminophores. Neither of the title compounds do however show any luminescence.

The general geometry of the Cu-I species is controlled by the presence of counter ions that impart constraints on the system. For naked Cu<sub>x</sub>I<sub>y</sub><sup>(y-x)-</sup> clusters the general tendency is that small counter ions tend to generate linear infinite species, and beyond a certain size, the Cu<sub>x</sub>I<sub>y</sub><sup>(y-x)-</sup> complexes break apart to form discrete clusters that grow in size with the size of the counter ion. There are also examples of intercalation-type compounds where neutral

sheets of composition CuI are interleaved with organic layers [3]. The situation for N based donors is essentially the same, although different effect may be achieved by the use of bulky groups attached to the donor. Regardless of this, a survey of structures from the CCDC shows that N donors tend to be terminal, and bridging occurs in principle only for polydentate ligands [4]. With sulphur, the situation is quite different. For large species, again, terminal coordination dominates, but for small species such as mercaptan and certainly for pure sulphide, S tends to be bridging [5]. For the pure sulphide, the presence of other, more highly charged metal centres is normally needed for charge balance, but small thio-compounds are capable of decorating pure Cu<sub>x</sub>I<sub>y</sub><sup>(y-x)-</sup> species, and to generate new connectivities. In this paper we present a new example of the interaction between such a small sulphur species, 4-mercaptopyridine, with CuI namely di- $\mu_3$ -4-mercaptopyridine catena-di- $\mu_2$ -iodo-di- $\mu_3$ -iodo- $\mu_4$ -iodo penta copper(I) [I] and di- $\mu_3$ -4-mercaptopyridine-di-catena-iodo-di- $\mu_3$ -iodo tri copper(I) [II].

## 2. Experimental

### 2.1. Synthesis

Copper (II) oxide powder, copper powder, 4-mercaptopyridine and hydroiodic acid were mixed in an autoclave (Parr Instruments Acid digestion Bomb model 276Ac, teflon lined 304 stainless steel,

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45 ml capacity) and heated under hydrothermal conditions. From both syntheses the product was red crystals. These were washed with deionized water and stored at room temperature. Conf. Table 1 for details.

## 2.2. Single crystal X ray diffraction

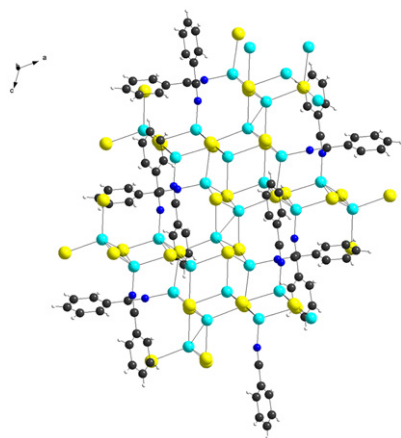
From previous experience, the structures of inorganic hybrid Cu–I compounds tends to be difficult to refine from room temperature data due to disorder. Therefore both measurements were performed at 100 K. Suitable single crystals for single crystal X-ray measurements were chosen based on their shape and appearance, and were attached to a glass fiber. Data collection at 100 K was carried out with an Oxford diffraction XCalibur3 system using MoKa radiation, with graphite monochromator. Reduction of data and absorption correction was performed using the software package CrysAlis Red [6].

## 2.3. Structural solution

The space group for both compounds is uniquely indicated by the Laue symmetry  $4/m$  and the systematic extinction conditions  $hkl, h+k+l=2n; hk0, h=2n, k=2n; 00l, l=4n$  as  $I4_1/a$ , and Charge Flipping [7] as implemented in Superflip [8] directly produces the heavy atom positions, and most of the C positions. Refinement using Jana2000 [9] was straight forward, and in the final model all non-hydrogen atoms were refined anisotropically. Hydrogen was refined in a riding model. In [I], one Cu position, Cu3 that was associated with a large anisotropic thermal parameter was closely inspected and deemed better modeled by a split position, while in [II] the splitting of one Cu position, Cu2, was generated directly in

**Table 1**  
Synthesis details for both compounds.

	Compound I	Compound II
<b>Cu [mmol]</b>	3.81	3.80
<b>CuO [mmol]</b>	3.83	3.80
<b>4-Mercaptopyrine [mmol]</b>	3.82	12.93
<b>HI [mmol]</b>	7.6	15.2
Temperature [°C]	180	180
Heating time [h]	26	22

