

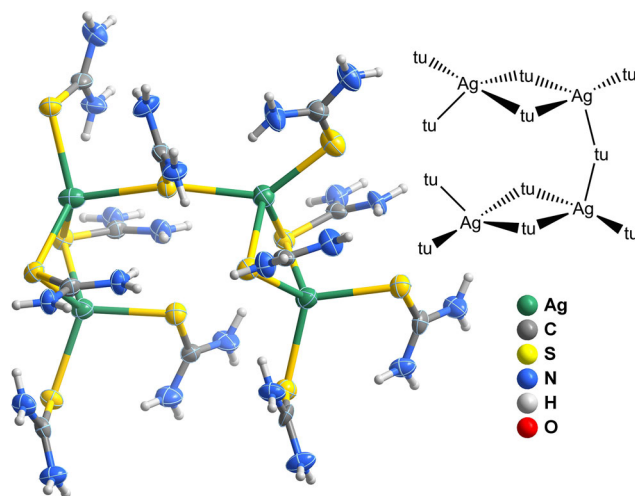
# A Tetranuclear Silver–Thiourea Cluster

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**Abstract** During the synthesis of the bioactive complex  $[\text{Ag}(\text{phen})(\mu\text{-tu})_2(\text{NO}_3)_2]$  (**1**), some crystals of a new compound were isolated. This crystalline compound,  $[\text{Ag}_4(\mu\text{-tu})_5(\text{tu})_6](\text{NO}_3)_4 \cdot 7\text{Phen}$  (**2**) (tu = thiourea, Phen = 1,10-phenanthroline), is a novelty for at least two reasons: (i) it is the first tetranuclear silver and thiourea cluster; (ii) it is the first crystal structure with seven neutral, and uncoordinated, phen molecules. Phen molecules pack forming an infinite column, and the tu ligands form an intricate network of hydrogen bonds with the Phen and nitrate entities.

**Graphical Abstract** The new compound  $[\text{Ag}_4(\mu\text{-tu})_5(\text{-tu})_6](\text{NO}_3)_4 \cdot 7\text{Phen}$  (tu = thiourea, Phen = 1,10-phenanthroline) is a novelty at least by two ways: (i) it is the first tetranuclear cluster of silver and thiourea; (ii) it is the first crystal structure with seven neutral, and uncoordinated, phen molecules.



**Keywords** Silver and thiourea cluster · Supramolecular interactions

## Introduction

A great deal of work has been devoted to studying the biological activity of polynuclearsilver(I) complexes [1–4]. The interest in polynuclear complexes has been stimulated by the remarkable antimicrobial and antifungal activity exhibited by silver sulfadiazine [5]. Used clinically to prevent bacterial infections in cases of severe burns, silver sulfadiazine is an insoluble polymeric compound that slowly releases the antibacterial  $\text{Ag}^+$  ion [6, 7]. The construction of such species requires linking silver centers by appropriate bridging species. From this point of view, thiourea-type ligands seem to be well suited for this purpose, since they display the ability to coordinate various

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metals via  $\eta^1$ -,  $\mu_2$ -S, and  $\mu_3$ -S bonding modes, and as an anionic ligand it can bind in a chelating N,S fashion [8–11].

In a recent report [12], we have described the synthesis and characterization of compounds of the type  $[\{Ag(N,N)(\mu-tu)\}_2](X)_2$  (N,N = 2,2'-bipyridine, 1,10-phenanthroline; tu = thiourea;  $X^- = NO_3^-$ ,  $CF_3SO_3^-$ ). Among them, 1,10-phenanthroline-based derivatives exhibited promising activity against promastigote and amastigote forms of *Leishmania (L.) amazonensis*, together with lower toxicity towards murine peritoneal macrophages than Amphotericin B.

Considering the isoleptic metallic clusters with thiourea, only the metal centers copper(I), silver(I) and Pd(I)/Pd(II) [13] can be found in numbers from 2 to 6 per cluster, whereas the number of tu ligands ranges from 6 to 14. The simplest arrangement of the clusters is the dinuclear cation  $[M(\mu-tu)_2]_2^{2+}$  (Scheme 1a), comprising all the previously existing silver clusters [14–16] and also a large part of the copper clusters [17–21]. The sole trinuclear arrangement is also the only palladium compound  $[Pd_3(\mu-tu)_4tu_4]^{4+}$  mentioned above [13] (Scheme 1b). Although there are no cyclic trinuclear clusters, the moiety  $cyclo-[Cu(\mu-tu)]_3^{3+}$  is present as a structural bridging block in clusters with higher number of atoms, such as in adamantane-like clusters with four copper atoms [22–24] (Scheme 1c) or a hexagonal prism with six copper atoms [25] (Scheme 1d). The remaining structures can be formed by connecting two dinuclear clusters  $[\{Cu(\mu-tu)_2\}_2(\mu-tu)]_2^{4+}$  [26] (Scheme 1e), or by a cyclic arrangement  $[Cu(\mu-tu)_2]_4^{4+}$  [27] (Scheme 1f).

