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## PAPER

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# Co-crystal synthesis of 2- and 4-mercaptopyridines with thiourea and its analogue, trithiocyanuric acid†

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This article describes the synthesis of four new co-crystals obtained *via* cross-crystallisation of 2- and 4-mercaptopyridines with thiourea and trithiocyanuric acid and examines their crystal structures. The resulting structures are the first four reported co-crystals of mercaptopyridines. In one case, the synthesis resulted in the production of a ternary co-crystal of unexpected composition instead of the desired product and the correct co-crystal needed to be obtained under dark room conditions; interestingly, when separated from solution, all four co-crystal samples were fully light resistant. The crystal state of the four co-crystals is stabilized by several N–H⋯S type hydrogen bonds. Additionally, in the case of thiourea co-crystals, additional short contacts of S⋯S type are also observed. This relatively complicated network of intermolecular interactions is fully characterized herein.

## Introduction

The organosulfur compounds possess a wide spectrum of applications in industry, pharmacology, biology, agrochemistry and synthetic organic chemistry, among others, and their chemistry and application have played significant roles in recent scientific advances. For example, mercaptopyridine derivatives are known for their antimicrobial, antifungal, and alkylation properties[1–4] and are used as effective ligands in the syntheses of transition metal complexes.[5] In contrast, thiourea demonstrates broad antiviral[6] and antibacterial[7] activities and has been reported to exhibit anticancer activity and inhibit HIV reverse transcriptase activity.[8] Moreover, one form of trithiocyanuric acid, which can be considered a result of cyclic condensation of three thiourea molecules, has been used in plating processes and anticorrosion agents,[9] and to remove the palladium formed during the production of drugs.[10,11] More information about the application, co-crystal synthesis and interactions of these three chemical species, as well as various theoretical studies, can be found in our earlier works.[12–17]

These previous papers also include a search for thiourea and trithiocyanuric acid crystals in the Crystal Structure

Database (CSD).[18] The search revealed only a few depositions of *para*- and *ortho*-mercaptopyridines, two of which were crystals of pure 4-mercaptopyridine (refcode: AKOVOL;[19] AKOVOL01;[20] AKOVOL02;[21] AKOVOL03;[21] AKOVOL04 (ref. 22)) and 2-mercaptopyridine (refcode: PYRIDS;[23] PYRIDS01;[24] PYRIDS02;[25] PYRIDS03;[26] PYRIDS11 (ref. 25)). Apart from these two entries, only three metal organic crystals containing 2-mercaptopyridine could be found (refcode: DAHTIP;[27] JEHTIC;[28] VIJNEH;[29] VIJNEH01 (ref. 30)). Clearly knowledge regarding the crystallography of mercaptopyridines is still in its infant stage. The present paper provides the first report of four co-crystal structures containing mercaptopyridines.

This paper reports the continuation of our studies on co-crystal synthesis with the use of thiourea and its analogue, trithiocyanuric acid, as components.[12,14–16] It employs a cross-crystallization approach (see graphical abstract) to obtain samples of four new co-crystals (**I–IV**) of sufficient quality to allow X-ray single-crystal analysis (Scheme 1).

## Results and discussion

In general, the synthesis of the reported co-crystals was relatively uncomplicated and spontaneous, with the important exception of **III**, as will be discussed in this section. Briefly, for each of the desired co-crystals, the components were dissolved in a water-ethanol mixture, and the solvents were removed by slow evaporation. From the remaining solid-state material, single crystals were selected for X-ray analysis. The obtained co-crystals were of good quality, and high-quality experimental data could be

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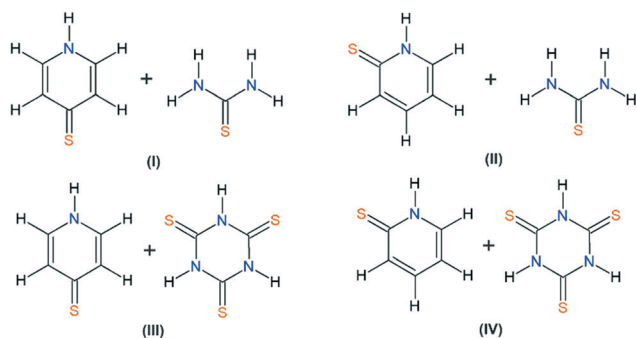


**Scheme 1** The molecular formulas of I–IV co-crystals (I – 4-mercaptopyridine and thiourea; II – 2-mercaptopyridine and thiourea; III – 4-mercaptopyridine and trithiocyanuric acid; IV – 2-mercaptopyridine and trithiocyanuric acid).

obtained, confirming the successful co-crystallization of **I, II** and **IV**. See Table 1 (with standard X-ray experimental data).