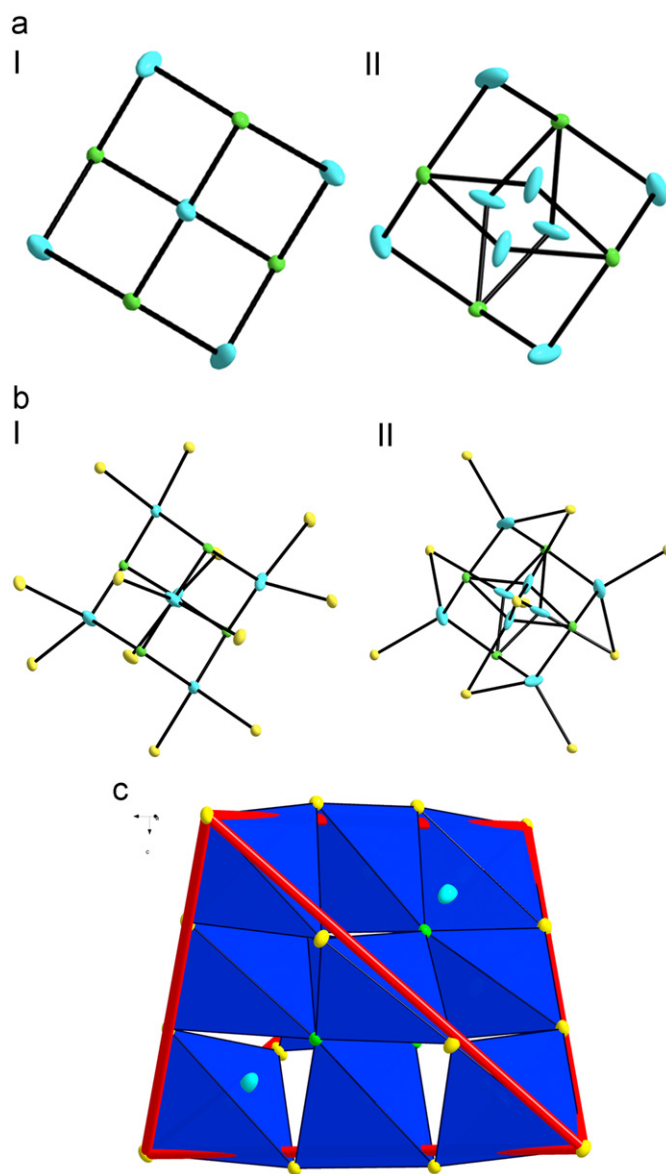


**Fig. 1.** The structure of catena (benzotrinitrile-( $\mu_4$ -iodo)-( $\mu_3$ -iodo)-di-copper(I)) showing the Cu–I network, and the protruding aromatic rings from the benzotrinitrile. Color code S: green, Cu: cyan, I: yellow, C: black, N: blue, H: white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the structural solution. Attempts to resolve the splitting by lowering the space group symmetry were unsuccessful. Final agreements were excellent,  $R/R_w(F^2)=3.6/6.7$  for (I) and  $3.1/9.5$  for (II).

## 3. Results and discussion

It is notable that in systems where an organic species is largely non-bonding with respect to the  $\text{Cu}_x\text{I}_y^{(y-x)-}$  species, or locally attached through a donor–acceptor mechanism that leaves the bulk of the organic species pointing away from the  $\text{Cu}_x\text{I}_y^{(y-x)-}$  cluster, the effect is a separation of the structure into distinct subvolumes reminiscent of the behaviour for amphiphile systems with hydrophilic head groups and hydrophobic tails, or of lone



**Fig. 2.** (a) Comparison between the tetrahedral core of the Cu–I–S network that is formed in (I) and (II) by four sulphur atoms that are each bound to two copper atoms forming a  $\text{Cu}_6\text{S}_4$ -cluster of almost perfect  $T_d$  symmetry, (b)  $\text{Cu}_6\text{S}_4\text{I}_{12}$  cluster showing Cu in tetrahedral coordination  $\text{CuS}_2\text{I}_2$ . There is still nothing in this local arrangement to break the  $T_d$  symmetry and (c)  $T_3$  supertetrahedron with the composition  $\text{Cu}_{10}\text{S}_4\text{I}_{16}$ . Note the protruding Cu atom in the vertex  $\text{CuI}_4$  tetrahedra. This is a split position with ca 1/6 occupancy. The remaining Cu-occupancy for this tetrahedron is in the central position.

