

## Note

## Solvent-dependent 2D-coordination polymers of Cu(I) containing a bridging triazolopyrimidine ligand

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## ABSTRACT

Two 2D-polymers of Cu(I), [Cu<sub>2</sub>(μ-tp)(CH<sub>3</sub>CN)(μ-1)(μ<sub>3</sub>-I)]<sub>n</sub> (**1**) and [Cu<sub>2</sub>(μ-tp)(μ<sub>3</sub>-I)]<sub>n</sub> (**2**), both obtained from the reaction between copper iodide and 1,2,4-triazolo[1,5-*a*]pyrimidine (tp) in the presence of KI are described. While in compound **1**, tp acts as bridging ligand via N1 and N3 between chair-like [Cu<sub>4</sub>I<sub>4</sub>] units, in compound **2**, tp moieties are placed at both sides of a [Cu<sub>n</sub>I<sub>n</sub>] kinked layer, displaying also a bridging mode but, in this case, through its atoms N3 and N4. These structural differences between both compounds seem to be due to the solvent of crystallization, being acetonitrile for **1** and water for **2**. These polymers are the first examples of Cu(I) compounds based on the nucleobase-analog ligand tp.

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## 1. Introduction

Copper complexes and clusters have been studied for decades, mostly because of the unique role these species play in both physical and biological research and applications [1]. Copper(I) halide aggregates constitute a large family of compounds studied mainly for their photochemical and photophysical properties [2] which are currently at the forefront of coordination chemistry and crystal engineering research [3,4]. Coordination systems based on copper halides show a remarkable structural diversity, which has been recently reviewed [4]. This variability arises from the many possible combinations of coordination numbers (two, three and four) available for copper(I) and geometries that can be adopted by the halide ions (from terminal to μ<sub>2</sub>- and up to μ<sub>8</sub>-bridging). Especially, copper(I) iodide has been used as the inorganic component in the building of novel coordination polymers with diverse structural motifs such as rhomboid [Cu<sub>2</sub>(μ-1)]<sub>2</sub> fragment [5–7], cubane-like or chair-like [Cu<sub>4</sub>(μ<sub>3</sub>-1)]<sub>4</sub> fragment [8], one-dimensional ladder strand [Cu<sub>2</sub>(μ<sub>3</sub>-1)]<sub>n</sub> [9] or zigzag [Cu(μ-1)]<sub>n</sub> chain [5,7,9,10]. These motifs could be further connected by N-heterocyclic linkers to form more complex [Cu<sub>n</sub>I<sub>n</sub>]-based frameworks [9]. Preparation of such compounds has been reported to be affected by many factors

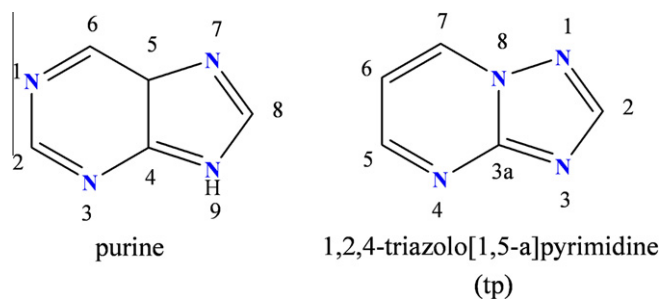
such as CuI-to-ligand ratio, flexibility and rigidity of the ligands, solvents and temperature [5,11].

On the other hand, 1,2,4-triazolo[1,5-*a*]pyrimidines have proved to be versatile ligands as they have several nitrogen atoms with accessible lone pairs to bind to Lewis acids like metal ions [12] (see Scheme 1). Moreover, their versatility can be increased by the ring-substitution with functional groups containing donor atoms like nitrogen, sulfur or oxygen, leading to a wider range of coordination modes and structural topologies in their metal complexes [13]. Previous studies reveal that the most frequent binding mode of these heterocycles is monodentate through its N3 position, followed by bidentate through N3 and N4 atoms [12]. The increasing interest, which aroused recently around these type of ligands, does not only lie in their great capacity to act as suitable building blocks for the synthesis of novel metal–organic multidimensional systems [11–14] but also in their biomimetic character, since they resemble the natural occurring purinic nucleobases adenine and guanine (Scheme 1).