The only exception was noted for **III**, for which a very interesting and relatively rare ternary co-crystal was repeatedly obtained. This molecule consisted of two trithiocyanuric acid molecules, two bis(pyridin-4-yl) sulfide molecules and 1,4-bis(pyridin-4-yl)tetrasulane, namely, 1,3,5-triazinane-2,4,6-trithione–4-(pyridin-4-ylsulfan-yl)pyridine–1,4-bis(pyridin-4-yl)tetrasulfane in a 2 : 2 : 1 stoichiometry. This single crystal structure has been published elsewhere.[12]

Although the obtained ternary co-crystal itself was a very interesting result, it did not suit our series of desired co-crystals. Any attempt to obtain the crystal sample of **III** was unsuccessful and always resulted in the production of a ternary co-crystal. Finally, we learned that hydroxyl radicals may be generated from mercaptopyridine *N*-oxides by photolysis, leading *inter alia* to the formation of *n*-sulfides.[31] Since our attempts to create **III** resulted in both the formation of *n*-sulfides (in reported ternary co-crystals *n* was equal to 1 and 4) and α-sulfur, it was probable that our substrates, mixed in solution, undergo such decomposition. Therefore, the entire experiment was repeated using only a faint red light source in the laboratory, finally allowing the desired co-crystal of **III** to be obtained. Interestingly, after the solvents evaporated, the obtained crystalline material was stable under standard conditions, including daylight. The crystallization process applied in our experiments is detailed in the experimental section.

In our four new co-crystals **I–IV**, all the components co-crystallise in a 1 : 1 stoichiometry. Molecular graphs, with atoms represented by thermal ellipsoids, can be found in Fig. 1. As can be seen, in crystal structures **I–IV**, the