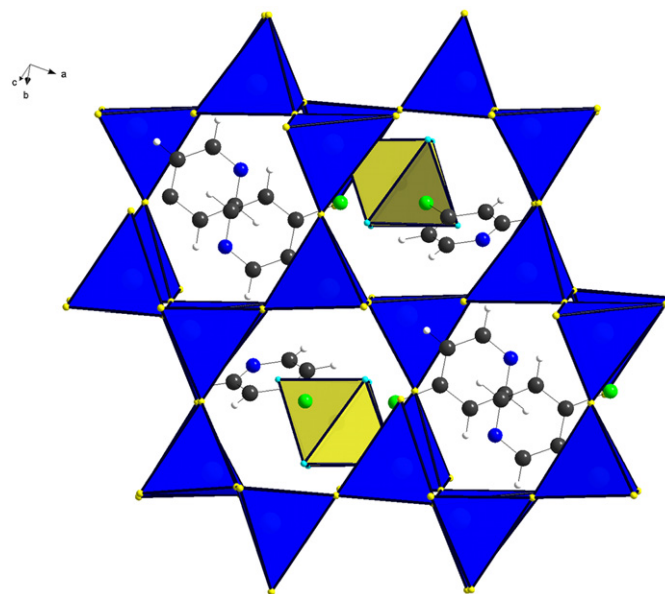
pair structures where individual atoms display bonding and non-bonding directions. This is unsurprising. After all, such systems constitute two separate modes of interaction, and there is a tendency to phase-separation on a local scale, which is counteracted by direct bonding in the case of amphiphile species or by charge neutrality in the case of Coulombically attracted systems. The geometry of such systems has been the subject of much analysis in the case of amphiphiles, and quite clearly the same analysis applies to any system where distinct subsystems may be identified. An important difference between amphiphile systems and hybrid organic–inorganic systems is the strong and often directional interaction within the inorganic subspace of the structure. This leads to a much more constrained configuration space than for true amphiphile systems where the weak intramolecular bonding allows both the hydrophilic head groups and the hydrophobic tails substantial configurational freedom on a short time scale. Due to the great flexibility of Cu–I interactions, the hybrid organic–inorganic systems based on  $\text{Cu}_x\text{I}_y^{(y-x)-}$  species are among those that most closely resemble the true amphiphile systems, and it is instructive to consider how such systems order to accommodate the rather lax bonding requirements of such a system. Those requirements are quite simple: Copper may adopt planar trigonal coordination, tetrahedral coordination, or a mongrel coordination somewhere between the two, but copper may never protrude outside the convex hull of the surrounding bonding network made up by iodide and whatever soft donor ligand that is used. This simply means that copper is excluded from the non-bonded region of the structure. Iodide on the other hand preferably sits on the interface between the bonding and non-bonding region of the structure. Iodide may coordinate to copper in a terminal fashion, or as a  $\mu_x$ -bonded ligand, but it is rarely found completely enveloped by copper in hybrid systems. Other ligands, such as N- and S-based donors, also define the interface between the bonding and the non-bonding region. The donor end of the molecule is part of the bonded network while the rest of the molecule simply protrudes into the non-bonding region. These simple constraints set up geometrical rules for the systems.

Starting with the naked species, the interaction between the organic and the inorganic part is purely Coulombic.  $\text{Cu}_x\text{I}_y^{(y-x)-}$  units grow to a certain size mainly determined by the size of the counter ion. Large counter ions tend to exceed a 3-dimensional percolation threshold and as a result, the  $\text{Cu}_x\text{I}_y^{(y-x)-}$