Among the silver compounds, even if the search is extended to  $\kappa$ -S-thiourea derivatives, only the dimer  $[Ag(\mu-tu')tu'_2]_2^{2+}$  is found (where tu' is a substituted thiourea) [14–16, 28–36]. This type of dimer can be found in two different conformations, one in which the polygon  $\{Ag \cdots S \cdots Ag \cdots S\}$  is planar (the majority) and the other in which the polygon deviates considerably from planarity [14, 16]. The cluster  $[Ag(\mu-tu)_2]_2^{2+}$  is found in both planar and non-planar conformations, and for this reason, there is apparently no rule of thumb to explain the existence of these two conformations.

During the synthesis of compound  $[Ag(phen)(\mu-tu)]_2(NO_3)_2$  [12], crystals of the complex  $[Ag_4(\mu-tu)_5(tu)_6](NO_3)_4 \cdot 7Phen$  containing a novel silver(I)/thiourea arrangement were obtained.

## Experimental

### Materials and Methods

Syntheses were performed at room temperature and under light protection. Commercial reagents and solvents were

employed without further purification. The title compound (2) comprises a crystalline impurity of compound  $[Ag(phen)(\mu-tu)]_2(NO_3)_2$  (1) synthesized by some of us [12].

### Synthesis

#### $[Ag(phen)(\mu-tu)]_2(NO_3)_2$ (1)

1,10-phenanthroline (0.58 mmol; 116.7 mg) dissolved in 10 mL of  $CH_3OH$  was added to a 15 mL  $CH_3CN$  solution containing  $AgNO_3$  (0.58 mmol; 100.0 mg). After stirring the obtained yellow suspension for 30 min, thiourea (1.16 mmol; 89.6 mg) dissolved in 10 mL of  $CH_3OH$  was added, affording a light brown solid which was isolated by simple filtration and washed with methanol.

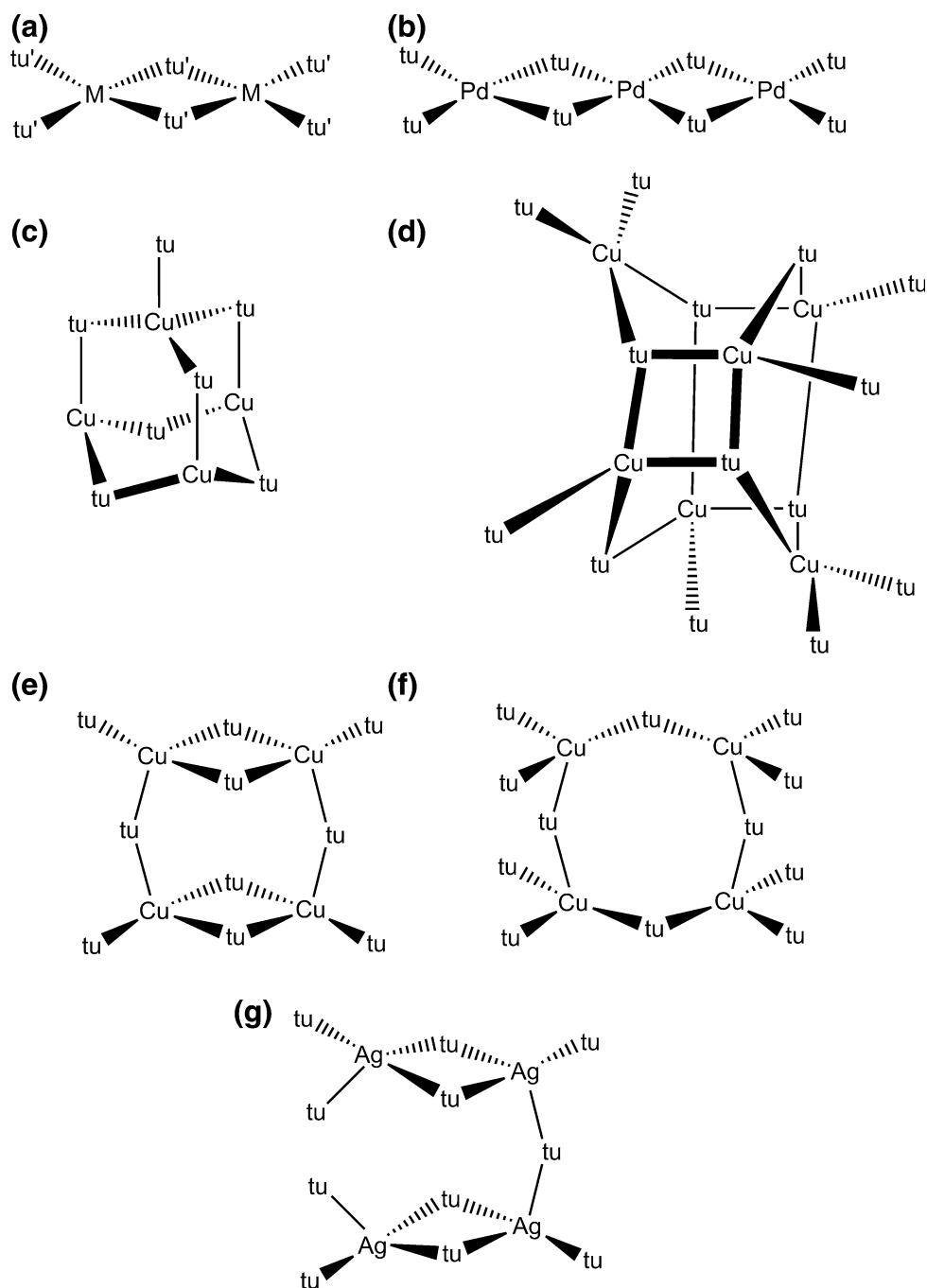
#### $[Ag_4(\mu-tu)_5(tu)_6](NO_3)_4 \cdot 7Phen$ (2)