**Table 1** Details of the crystal structure determination

| Structure | I | II | III | IV |
|---|---|---|---|---|
| Empirical formula | $C_5H_5NS\cdot CH_4N_2S$ | $C_5H_5NS\cdot CH_4N_2S$ | $C_5H_5NS\cdot C_3H_3N_3S_3$ | $C_5H_5NS\cdot C_3H_3N_3S_3$ |
| Formula weight | 187.28 | 187.28 | 288.42 | 288.42 |
| Temperature [K] | 298 | 298 | 298 | 298 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Triclinic |
| Space group | $Pbca$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| $a$ [Å] | 11.4353(2) | 10.5170(2) | 4.1140(1) | 4.1956(1) |
| $b$ [Å] | 8.3568(1) | 10.8672(1) | 12.3715(1) | 10.848(3) |
| $c$ [Å] | 18.7182(2) | 8.4287(1) | 23.8214(2) | 13.5301(4) |
| $\alpha$ [°] | 90 | 90 | 90 | 99(2) |
| $\beta$ [°] | 90 | 107(2) | 90(1) | 93(2) |
| $\gamma$ [°] | 90 | 90 | 90 | 93(2) |
| Volume [Å³] | 1788.76(4) | 916.59(2) | 1212.40(3) | 605.53(3) |
| Z | 8 | 4 | 4 | 2 |
| $\rho_{calc}$ [g cm$^{-3}$] | 1.391 | 1.357 | 1.580 | 1.582 |
| $\mu$ [mm$^1$] | 4.922 | 4.802 | 7.026 | 7.034 |
| $F(000)$ | 784.0 | 392.0 | 592.0 | 296.0 |
| Crystal size [mm³] | 0.262 × 0.069 × 0.048 | 0.355 × 0.316 × 0.143 | 0.056 × 0.033 × 0.027 | 0.520 × 0.050 × 0.045 |
| Radiation | Cu Kα | Cu Kα | Cu Kα | Cu Kα |
| 2Θ range for data collection [°] | 9.45 to 136.978 | 8.836 to 136.988 | 7.422 to 137 | 6.632 to 136.962 |
| Index ranges | $-13 \leq h \leq 13$ | $-12 \leq h \leq 12$ | $-4 \leq h \leq 4$ | $-4 \leq h \leq 5$ |
| | $-8 \leq k \leq 9$ | $-13 \leq k \leq 11$ | $-14 \leq k \leq 14$ | $-13 \leq k \leq 12$ |
| | $-22 \leq l \leq 22$ | $-10 \leq l \leq 6$ | $-28 \leq l \leq 28$ | $-16 \leq l \leq 16$ |
| Reflections collected | 13 805 | 5349 | 52 585 | 5954 |
| Independent reflections | 1630 | 1685 | 2210 | 2201 |
| | $R_{int} = 0.0601$ | $R_{int} = 0.0308$ | $R_{int} = 0.0524$ | $R_{int} = 0.0365$ |
| | $R_{sigma} = 0.0251$ | $R_{sigma} = 0.0306$ | $R_{sigma} = 0.0161$ | $R_{sigma} = 0.0398$ |
| Data/restraints/parameters | 1630/0/120 | 1685/0/121 | 2210/0/162 | 2201/0/162 |
| Goodness-of-fit on $F^2$ | 1.076 | 1.089 | 1.054 | 1.061 |
| Final R indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0412$ | $R_1 = 0.0383$ | $R_1 = 0.0258$ | $R_1 = 0.0312$ |
| | $wR_2 = 0.1197$ | $wR_2 = 0.1085$ | $wR_2 = 0.0622$ | $wR_2 = 0.0809$ |
| Final R indexes [all data] | $R_1 = 0.0440$ | $R_1 = 0.0412$ | $R_1 = 0.0282$ | $R_1 = 0.0350$ |
| | $wR_2 = 0.1229$ | $wR_2 = 0.1115$ | $wR_2 = 0.0633$ | $wR_2 = 0.0832$ |
| Largest diff. peak/hole [e Å$^{-3}$] | 0.37/−0.34 | 0.34/−0.21 | 0.26/−0.21 | 0.30/−0.27 |
| CCDC deposit number | 2165358 | 2165361 | 2165360 | 2165359 |
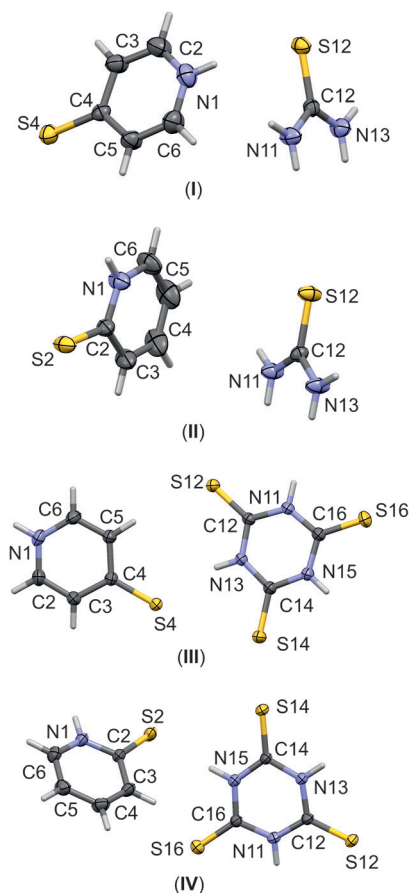
**Fig. 1** The labelling schemes of molecular components of I–IV co-crystals. The anisotropic displacement parameters of non-hydrogen atoms are drawn as ellipsoids with a 30% probability level.

mercaptopyridine derivatives adopt an N-protonated form, that is, the sulfur analogue of pyridone tautomers, *i.e.* pyridinethione. This appears to be the standard arrangement for the crystalline state,[12] possibly due to the fact that this tautomeric form is characterized by N–H⋯A type hydrogen bonds, which are stronger than the S–H⋯A type.[32,33] However, it must be emphasized that pyridinethione not always is the generally preferred tautomeric form, as the tautomeric preferences of that species depend on a range of factors, including chemical environment (*e.g.*, the type of solvent), the state of matter or even the temperature.[34–38]

A similar observation can be made for trithiocyanuric acid, which, out of four possible forms, also favors the non-aromatic tautomeric form with protonated N atoms, *i.e.*, the all-keto 1,3,5-triazi-nane-2,4,6-trithione tautomer. This issue was recently addressed by a combination of structural analysis of experimental data collected in the CSD[18] and computational studies for representative molecular models.[14,15]

Due to the fact that all the components of co-crystals I–IV possess proton-donating amino groups and potential proton-accepting centers, *e.g.*, N and S atoms, it is reasonable to assume that the key effect stabilizing the crystal state would

be hydrogen bond formation. In fact, this was found to be the case, and the hydrogen bonding network is relatively expanded. Therefore, to systemize the discussion on the intermolecular interactions present in I–IV, it is divided into two parts. The first discusses the interactions formed by molecules of the same type, and the second examines the H-bridges formed between mercaptopyridines and their co-crystal counterparts. The geometric parameters of all discussed interactions are collected in Table 2.