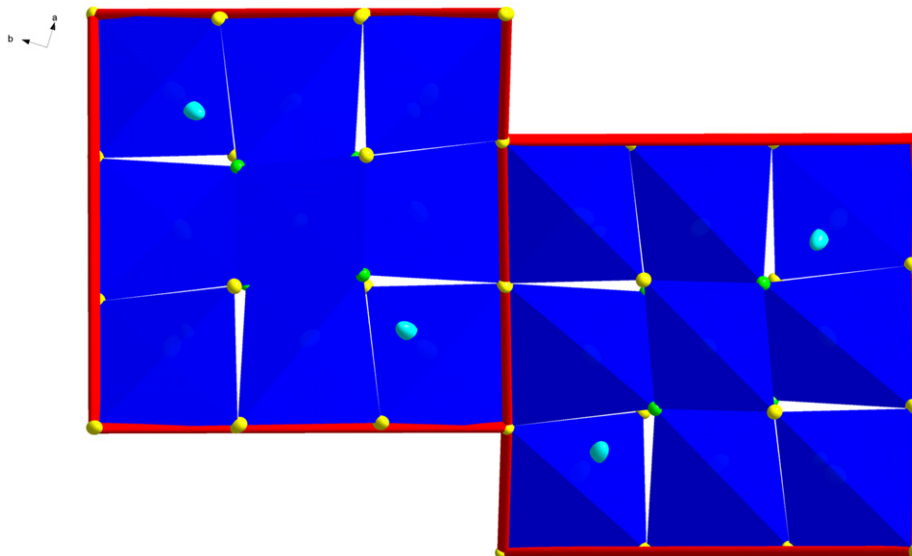
units in such systems are finite objects dispersed in a continuous organic matrix. The cluster presents a non-bonding iodide surface to the organic part of the structure. This is entirely analogous to the formation of spherical micelles in amphiphile systems.

If the size of the organic counter ion is reduced, the interface between organic and inorganic regions needs to increase to counteract charge separation. This can lead to the formation of very small, discrete  $\text{Cu}_x\text{I}_y^{(y-x)-}$  units such as the  $\text{Cu}_2\text{I}_4^{2-}$  species [2,10], but often the result is instead one dimensionally infinite arrangements [11]. Again the analogy with amphiphiles is simple. We have the formation of a typical hexagonal phase with cylindrical micelles.

Molecular species that pack well in sheets may be conducive to planar arrangements, and there are reports of such systems



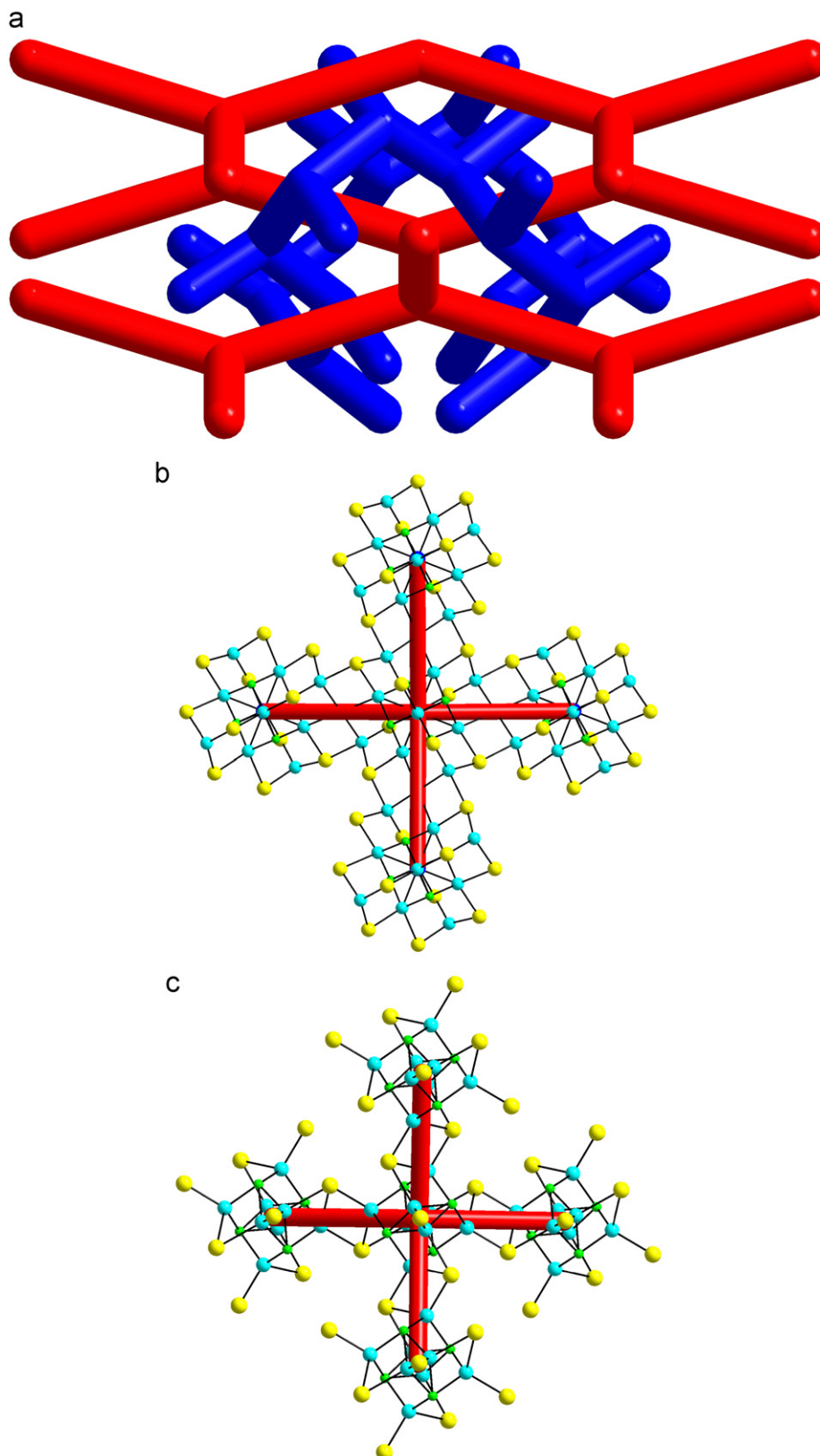
**Fig. 4.** Bounded projection of the structure of the title compound represented by the formal network formed by the iodide atoms. Looking down rows of face-sharing truncated tetrahedral cavities, it is clear that these contain  $\text{Cu}_6\text{S}_4$  units or pyridine rings.