In order to obtain suitable crystals for X-ray diffraction, the supernatant solvent of the previous synthesis was submitted to further evaporation. Ultimately, a mixture of colourless and brown crystals was obtained, identified by the conjugation of powder and single crystal X-ray diffraction data as a mixture of  $[Ag(tu)_2(\mu-tu)]_2(NO_3)_2$  (1), described by ourselves elsewhere [12], and the new compound 2.

### Single-Crystal X-ray Diffraction Studies

A suitable colourless single-crystal of the title compound was manually harvested from a material mainly composed by brown needles (from 1) and immediately immersed in FOMBLIN Y. The crystal was mounted on a Hampton Research CryoLoop with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses [37]. Data were collected on a Bruker X8 Kappa APEX II CCD area-detector diffractometer (Mo  $K\alpha$  graphite-monochromated radiation,  $\lambda = 0.71073 \text{ \AA}$ ) controlled by the APEX2 software package [38] and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad [39]. Images were processed using the software package SAINT+ [40], and data were corrected for absorption by the multi-scan semi-empirical method implemented in SADABS [41].

The structure was solved using the Patterson synthesis algorithm implemented in *SHELXS-97* [42], which allowed the immediate location of the metal centres and most of the heaviest atoms. All remaining non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on  $F^2$  using *SHELXL-2014* [43].

**Scheme 1** Metallic clusters of thiourea derivatives

Hydrogen atoms bound to carbon and nitrogen atoms were placed at their idealised positions using *HFIX* instructions (43 for aromatic and 93 for amino groups). All these hydrogen atoms were included in the final structural model in riding-motion approximation with isotropic thermal displacement parameters fixed at  $1.2 \times U_{\text{eq}}$  (for C) or  $1.5 \times U_{\text{eq}}$  (for N) of the atom to

which they are attached. The refinement of totally independent thermal displacement parameters for all the atoms converged into a solution with eight atoms of the phenanthroline molecules (from a total of 162) with non-positive defined or with very prolate or oblate ellipsoids. We managed to solve this problem by considering the atoms in each specific position in approximately parallel

**Table 1** Crystal and structure refinement data for compound [Ag<sub>4</sub>(μ-tu)<sub>5</sub>(tu)<sub>6</sub>](NO<sub>3</sub>)<sub>4</sub>·7Phen (**2**)

Formula	C <sub>95</sub> H <sub>100</sub> Ag <sub>4</sub> N <sub>40</sub> O <sub>12</sub> S <sub>11</sub>
Formula weight	2778.29
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	19.1789 (9)
<i>b</i> (Å)	24.5910 (14)
<i>c</i> (Å)	24.9467 (11)
Volume (Å <sup>3</sup> )	11,093.5 (10)
β (°)	109.459 (3)
<i>Z</i>	4
Temperature (K)	150 (2)
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.663
μ(Mo-Kα) (mm <sup>-1</sup> )	0.982
Crystal size (mm)	0.12 × 0.03 × 0.01
Crystal type	Colourless needle
θ range	2.25–25.35
Index ranges	–22 ≤ <i>h</i> ≤ 23 –29 ≤ <i>k</i> ≤ 26 –28 ≤ <i>l</i> ≤ 30
Reflections collected	51,688
Independent reflections	20,070 [ <i>R</i> <sub>int</sub> = 0.1408]
Completeness to θ = 25.35°	98.9 %
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a,b</sup>	<i>R</i> 1 = 0.0972 <i>wR</i> 2 = 0.1172
Final <i>R</i> indices (all data) <sup>a,b</sup>	<i>R</i> 1 = 0.2270 <i>wR</i> 2 = 0.1480
Weighting scheme <sup>c</sup>	<i>m</i> = 0.0183 <i>n</i> = 0.0000
Largest diff. peak and hole	0.849 and –0.635 e Å <sup>-3</sup>
CCDC No.	1031660