Thiourea, present in co-crystals of I and II, forms chains involving two –NH groups and one S-atom per each molecule, as shown in Fig. 2(a), together with other interactions discussed later. This interaction motif has already been reported[16] for other co-crystals containing thiourea, together with a more comprehensive review of crystal structures stabilized using this hydrogen bonding pattern.

Regarding the hydrogen bonds present in I and II, the calculated H-bridge structural parameters indicate slightly more effective bonding in the case of structure II than structure I, with shorter distances in I (3.418(2) Å and 3.468(2) Å) than in II (3.381(2) Å and 3.402(2) Å) (Table 2). Similarly, the interacting thiourea molecules are closer to a planar arrangement in II than in I. The appropriate dihedral angles are 18(2)° and 0(2)° for I and II, respectively. This hydrogen bonding motif can be described as a C(6) second order graph and an $R_2^2(8)$ first order graph according to the graph set method.

The trithiocyanuric acid present in crystals of III and IV, *i.e.*, the thiourea analogue, also connects into chain-like patterns; however, two different structural types exist, and these are given in Fig. 2(b) and (c). In both cases, the molecules are linked by the same type of hydrogen bonding, *i.e.*, N–H⋯S; however, this motif is straight in III but kinked in IV. Nevertheless, in both cases, when arranged in dimers, the molecules are symmetrically equivalent *via* an inversion operation located at the centers of $R_2^2(8)$ extra rings.

As can be seen in Table 2, the H-bridges in III demonstrate more closely spaced structural parameters than those of IV. For example, the difference between the two extra rings is smaller in III (H⋯S distances of 2.50(2) Å and 2.57(2) Å) compared to 2.45(2) Å and 2.56(3) Å in IV. Also, the whole chain is practically planar in IV, with an interplanar distance of 0.192(2) Å, while III demonstrates a small shift of dimers linked by an H-bridge with a longer hydrogen bond (0.415(2) Å).

Regarding the interactions involving mercaptopyridines, a graphical presentation of contacts corresponding to mercaptopyridine self-assembly hydrogen bonding is given in Fig. 3. Interestingly, only structure I was found to possess (N) H proton-donating and S proton-accepting centers involved in the interaction with the second co–crystal component, that is, the thiourea molecules. Therefore, although 4-mercaptopyridine forms N–H⋯S type hydrogen bonds in this case, this species does not undergo self-assembly in I; it also forms C(6) type chains *via* N–H⋯S bridges in III (Fig. 2(b)). The same motif, a $R_2^2(8)$ type dimer, is formed by molecules of the second derivative, 2-mercaptopyridine, in II