**Fig. 3.** Misaligned edge sharing between two  $T_3$  tetrahedra. Each  $T_3$  unit shares partial edges with four surrounding units.

with naked  $\text{Cu}_x\text{I}_y^{(y-x)-}$  sheets, but so far the examples are few. A probable cause of this is the limited flexibility of such a sheet [12]. There are far more examples of such structures with compound

sheets terminated by a non-iodine ligand and in such cases the  $\text{Cu}_x\text{I}_y\text{L}_z^{(y-x)-}$  sheets often undulate [13]. The analogy with lamellar phases is obvious.



**Fig. 5.** (a) The interpenetrating dual graph of the inorganic network generated from the centres of the  $\text{Cu}_6\text{S}_4$  units (red) and the organic subspace generated from the centres of the aromatic rings (blue), (b) The cluster structure of compound (I) forming the inorganic subspace that defines the diamond network and (c) The cluster structure of compound (II). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



The final class of archetypical amphiphile system is constituted by the bi-continuous phases. One example of such a system is [14] where the nitrogen of benzonitrile acts as a terminator in a 3-dimensionally connected network of overall composition  $\text{Cu}_2\text{I}_2\text{N}$  and the aromatic rings fill a contiguous subspace (Fig. 1) and the topology of a system such as this may be described as a pair of complementary, interpenetrating graphs. The structures presented in this paper are two more examples of this class of bi-continuous phases. One part of the structures is bonding and consists of copper, iodide and the sulphur from the 4-mercapto pyridine, and the “non-bonding” part of the structure consists of the rest of the 4-mercaptopyridine molecule. The arrangement is deceptively simple: in compound (I) four 4-mercaptopyridine sulphur atoms come together in a tetrahedral centre where each sulphur bonds to three copper atoms forming a  $\text{Cu}_6\text{S}_4$  core (Fig. 2a). Each copper atom is also bound to two iodides, yielding a tetrahedral environment for all copper (Fig. 2b). The cluster is completed by four further copper positions and four further iodide positions. Those outer copper positions are exclusively bonded to iodide. The entire complex is composed by ten Cu-centred tetrahedra sharing vertices to build a  $T_3$ -supertetrahedron (Fig. 2c). Each such  $T_3$  unit shares four out of six edges with surrounding  $T_3$  units, and this connectivity lowers the symmetry of the ensemble from  $T_d$  to  $C_4$ . The edge sharing is imperfect in that only two out of three sub-tetrahedra of the edge of the  $T_3$  unit are joined. This leads to a misalignment of the edge-sharing  $T_3$  units with respect to each other (Fig. 3). The only copper position that is not directly bonded to S is Cu3. This is also the position that is disordered over two positions with an occupancy of ca 5/6 in the centre of an  $I_4$  tetrahedron, and about 1/6 on the face of that same tetrahedron (Conf. Fig. 2c).