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}$$

$$^c w = 1 / [\sigma^2(F_o^2) + (mP)^2 + nP] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

residues to share common displacement parameters, using the *EADP* instruction. The refinement in the *SHELXL* package converged to a solution in which the highest difference peak and deepest hole are located 1.07 and 0.50 Å away from Ag<sub>3</sub>, with respective values of 0.849 and –0.635 e Å<sup>-3</sup>.

Crystallographic data collection and structure refinement details are summarized in Table 1. Selected bond lengths and angles for the metallic coordination environments and hydrogen bonding geometry are presented in Tables 2 and 3, respectively.

## Results and Discussion

### Crystal Structure Description of [Ag<sub>4</sub>(μ-tu)<sub>5</sub>(tu)<sub>6</sub>](NO<sub>3</sub>)<sub>4</sub>·7Phen (**2**)

The asymmetric unit of **2**, [Ag<sub>4</sub>(μ-tu)<sub>5</sub>(tu)<sub>6</sub>](NO<sub>3</sub>)<sub>4</sub>·7Phen, is composed by twelve crystallographically independent entities, namely a tetracationic cluster, four charge balancing nitrate anions and seven cocrystallising 1,10-phenanthroline molecules (Fig. 1). The cluster is composed by four Ag<sup>+</sup> centres (Scheme 1g), each of them coordinated to four thiourea ligands. The coordination environment around each metal centre resembles a distorted tetrahedron with the S–Ag–S angles ranging from 87.00(11) to 134.36(11)°. The metal centres are arranged in two close pairs, with Ag⋯Ag distances of 2.9820(12) and 3.0661(11) Å, each connected by bridging thiourea ligands with Ag–S–Ag angles varying from 67.01(8) to 70.90(8)°. A further bridging thiourea ligand connects the two silver pairs with a Ag2⋯Ag3 distance of 5.2686(16) Å, and a Ag2–S6–Ag3 angle of 157.87(12)°. The cluster does not comprise a closed ring, since S8 (bound to Ag<sub>4</sub>) is located at a distance of 3.771(4) Å from Ag<sub>1</sub>, which is too long to correspond to a real Ag–S bond. While the bridging between Ag<sub>2</sub> and Ag<sub>3</sub> is assured by S<sub>6</sub>, the bridging between Ag<sub>1</sub> and Ag<sub>4</sub> could be made, in principle, by S<sub>1</sub> or S<sub>8</sub> (giving a structure as the one in Scheme 1e). However, the mutual steric hindrance of the two ligands widens the gap between the metal atoms, and ultimately, interrupts the polygon {Ag<sub>1</sub>⋯Ag<sub>2</sub>⋯Ag<sub>3</sub>⋯Ag<sub>4</sub>}. Additionally to the bridging ligands, the metals are coordinated to terminal thiourea ligands: One to Ag<sub>2</sub> and Ag<sub>3</sub> and two to Ag<sub>1</sub> and Ag<sub>4</sub>.

The present cluster can be compared to the connection of two dinuclear clusters of the non-planar type described in the introduction, with an additional S<sub>6</sub> bridge replacing one terminal ligand from each cluster. All the geometrical features such as distances and angles are close to or within the interval of values defined by the corresponding features of the non-planar clusters [14, 16].

The existence of a large number of proton donors and acceptors gives the structure of **2** a highly intricate hydrogen network (Fig. 2b and c). The donation of the *anti* protons (with respect to the S atoms) depends on the function of the tu ligands they belong to. While the four bridging tu ligands with short Ag–S–Ag angles donate their *anti* protons to the nitrate anion, the remaining seven tu ligands donate their *anti* protons to the cocrystallising phen ligands. The *syn* protons are substantially, but not completely, involved in N–H⋯S bonding. Additionally to hydrogen bonding, the column of phenanthroline ligands is

**Table 2** Selected bond distances (in Å) and angles (in degrees) for the coordination environments present in compound [Ag<sub>4</sub>(μ-tu)<sub>5</sub>(tu)<sub>6</sub>](NO<sub>3</sub>)<sub>4</sub>·7Phen (**2**)