**Table 2** Parameters of the selected hydrogen bonds for co-crystal structures **I–IV** [Å, °]

| D–H…A | | $d$(D–H) | $d$(H…A) | $d$(D…A) | <(D–H…A) | Symmetry |
|---|---|---|---|---|---|---|
| Pyridine–pyridine | | | | | | |
| **II** | N(1)–H(1)⋯S(2) | 0.83(3) | 2.54(3 | 3.350(2) | 166(2) | $1 - x, -y, 1 - z$ |
| **III** | N(1)–H(1)⋯S(4) | 0.84(3) | 2.45(2) | 3.256(2) | 160(2) | $3/2 - x, -1/2 + y, 1/2 - z$ |
| **IV** | N(1)–H(1)⋯S(2) | 0.86(3) | 2.45(3) | 3.287(2) | 165(2) | $-x, 1 - y, 1 - z$ |
| Thiourea–thiourea | | | | | | |
| **I** | N(11)–H(11A)⋯S(12) | 0.89(3) | 2.53(3) | 3.418(2) | 175(2) | $1 - x, -1/2 + y, 1/2 - z$ |
| | N(13)–H(13A)⋯S(12) | 0.85(2) | 2.69(2) | 3.468(2) | 155(2) | $1 - x, 1/2 + y, 1/2 - z$ |
| **II** | N(11)–H(11A)⋯S(12) | 0.87(2) | 2.52(2) | 3.381(2) | 170(2) | $-x, 1 - y, 1 - z$ |
| | N(13)–H(13A)⋯S(12) | 0.83(2) | 2.58(2) | 3.402(2) | 172(3) | $-x, 1 - y, -z$ |
| Trithiocyanuric acid–trithiocyanuric acid | | | | | | |
| **III** | N(11)–H(11)⋯S(12) | 0.80(2) | 2.57(2) | 3.355(2) | 169(2) | $1 - x, -y, -z$ |
| | N(15)–H(15)⋯S(14) | 0.85(2) | 2.50(2) | 3.342(2) | 172(2) | $2 - x, 1 - y, - z$ |
| **IV** | N(11)–H(11)⋯S(12) | 0.81(3) | 2.56(3) | 3.361(2) | 177(2) | $1 - x, 2 - y, -z$ |
| | N(13)–H(13)⋯S(14) | 0.84(2) | 2.45(2) | 3.286(2) | 178(2) | $-x, 1 - y, -z$ |
| Thiourea–pyridinie | | | | | | |
| **I** | N(11)–H(11B)⋯S(4) | 0.72(2) | 2.71(3) | 3.392(2) | 158(2) | $x, 1/2 - y, -1/2+$ |
| | N(13)–H(13B)⋯S(4) | 0.79(3) | 2.72(3) | 3.442(2) | 153(2) | $x, 1/2 -y, -1/2 + z$ |
| **II** | N(11)–H(11B)⋯S(2) | 0.84(3) | 2.66(3) | 3.466(2) | 163(2) | $x, y, z$ |
| | N(13)–H(13B)⋯S(2) | 0.86(3) | 2.78(3) | 3.574(2) | 155(2) | $x, y, z$ |
| Trithiocyanuric acid–pyridine | | | | | | |
| **III** | N(13)–H(13)⋯S(4) | 0.81(2) | 2.42(2) | 3.216(2) | 168(2) | $1 + x, y, z$ |
| **IV** | N(15)–H(15)⋯S(2) | 0.86(3) | 2.34(2) | 3.194(2) | 174(2) | $1 - x, 1 - y, 1 - z$ |
| Pyridine–thiourea | | | | | | |
| **I** | N(1)–H(1)⋯S(12) | 0.85(3) | 2.54(3) | 3.359(2) | 162(2) | $1 - x, 1/2 + y, 1/2 - z$ |
| Pyridine–trithiocyanuric acid | | | | | | |
| **III** | C(5)–H(5)⋯S(12) | 0.93 | 2.92 | 3.832(2) | 169 | $x, y, z$ |
| **IV** | C(6)–H(6)⋯S(14) | 0.93 | 2.90 | 3.794(2) | 161 | $-x + 1, -y + 1, -z + 1$ |
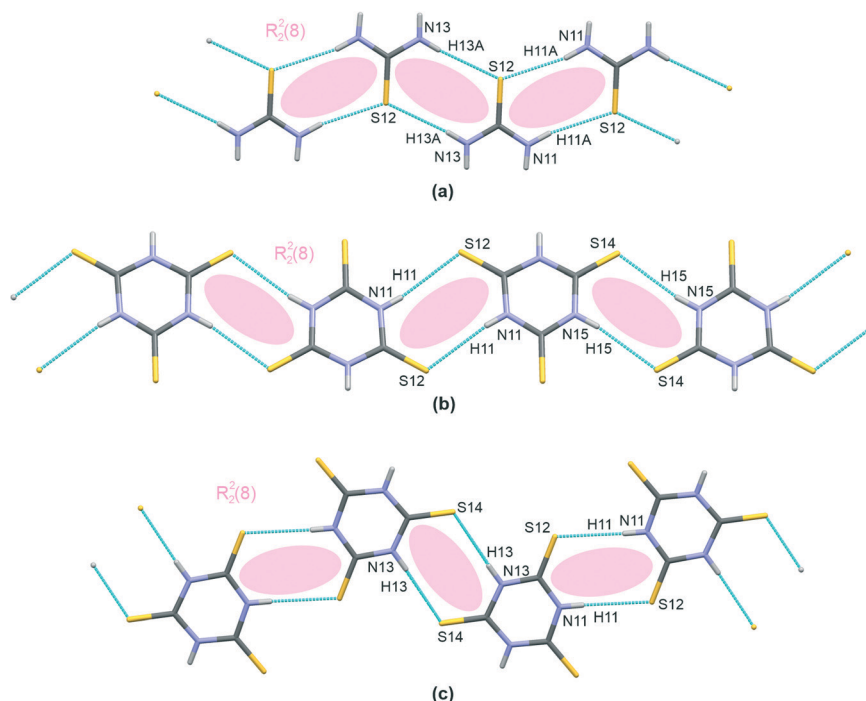