An alternative view of the structure of compound (I) is that the iodides of the structure form an arrangement topologically identical to that of Cu in the cubic Laves phase  $\text{MgCu}_2$  and that the  $\text{Cu}_6\text{S}_4$  cluster occupies part of the positions of the Mg atom in that structure, that is in the large cavity surrounded by a truncated tetrahedron. The ratio of Mg to Cu in the Laves phase indicates that there should be one truncated tetrahedral cavity in the structure for every two iodides, and the stoichiometry of the compound is  $\text{Cu}_{10}\text{I}_{10}(\text{SC}_5\text{H}_4)_4$  implying that only one fifth of the cavities can be filled by the  $\text{Cu}_6\text{S}_4$  units. The remaining four fifths of the cavities are inhabited by the pyridine ring that protrudes from the  $\text{Cu}_6\text{S}_4$  units into the four surrounding cavities (Fig. 4). The I-arrangement allows perfect  $T_d$  symmetry, but the filling of the cavities does not.

Compound (II) can be described similarly. This compound also consists of a  $\text{Cu}_6\text{S}_4$  core (Fig. 2a), where each S atom is coordinated to three Cu atoms. The  $\text{Cu}_6\text{S}_4$  units are connected via double bridges of  $\text{I}^-$  ions forming a network. (Fig. 2b). Again,

**Table 2**  
Overview of both compounds.

	Compound I	Compound II
<b>Composition</b>	$\text{Cu}_5\text{I}_5\text{S}_2\text{N}_2\text{C}_{10}\text{H}_8$	$\text{Cu}_3\text{I}_3\text{S}_2\text{N}_2\text{C}_{10}\text{H}_8$
<b>Crystal system</b>	Tetragonal	Tetragonal
<b>Space group</b>	$I4_1/a$	$I4_1/a$
<b>Color</b>	Colorless	Red
<b>a [Å]</b>	19.0120(4)	15.6543(1)
<b>c [Å]</b>	11.7253(4)	13.5978(2)
<b>V [Å<sup>3</sup>]</b>	4238.2(2)	3332.24(6)
<b>Z</b>	8	8
<b><math>\mu</math> [mm<sup>-1</sup>]</b>	12.42	9.59
<b>Cu–I [Å]</b>	2.440(7)–2.9095(7)	2.560(2)–2.9746(14)
<b>Cu–S [Å]</b>	2.2636(12)–2.3158(12)	2.258(3)–2.308(3)

similar to in the case of compound (I), the organic part is non-bonding and fills the cavities in this network. Although the connections between the  $\text{Cu}_6\text{S}_4$  units are different in the two compounds, and the composition of the inorganic networks differs markedly, the bonded networks themselves are topologically equivalent. They each form a diamond type graph. The dual of this graph is the loci of the non-bonding part of the structure. It is an interesting 3-connected system built from the interconnection of  $4_1$  and  $4_3$  helices. This graph is uninodal, but not uniform since there are two distinct kind of connections: within the helices and between them. The complex of the two dual interpenetrating graphs that make up both structures much resembles that of a Nowotny chimney ladder system [15] (Fig. 5).

Table 2 shows an overview of both compounds presented in this paper.

#### 4. Conclusion

The subdivision of a structure into subspaces is an arbitrary one inasmuch that it is not necessarily based on direct interaction. If we decide to look at the structure through subspace glasses, we are bound to find subspaces in it. But the spontaneous segregation of the structure into distinct subspaces is a necessary effect of the bonding (or absence of it) in the system. Non-bonding unit will agglomerate not because they gravitate towards each other, but because of confluent expulsion. To optimize bonding between units that may bond, non-bonding entities are excluded, and this has a strong structure directing effect. The same phenomenon is seen in lone pair element oxyhalides. In these compounds the lone pairs flock together with halide ions in non-bonding subspaces, like micelles in the oxide matrix.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.09.009.

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