Ag1–S1	2.563 (3)	Ag3–S6	2.759 (4)
Ag1–S2	2.568 (4)	Ag3–S9	2.670 (3)
Ag1–S3	2.733 (3)	Ag3–S10	2.683 (3)
Ag1–S4	2.645 (3)	Ag3–S11	2.538 (3)
Ag2–S3	2.588 (3)	Ag4–S7	2.600 (3)
Ag2–S4	2.754 (3)	Ag4–S8	2.539 (4)
Ag2–S5	2.459 (4)	Ag4–S9	2.615 (3)
Ag2–S6	2.609 (4)	Ag4–S10	2.688 (3)
Ag1…Ag2	2.9820 (12)	Ag3…Ag4	3.0661 (11)
Ag1–S3–Ag2	68.11 (8)	S <sub>T</sub> –Ag–S <sub>T</sub>	106.11 (10)–110.38 (11)
Ag1–S4–Ag2	67.01 (8)	S <sub>T</sub> –Ag–S <sub>μ</sub>	103.70 (11)–127.73 (10)
Ag3–S9–Ag4	70.90 (8)	S <sub>T</sub> –Ag–S6	94.69 (10)–134.36 (11)
Ag3–S10–Ag4	69.62 (8)	S <sub>μ</sub> –Ag–S <sub>μ</sub>	98.27 (9)–107.67 (9)
Ag2–S6–Ag3	157.87 (12)	S <sub>μ</sub> –Ag–S6	87.00 (11)–115.88 (10)
Ag–S–C	97.7 (4)–112.6 (4)		

S<sub>T</sub>(terminal): S1, S2, S5, S7, S8, S11; S<sub>μ</sub>(bridging):S3, S4, S9, S10**Table 3** Hydrogen bonding geometry for compound [Ag<sub>4</sub>(μ-tu)<sub>5</sub>(tu)<sub>6</sub>](NO<sub>3</sub>)<sub>4</sub>·7Phen (**2**) (distances in Å and angles in °)

D–H…A	d (D…A)	<(DHA)	D–H…A	d (D…A)	<(DHA)
N1–H1A…N1_3	2.890 (13)	164	N12–H12A…N2_6	2.996 (13)	164
N1–H1B…S1 <sup>i</sup>	3.388 (8)	169	N12–H12B…S11	3.419 (10)	129
N2–H2A…N2_3	2.972 (13)	170	N13–H13A…N1_5	2.800 (13)	157
N2–H2B…S4	3.416 (8)	170	N13–H13B…S11 <sup>iii</sup>	3.526 (9)	165
N3–H3A…N2_4	2.938 (13)	161	N14–H14A…N2_5	3.021 (13)	173
N3–H3B…S1	3.345 (10)	147	N14–H14B…S9	3.598 (9)	157
N4–H4A…N1_4	2.909 (13)	148	N15–H15A…N2_2	2.966 (13)	163
N4–H4B…S9 <sup>ii</sup>	3.368 (10)	158	N15–H15B…S7	3.317 (11)	143
N5–H5A…O2_11	2.938 (13)	162	N16–H16A…N1_2	2.924 (14)	142
N5–H5B…S2	3.336 (10)	141	N16–H16B…S3	3.395 (9)	159
N6–H6A…O1_11	2.936 (14)	168	N17–H17A…O1_8	2.906 (13)	171
N6–H6B…O2_10	2.920 (13)	170	N17–H17B…O3_11 <sup>iv</sup>	2.884 (14)	172
N7–H7A…O2_9	2.906 (13)	152	N18–H18A…O2_8	2.919 (13)	168
N7–H7B…S2	3.686 (10)	144	N18–H18B…S6	3.483 (10)	139
N8–H8A…O1_9	2.906 (13)	162	N19–H19A…O2_10	2.888 (12)	172
N8–H8B…O2_8	2.842 (13)	171	N19–H19B…S8	3.318 (10)	140
N9–H9A…N2_7	2.944 (14)	160	N20–H20A…O1_10	3.017 (13)	169
N9–H9B…S7 <sup>ii</sup>	3.382 (11)	161	N20–H20B…O2_9 <sup>iv</sup>	2.917 (12)	168
N10–H10A…N1_7	2.908 (14)	142	N21–H21A…N2_1	2.988 (13)	172
N10–H10B…N11	3.107 (14)	151	N21–H21B…S10	3.716 (9)	176
N11–H11A…N1_6	2.848 (13)	154	N22–H22A…N1_1	2.827 (13)	154
N11–H11B…S4	3.378 (9)	148	N22–H22B…S7 <sup>v</sup>	3.465 (9)	160