**Fig. 2** Characteristic patterns of hydrogen bonding found in **I–IV**. Thiourea motif in **I** and **II** – (a), trithiocyanuric acid motif in **III** – (b), and **IV** – (c). Atoms are marked with colours, as follows: N – blue, S – yellow, C – grey, H – white. Classification of synthons according to the graph set method is also given.

and **IV**, (Fig. 3(a)). As can be seen from structural parameters collected in Table 2, this hydrogen bonding seems to be slightly more effective in the case of **IV** than **II**, with (N)H⋯S distances of 2.45(3) Å and 2.54(3) Å for **IV** and **II**.
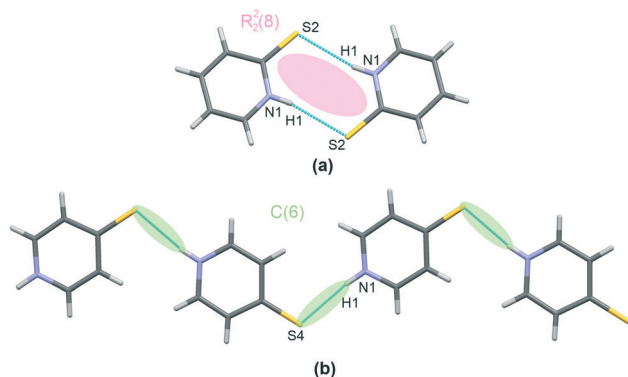
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**Fig. 3** I–IV characteristic patterns of the self-assembly of mercaptopyridines *via* hydrogen bonding. The $R_2^2(8)$ dimer present in II and IV – (a), and the C(6) chain in III – (b). Atoms are marked with colours, as follows: N – blue, S – yellow, C – grey, and H –white. The classification of synthons according to graph set method is also given.

The co-crystal structures I–IV are finally stabilized by a few hetero–molecular N–H⋯S bond linking motifs, as discussed above; all are shown in Fig. 4(a–d). Clearly, I and II demonstrate a characteristic pattern of a bifurcated $R_1^2(6)$ hydrogen bond linking mercaptopyridines with thiourea chains. The co-crystals formed with trithiocyanuric acid, *i.e.* III and IV, both demonstrate a single N–H⋯S hetero-molecular bond, which is responsible for co-crystal structure stabilization. Additionally, I demonstrates an N–H⋯S hydrogen bond, with 4-mercaptopyridine acting as a proton donor and thiourea as a proton acceptor (pyridine–thiourea dimer in Table 2). Structure III is characterized by two hydrogen bonds, N–H⋯O and C–H⋯N; thus, both molecules in the co-crystal (trithiocyanuric acid and 4-marcaptopyridine) serve simultaneously as a proton donor and an acceptor.

Finally, it is worth mentioning the short S⋯S type bond found in I and II (see Fig. 5). This interaction connects the molecules of both co–crystal components and can potentially be classified as chalcogen bonding. This type of interaction has been noted previously in co-crystals of thiourea. In Table 3 there is a brief comparison of the structural properties selectively collected for such contacts found in thiourea crystal structures deposited at the CSD.[18] Additionally, Table S1 (see the ESI† associated with this paper) shows a collection of refcodes together with structural data and literature references that can be found in regard to all urea crystals in which such short S⋯S contacts can be observed.

## Experimental

### Co-crystals synthesis

**Preparation of crystallization from 4-mercaptopyridine and thiourea (structure I).** Exact amounts of substrates, 0.0039 g of thiourea and 0.0056 g of 4-mercaptopyridine, were weighed out on an analytical balance and transferred to a crystallizing dish with a capacity of 50 ml. The selected substances were mixed in a 1:1 ratio and dissolved in

ethanol. After dissolving the substance in the solvent, the crystallizing dish was covered with a parafilm and allowed to crystallize for more than a week.

**Preparation of crystallization from 2-mercaptopyridine and thiourea (structure II).** Exact amounts of substrates, 0.0039 g of thiourea and 0.0056 g of 2-mercaptopyridine, were weighed out on an analytical balance and transferred to a crystallizing dish with a capacity of 20 ml. The selected substances were mixed in a 1:1 ratio and dissolved in ethanol. After dissolving the substance in the solvent, the crystallizing dish was covered with a parafilm and allowed to crystallize for more than a week.

**Preparation of crystallization from 4-mercaptopyridine and trithiocyanuric acid (structure III).** Exact amounts of substrates, 0.0089 g of trithiocyanuric acid and 0.0056 g of 4-mercaptopyridine, were weighed out on an analytical balance and transferred to a crystallizing dish with a capacity of 50 ml. The selected substances were mixed in a 1:1 ratio and dissolved in ethanol. Due to poor solubility, the mixture was heated on a magnetic stirrer with a heating plate. After dissolving the substance in the solvent, the crystallizing dish was covered with a parafilm and allowed to crystallize for more than a week. All the above activities were performed under dark room conditions. The crystallization mixture was protected from light and kept at 5 °C.