In the present paper, we report the syntheses and the crystal structures of two new copper(I) 2D-polymers, both obtained from the reaction between CuI and 1,2,4-triazolo[1,5-*a*]pyrimidine (tp): 2D-[Cu<sub>2</sub>(μ-tp)(CH<sub>3</sub>CN)(μ-1)(μ<sub>3</sub>-I)] (**1**) and 2D-[Cu<sub>2</sub>(μ-tp)(μ<sub>3</sub>-I)] (**2**). The solvent used seems to play a critical role on the structures of both compounds, being acetonitrile for **1** and water for **2**. These are the first examples of Cu(I) compounds based on the nucleobase-analog ligand tp.

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**Scheme 1.** Structural comparison between purine and 1,2,4-triazolo[1,5-*a*]pyrimidine (tp).

## 2. Experimental

### 2.1. General

All analytical reagents were purchased from commercial sources and used without further purification. Microanalysis of C, H and N were performed on a Fisons Instruments EA-1008 analyzer. Thermal behavior was studied under an air flow in Shimadzu TGA-50 and Shimadzu DSC-50 equipments, at heating rates of 20 and 10 °C min<sup>-1</sup>, respectively. All this equipment is sited at the Centro de Instrumentación Científica of the University of Granada. IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr pellets.

### 2.2. Preparation of the complexes 2D-[Cu<sub>2</sub>(μ-tp)(CH<sub>3</sub>CN)(μ-I)(μ<sub>3</sub>-I)] (**1**) and 2D-[Cu<sub>2</sub>(μ-tp)(μ<sub>3</sub>-I)<sub>2</sub>] (**2**)

CuI (0.30 mmol, 57.1 mg) was dissolved in 10 ml of a KI-saturated aqueous solution. Over the resulting clear solution an aqueous solution (10 ml) of tp (0.60 mmol, 72.1 mg) was poured. Immediately, a red precipitate appeared which was filtrated, washed with mother liquor (which was kept for the later isolation of compound **2**) and ethanol, and dried with diethyl ether. Afterwards, this precipitate was redissolved in 20 ml of hot acetonitrile. The resulting yellow clear solution was kept standing at room temperature and after 1 week, yellow prismatic crystals of **1** suitable for X-ray analysis were isolated. From the former aqueous mother liquor (slightly colored and clear solution) brown needle-shaped crystals of **2** were formed after standing at room temperature for 5–10 days.

Yield (**1**) ~60%. *Anal. Calc.* for C<sub>7</sub>H<sub>7</sub>Cu<sub>2</sub>N<sub>5</sub>I<sub>2</sub> (**1**): C, 15.51; H, 1.30; N, 12.92. Found: C, 15.54; H, 1.11; N, 13.04%. Main IR bands (cm<sup>-1</sup>): 1616s (ν<sub>tp</sub>), 1535s (ν<sub>pym1</sub>), 1517s (ν<sub>pym2</sub>), 3085w, 3063w (ν<sub>C-H</sub>).

Yield (**2**) ~10%. *Anal. Calc.* for C<sub>5</sub>H<sub>4</sub>Cu<sub>2</sub>N<sub>4</sub>I<sub>2</sub> (**2**): C, 11.99; H, 0.80; N, 11.18. Found: C, 11.06; H, 0.90; N, 12.33%. Main IR bands (cm<sup>-1</sup>): 1616s (ν<sub>tp</sub>), 1543s (ν<sub>pym1</sub>), 1520s (ν<sub>pym2</sub>), 3048w, 2994w (ν<sub>C-H</sub>).

### 2.3. Single-crystal structure determination

#### 2.3.1. Compound **1**

*Data collection:* Rigaku R-axis Spider Image plate detector diffractometer, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, double-pass method ω-scan; data collection, cell refinement and data reduction with CrystalClear [15], empirical (multi-scan) absorption correction with ABCOR [16].

#### 2.3.2. Compound **2**

Bruker SMART APEX CCD system with Mo Kα radiation (λ = 0.7107 Å). The data were processed with APEX2 [17] and corrected for absorption using SADABS [18].