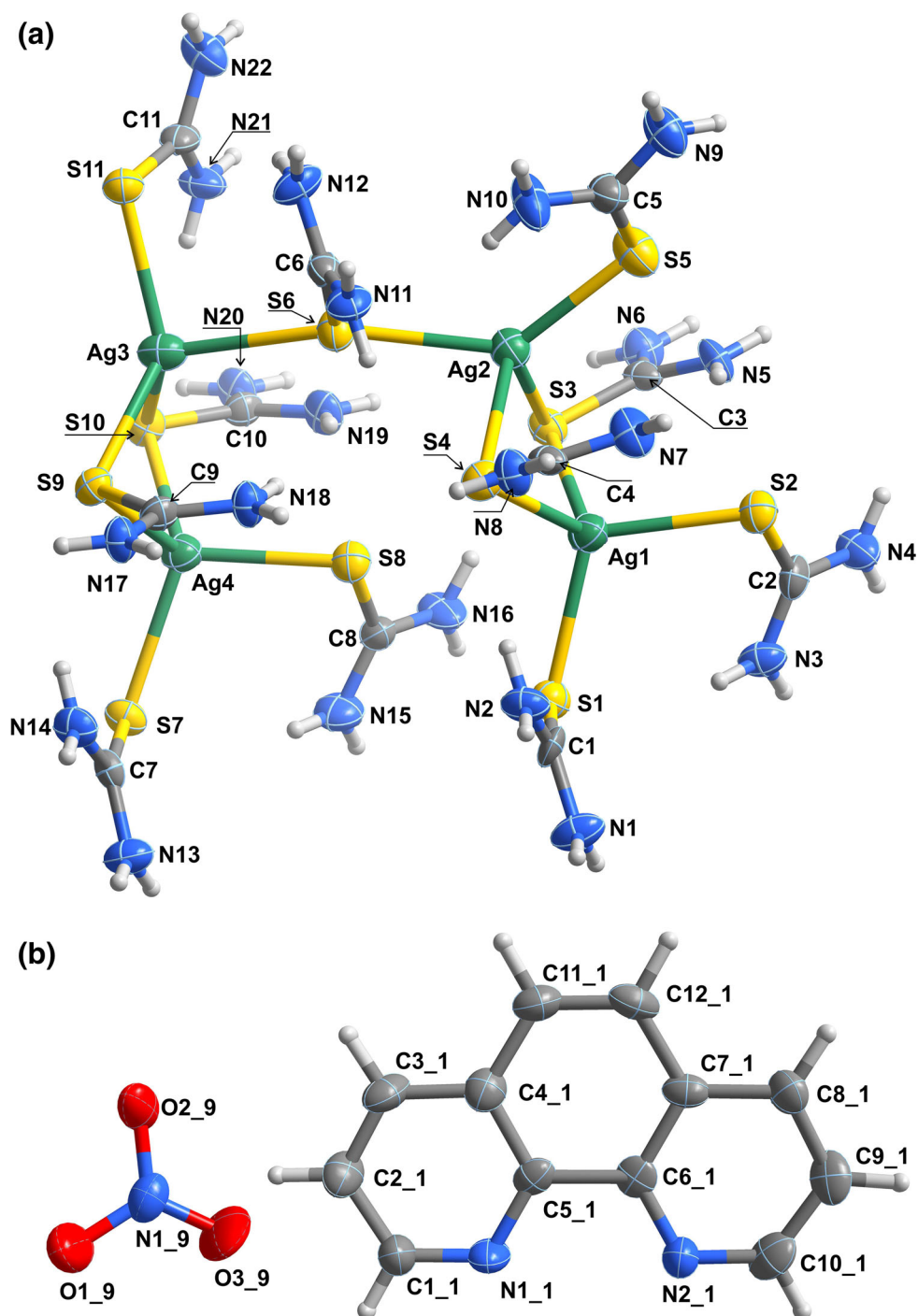
Symmetry transformations used to generate equivalent atoms

<sup>i</sup> 1 – x, 1 – y, 1 – z; <sup>ii</sup> 1 – x, ½ + y, ½ – z; <sup>iii</sup> x, ½ – y, ½ + z; <sup>iv</sup> 1 – x, ½ + y, ½ – z; <sup>v</sup> x, ½ – y, ½ – z

maintained by adjacent π–π stacking interactions parallel to the *b* axis of the unit cell (Figs. 2a and 3). Considering the medium planes formed by each of the six atoms of an

aromatic ring and its corresponding centroid, the geometrical relationship between centroids on the medium planes can be discussed [44]. The shortest distance between