**Preparation of crystallization from 2-mercaptopyridine and trithiocyanuric acid (structure IV).** Exact amounts of substrates, 0.0089 g of trithiocyanuric acid and 0.0056 g of 2-mercaptopyridine, were weighed out on an analytical balance and transferred to a crystallizing dish with a capacity of 50 ml. The selected substances were mixed in a 1:1 ratio and dissolved in ethanol. After dissolving the substance in the solvent, the crystallizing dish was covered with a parafilm and allowed to crystallize for more than a week.

### Data collection and refinement

X-ray diffraction data were collected on an XtaLAB Synergy, Dualflex, HyPix diffractometer. Integration of the intensities and corrections for Lorentz effects, polarization effects, and analytical absorption were performed with CrysAlis PRO.[41] Using Olex2,[42] the structure was solved with the SHELXT[43] structure solution program using intrinsic phasing and refined with the SHELXL[44] refinement package using least squares minimization. The hydrogen atoms of aromatic rings were introduced in the calculated positions with an idealized geometry and constrained using a rigid body model with isotropic displacement parameters equal to 1.2 of the equivalent displacement parameters of their parent atoms. The positions of the hydrogen atoms of the NH– groups were found on a Fourier difference map and refined isotropically without any restrains. The molecular geometries were calculated by the Platon program.[45] Atomic coordinates, displacement parameters, and structure factors of the analyzed crystal structures are deposited with the Cambridge Crystallographic Data Centre (CCDC).[46]
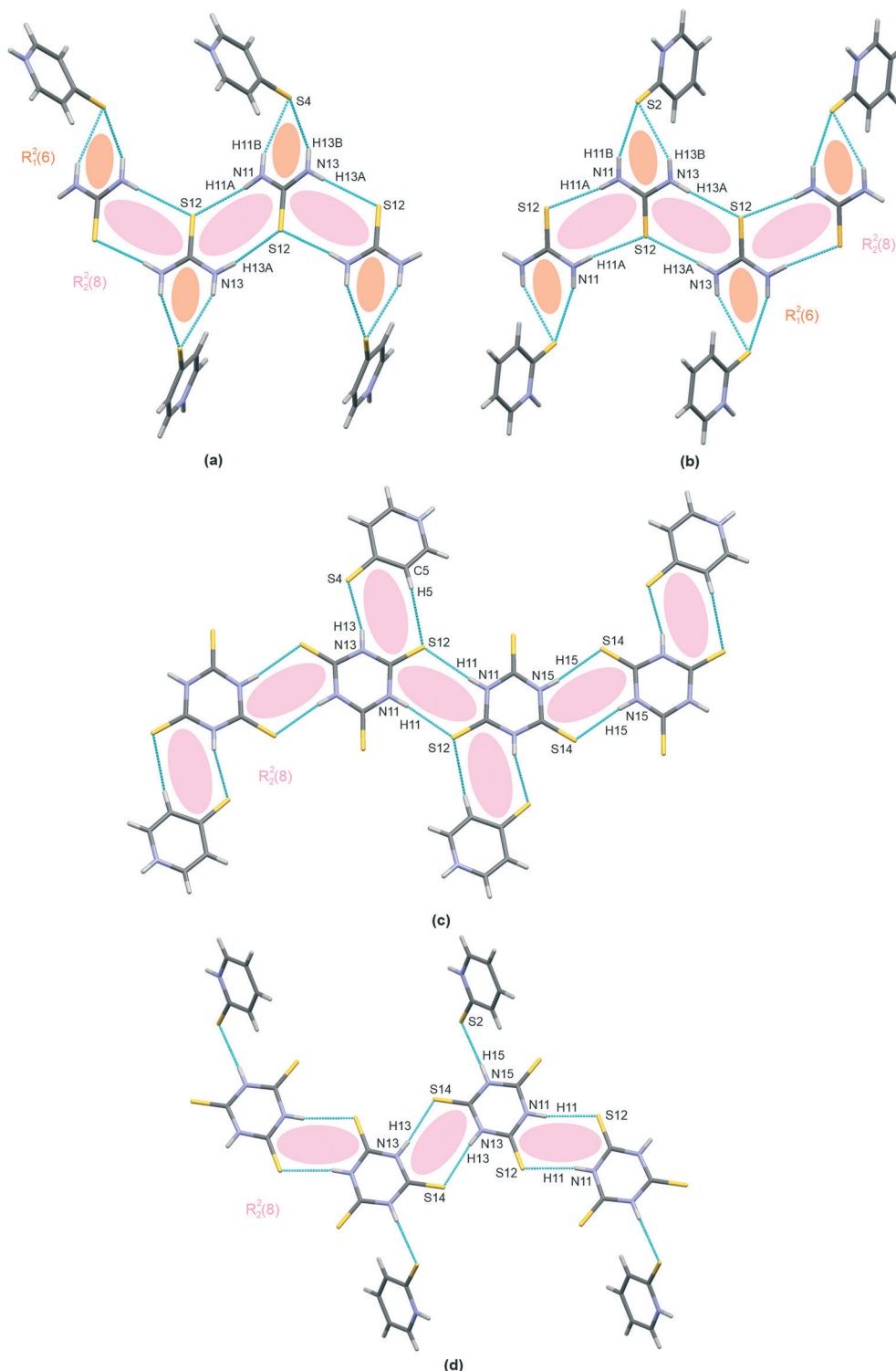
**Fig. 4** Selected large patterns of hydrogen bonding stabilizing the co-crystal state in the **I–IV** characteristic patterns of the self-assembly of mercaptopyridines *via* the hydrogen bonding. The $R_1^2(6)$ hydrogen bonding linking thiourea chains with mercaptopyridine molecules in **I** (a) and **II** (b), and the hydrogen bonding scheme between trithiocyanuric acid chains and mercaptopyridine molecules in **III** (c) and **IV** (d). Atoms are marked with colours, as follows: N – blue, S – yellow, C – grey, and H –white. The classification of synthons according to graph set method is also given.