**Table 1**  
Crystal data and structure refinement for **1** and **2**.

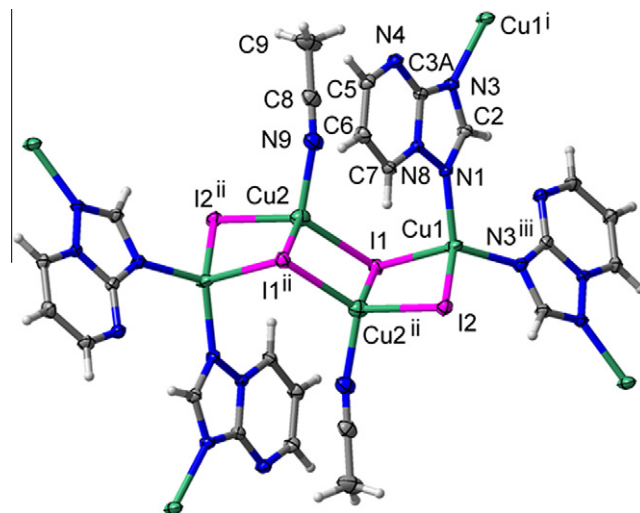
Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>7</sub> H <sub>7</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>5</sub>	C <sub>5</sub> H <sub>4</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub>
<i>M</i> (g mol <sup>-1</sup> )	542.06	501.00
Crystal size (mm)	0.20 × 0.16 × 0.12	0.37 × 0.05 × 0.01
Crystal appearance	block, yellow	needle, yellow
2θ range (°)	6.00–54.96	2.14–52.90
<i>h</i> ; <i>k</i> ; <i>l</i> range	±13; –12, 13; ±17	±5; 0, 15; 0, 23
Crystal system	monoclinic	monoclinic
<i>T</i> (K)	173(2)	100(2)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	10.019(2)	4.2256(2)
<i>b</i> (Å)	10.264(2)	12.0889(6)
<i>c</i> (Å)	13.495(5)	19.0076(10)
β (°)	115.60(2)	90.007(4)
<i>V</i> (Å <sup>3</sup> )	1251.5(6)	970.96(8)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.877	3.427
<i>F</i> (0 0 0)	992	904
μ (mm <sup>-1</sup> )	8.311	10.694
Maximum/minimum transmission	0.4354/0.2872	0.9006/0.1098
Reflections collected	55,585	2108
Independent reflections ( <i>R</i> <sub>int</sub> )	2866 (0.0230)	1998 (0.0000)
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	2800	1891
Parameters refined	146	119
Maximum/minimum Δρ <sup>a</sup> (e Å <sup>-3</sup> )	0.444/–0.792	0.956/–1.015
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0158, <i>wR</i> <sub>2</sub> = 0.0371	<i>R</i> <sub>1</sub> = 0.0246, <i>wR</i> <sub>2</sub> = 0.0562
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (All reflections) <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0165, <i>wR</i> <sub>2</sub> = 0.0374	<i>R</i> <sub>1</sub> = 0.0279, <i>wR</i> <sub>2</sub> = 0.0577
Goodness-of-fit (GOF) on <i>F</i> <sup>2c</sup>	1.289	1.138
Weight. scheme <i>w</i> ; <i>a</i> / <i>b</i> <sup>d</sup>	0.0140/1.6535	0.0270/1.3639

<sup>a</sup> Largest difference peak and hole.

<sup>b</sup> *R*<sub>1</sub> = [Σ(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)|Σ|*F*<sub>o</sub>|]; *wR*<sub>2</sub> = [Σ[*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

<sup>c</sup> Goodness-of-fit = [Σ[*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/(n – p)]<sup>1/2</sup>.

<sup>d</sup> *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*aP*)<sup>2</sup> + *bP*] where *P* = (max(*F*<sub>o</sub><sup>2</sup> or 0) + 2*F*<sub>c</sub><sup>2</sup>)/3.