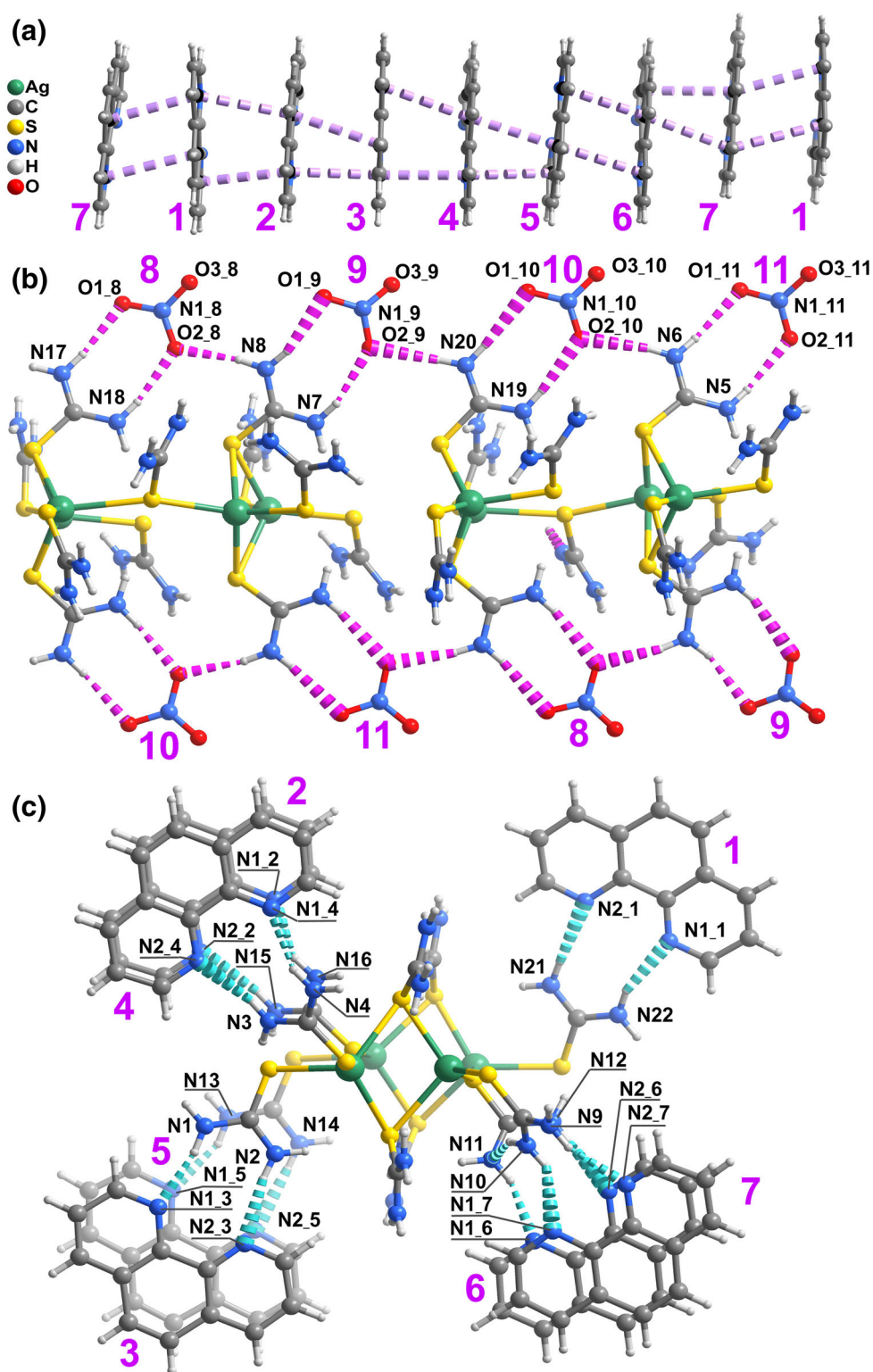
**Fig. 1** Representation of the molecular units present in  $[\text{Ag}_4(\mu\text{-tu})_5(\text{tu})_6](\text{NO}_3)_4 \cdot 7\text{Phen}$  (**2**) showing representative non-hydrogen atoms as displacement ellipsoids drawn at 50 % probability level and hydrogen atoms represented as spheres with arbitrary radii. Labels are provided for all non-hydrogen atoms. **a**  $[\text{Ag}_4(\mu\text{-tu})_5(\text{tu})_6]^{4+}$  cluster; **b** The asymmetric unit also contains four nitrate anions and seven phenanthroline molecules. The labeling scheme is common to similar entities, with addressing to the residue number. As an example, the complete labels are shown for residues 1 (phenanthroline) and 9 (nitrate)



centroids is formed by the atoms N1 and C1 through C6 of residues 3 and 4, with a value of 3.519(7) Å. The other 14 of such contacts happen at distances smaller than 3.8 Å. While the angle between the medium planes oscillates between 1.0(6)° and 5.8(6)°, the angle between the normal to the planes and the segment between centroids ranges between 9.8(6)° and 25.8(6)°.