### Cambridge Structural Database search

A search of the Cambridge Structural Database[18] [CSD, Version 5.43, Release of November 2021] was performed. In the case of mercaptopyridines the structure of 4- and 2-mercaptopyridines was the only criterion for the search. The following entries were the result of the search: AKOVOL,[19–22] DAHTIP,[27] JEHTIC,[28] PYRIDS,[23–26] and VIJNEH.[29,30] When searching S···S contacts
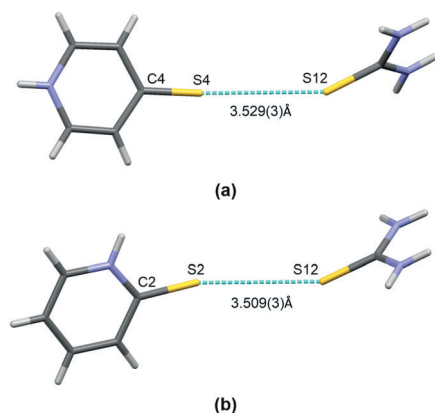
**Fig. 5** A short contact of S···S type found in co-crystals of thiourea: **I** (a) and **II** (b). Atoms are marked with colours, as follows: N – blue, S – yellow, C – grey, H –white.

**Table 3** Parameters of the S···S chalcogen contact for **I**, **II** and thiourea co-crystal structures deposited at the Cambridge structural Database[18] [Å, °]

|  | $d$(C···S) | $d$(S···S) | <(C–S···S) |
|---|---|---|---|
| **I** | 1.705(2) | 3.529(3) | 160(2) |
| **II** | 1.708(2) | 3.509(3) | 160(2) |
| PUZMIJ[39] | 1.705 | 3.283 | 169 |
| YOTJAT[40] | 1.698 | 3.348 | 180 |

with thiourea contribution, the main criterion was the structure of thiourea and the presence of the S(thiourea)···S(any) contact with a vdW distance limit.

## Conclusions

This paper describes the results of the cross-crystallization of four new co-crystals composed of 2- and 4-mercaptopyridines with thiourea and its cyclic analogue, trithiocyanuric acid. Our data represents the first accurate description of mercaptopyridine co-crystals. In one case (**III**), the crystallization procedure led to the production of an unexpected co-crystal; however, this was later found to result from the photoreactivity of the initial compound. The collection of the four obtained co-crystal structures has been characterized by X-ray single crystal analysis. While a relatively complicated network of N–H···S hydrogen bonds was found to be responsible for co-crystal state stabilization, additional short S···S type contacts seem to support the activity of hydrogen bonds in the case of thiourea co-crystals.

## Conflicts of interest

There are no conflicts to declare.

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