**Fig. 1.** Thermal ellipsoid plot (50% probability) of the building unit of **1**, showing the full coordination spheres for each Cu1 and Cu2 and the ligand bridging action. Selected distances (Å) and angles (°): Cu1–I1 2.7521(6), Cu1–I2 2.5932(9), Cu2–I1 2.6456(6), Cu2<sup>ii</sup>–I1 2.6754(11), Cu2–I2<sup>ii</sup> 2.6576(6), Cu1–N1 2.015(2), Cu1–N3<sup>iii</sup> 2.039(2), Cu1–I1–Cu2 99.056(19), Cu1–I1–Cu2<sup>ii</sup> 68.16(2), Cu1–I2–Cu2<sup>ii</sup> 70.80(2), Cu2–I1–Cu2<sup>ii</sup> 70.17(2), I1–Cu1–I2 108.52(2), I1–Cu2<sup>ii</sup>–I2 108.92(2), I1–Cu2–I1<sup>ii</sup> 109.83(2), I1–Cu2–I2<sup>ii</sup> 112.32(2), N1–Cu1–I1 102.75(6), N1–Cu1–I2 118.21(6), N3<sup>iii</sup>–Cu1–I1 106.41(6), N3<sup>iii</sup>–Cu1–I2 106.83(6), N1–Cu1–N3<sup>iii</sup> 113.40(8), N9–Cu2–I1 112.12(8), N9–Cu2–I1<sup>ii</sup> 112.39(7), N9–Cu2–I2<sup>ii</sup> 100.98(7). Symmetry transformations: (i) –*x*, –0.5 + *y*, 0.5 – *z*; (ii) 1 – *x*, 1 – *y*, 1 – *z*; (iii) –*x*, 0.5 + *y*, 0.5 – *z*.

## 2.4. Structural analysis and refinement

The structure was solved by direct methods (SHELXS for **1** and SIR97 [19] for **2**), refinement was done by full-matrix least squares on  $F^2$  using the SHELXL program suite [20]; all non-hydrogen positions refined with anisotropic temperature factors; hydrogen atoms for aromatic CH groups were positioned geometrically ( $C-H=0.94 \text{ \AA}$ ) and refined using a riding model, with  $U_{iso}(H)=1.2U_{eq}(C)$ ; H atoms of the acetonitrile group were found and refined with  $U_{iso}(H)=1.5U_{eq}(C)$ . Graphics were drawn with DIAMOND [21]. Computations on the supramolecular interactions were carried out with PLATON for Windows [22]. Crystal data and details on the structure refinements are given in Table 1.

## 3. Results and discussion

### 3.1. Description of the structures

Compound  $[\text{Cu}_2(\mu\text{-tp})(\text{CH}_3\text{CN})(\mu\text{-I})(\mu_3\text{-I})]_n$  (**1**) consists of chair-like tetrameric  $\text{Cu}_4\text{I}_4$  units which are bridged into a 2D network through the N1,N3-bridging action of the tp ligand (Figs. 1 and 2). There are two crystallographically different Cu and I atoms, respectively, in the asymmetric unit. Only the Cu1 atom types are connected to the tp donor atoms. Their coordination sphere is constructed from two bridging iodine atoms and two tp nitrogen donors. The Cu2 atoms are coordinated by three bridging iodine atoms and an acetonitrile ligand. Both copper(I) ions display an almost perfect tetrahedral coordination environment ( $\tau_4=0.91$  (Cu1), 0.96 (Cu2)) [23]. The geometry index  $\tau_4$  for four-coordinate complexes is defined as  $\tau_4=[360^\circ-(\alpha+\beta)]/141^\circ$  with  $\alpha$  and  $\beta$  being the two largest angles in the four-coordinate species. Intermediate structures, including trigonal pyramidal and seesaw, fall within the range of 0–1.00 [23]. One iodine atom bridges between two Cu atoms, the other one between three Cu atoms.