The number of seven uncoordinated phen molecules in the asymmetric unit is unprecedented. Actually, a survey in the Cambridge Structural Database (version 5.35 update May 2014) [45] revealed that this is the first structure with more than six phen protonated or neutral molecules in the asymmetric unit. Among the different pairs of interactions between neighboring phen molecules

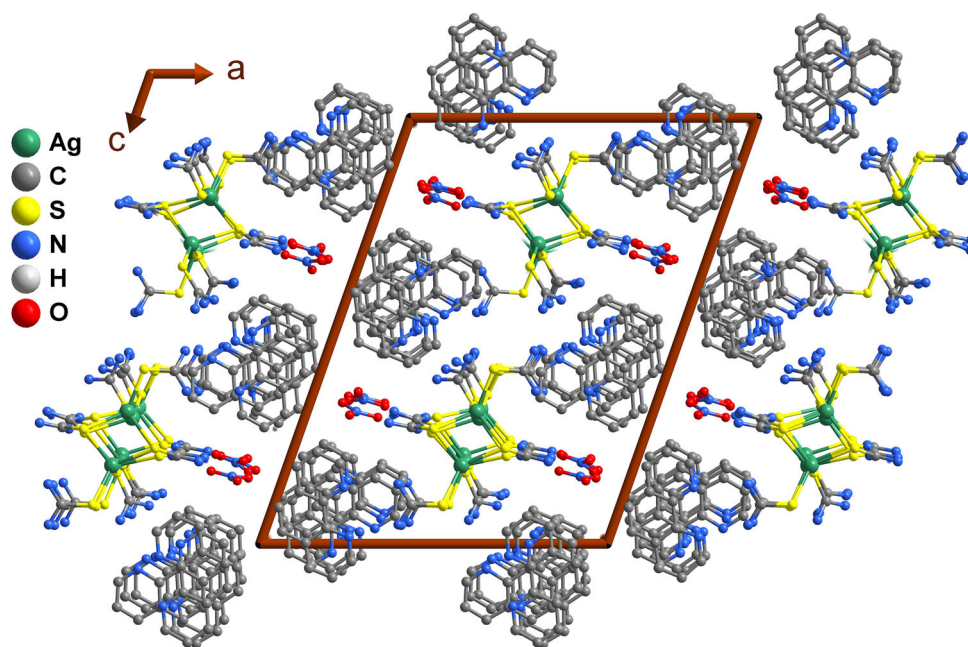
**Fig. 2** Schematic representation of the supramolecular interactions present in the crystal structure of  $[\text{Ag}_4(\mu\text{-tu})_5(\text{tu})_6](\text{NO}_3)_4 \cdot 7\text{Phen}$  (**2**): **a**  $\pi$ – $\pi$  stacking in column composed of phenanthroline molecules; **b** Hydrogen bonds formed between tu ligands and nitrate anions; **c** Hydrogen bonds formed between tu ligands and phenanthroline molecules. The weak  $\text{N}\cdots\text{S}$  bonds and symmetry operations are not represented for the sake of clarity



only phen molecules 6 and 7 interact with all the three aromatic rings as seen in Fig. 2, this phenomenon being observed several times in phen clusters in the literature

[46–49]. Phenanthroline molecules 1 through 5 interpose between each other causing the overlapping effect of two aromatic rings [50–53].

**Fig. 3** Perspective view along the *b* axis of  $[Ag_4(\mu\text{-tu})_5(\text{tu})_6](\text{NO}_3)_4 \cdot 7\text{Phen}$  (**2**) cell packing. Hydrogen atoms have been omitted for the sake of clarity



## Conclusion

Crystals of a new silver compound of the general formula  $[Ag_4(\mu\text{-tu})_5(\text{tu})_6](\text{NO}_3)_4 \cdot 7\text{Phen}$  were obtained. The cation is the first tetranuclear cluster with silver and thiourea, and the crystal structure is the first with seven uncoordinated 1,10-phenanthroline molecules in the asymmetric unit. The 1,10-phenanthroline molecules pack by forming an infinite column, supported by  $\pi$ - $\pi$  stacking. Additionally, the thiourea ligands control the packing by the formation of a plethora of hydrogen bonding interactions.

## Supporting Information

Crystallographic Information File (CIF) for the title compound. CCDC 1031660 contains the supplementary crystallographic data for molecule **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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