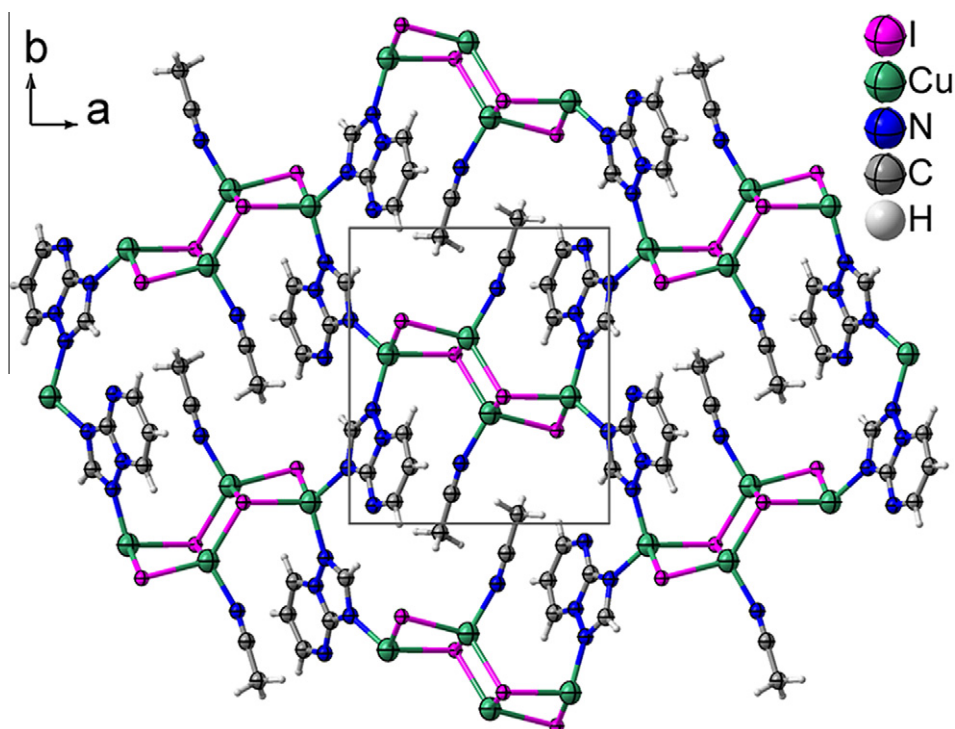


Fig. 2. View of the 2D network of complex **1** along the crystallographic  $c$  axis.

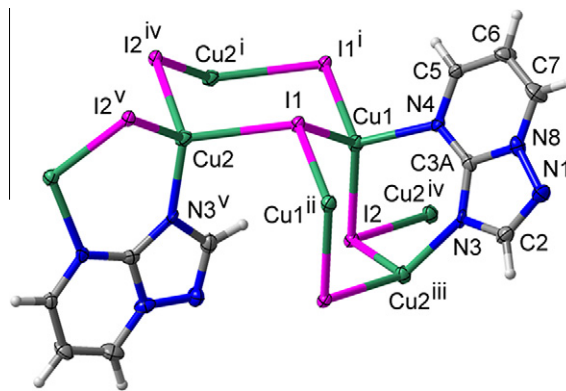
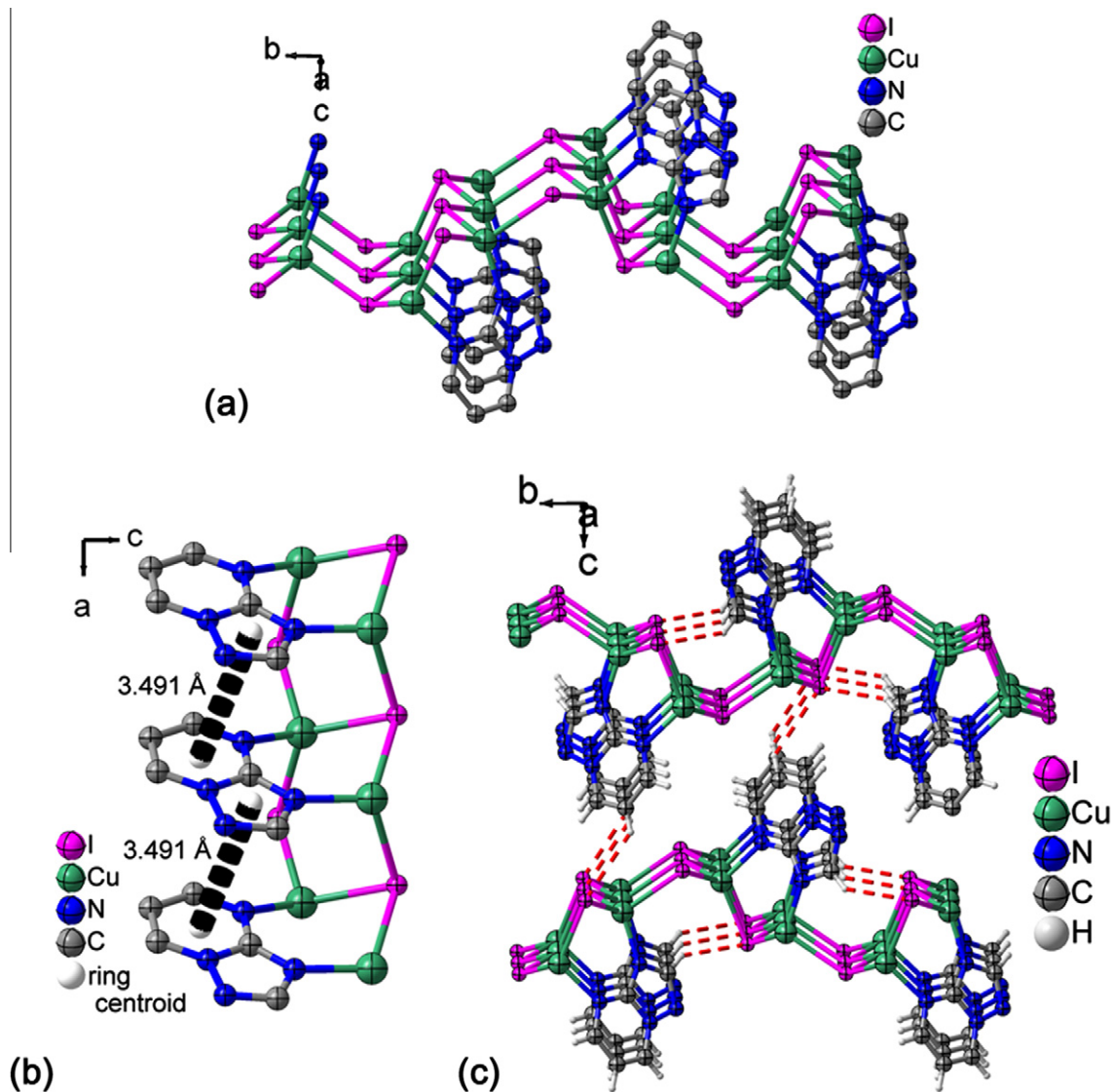


Fig. 3. Thermal ellipsoid plot (50% probability) of the asymmetric unit of **2**, also showing the full coordination spheres for Cu1 and Cu2 and the ligands bridging action. Selected distances (Å) and angles ( $^\circ$ ): Cu1–I1 2.6389(11), Cu1–I1<sup>i</sup> 2.6333(10), Cu1–I2 2.5944(10), Cu2–I1 2.6949(9), Cu2–I2<sup>v</sup> 2.6438(10), Cu2–I2<sup>v</sup> 2.5839(10), Cu1–N4 2.094(5), Cu2–N3<sup>v</sup> 2.020(6), Cu1–I1–Cu1<sup>ii</sup> 106.55(3), Cu1<sup>ii</sup>–I1–Cu2 102.98(3), Cu1–I1–Cu2 116.05(3), Cu2<sup>iii</sup>–I2–Cu1 81.01(3), Cu2–I2<sup>v</sup>–Cu2<sup>i</sup> 107.86(3), Cu1–I2–Cu2<sup>iv</sup> 96.75(3), I1–Cu1–I1<sup>i</sup> 106.55(3), I1–Cu1–I2 123.11(4), I2–Cu1–I1<sup>i</sup> 106.03(4), I1–Cu2–I2<sup>v</sup> 115.00(4), I1–Cu2–I2<sup>v</sup> 101.44(3), I2<sup>v</sup>–Cu2–I2<sup>v</sup> 107.86(3), N4–Cu1–I2 112.90(15), N4–Cu1–I1 98.66(17), N4–Cu1–I1<sup>i</sup> 108.91(17), N3<sup>v</sup>–Cu2–I1 105.97(15), N3<sup>v</sup>–Cu2–I2<sup>v</sup> 113.72(17), N3<sup>v</sup>–Cu2–I2<sup>v</sup> 112.28(17). Symmetry transformations: (i)  $-1+x, y, z$ ; (ii)  $1+x, y, z$ ; (iii)  $-x, -0.5+y, 1.5-z$ ; (iv)  $-1-x, -0.5+y, 1.5-z$ ; (v)  $-x, 0.5+y, 1.5-z$ .

The packing of adjacent layers in compound **1** appears controlled by van der Waals contacts. There are no  $\pi$ – $\pi$  or  $C-H \cdots \pi$  interactions.

Compound  $[\text{Cu}_2(\mu\text{-tp})(\mu_3\text{-I})_2]_n$  (**2**) consists of a 2D network made of condensed six-membered  $[\text{Cu}_3\text{I}_3]$  rings with chair-like conformation, and bridging tp ligands placed at both sides of the sheet (Figs. 3 and 4). In the structure, there are two crystallographically non-equivalent metal centers connected by a tp ligand through N3 and N4 atoms and one iodide (Fig. 3) at a  $\text{Cu1} \cdots \text{Cu2}$  distance of 3.363(1) Å. Both copper(I) ions display a slightly distorted tetrahe-



**Fig. 4.** Views of the 2D kinked-layer network of complex **2**, (a) showing one layer approximately along the crystallographic *a* axis; (b) showing the intra-layer  $\pi$ -stacking between the triazolo and the pyrimidine rings and (c) showing two adjacent layers with their intra- and inter-layer C-H...I contacts suggested by PLATON (down). Intra-layer H...I contact 2.96 Å, C-H...I angle 144°; inter-layer H...I contact 3.03 Å, C-H...I angle 133°.

dral coordination environment ( $\tau_4 = 0.88$  (Cu1), 0.93 (Cu2)) [23] with  $\text{CuNi}_3$  stoichiometry, but different connectivity; Cu1 is bound to N4 atom of tp and Cu2 is bound to N3 atom. In the absence of a coordinating solvent molecule like acetonitrile both Cu atoms have to coordinate to a nitrogen atom of the tp ligand.

As a result, a  $[\text{Cu}_n\text{I}_n]$  kinked layer (Fig. 4a) is formed whose structure is intermediate between the layer structures of black phosphorus and gray arsenic. Strong intra-layer  $\pi$ -stacking forces involving triazole and pyrimidine rings of tp ligands contribute to the stabilization of the structure (short centroid-centroid distance between pyrimidine and triazole rings = 3.491 Å and small slip angles ( $\beta = 19.80^\circ$ ,  $\gamma = 19.08^\circ$ ) between the slightly ( $0.8^\circ$ ) tilted ring planes) (Fig. 4b) [24,25].

In both structures **1** and **2** the tp ligand only engages two N atoms in metal coordination. Most likely, the coordination of two metal atoms already withdraws considerable electron density from the third N donor so that its coordinating ability becomes very low.

The packing of adjacent layers in **2** is probably mostly due to van der Waals contacts and perhaps a weak inter-layer C-H...I

contact as suggested by the calculations of the supramolecular interactions with PLATON (Fig. 4c). There are no inter-layer  $\pi$ - $\pi$  or C-H... $\pi$  interactions.

### 3.2. Spectroscopic and thermal analysis

A comparison of the infrared spectra of tp ligand and its Cu(I) complexes **1** and **2** reveals in both cases a small displacement to higher wavenumbers of tp bands ( $1621$ ,  $1534$  and  $1515\text{ cm}^{-1}$ ) due to combined C=C and C=N stretching vibrations of the ligand [26]. These minor displacements confirm a coordination of the triazolopyrimidine derivatives to the metal centers. In addition, several bands corresponding to C-H bond stretching vibration modes are also observed in the  $2900$ – $3300\text{ cm}^{-1}$  region of the IR spectra.

On the other hand, the first step of the thermal decomposition of the complex **1** is the loss of the acetonitrile (solvent) molecules, which is displayed in TG diagram as a well-defined single weight loss (% cal./exp.: 7.56/7.47) in the  $150$ – $175^\circ\text{C}$  temperature range.

From DSC diagram, a value of  $-45$  kJ per acetonitrile mol was obtained for desolvation. The pyrolysis of the organic moiety (tp) in both compounds occurs in several steps beginning around  $250$  °C and finishing at  $600$  °C, giving CuO as residue.

#### 4. Conclusions

Herein are reported the synthesis and structural characterization of two new 2D-polymers of Cu(I), **1** and **2**, both obtained from the reaction between copper iodide and 1,2,4-triazolo[1,5-*a*]pyrimidine (tp). Their structures reveal a clear influence of the solvent of crystallization, showing tp ligand different bridging modes: via N1 and N3 between chair-like  $[Cu_4L_4]$  units in compound **1**, and through N3 and N4 at both sides of a  $[Cu_nL_n]$  kinked layer in compound **2**. These polymers are the first examples of Cu(I) compounds based on the nucleobase-analog ligand tp.

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#### Appendix A. Supplementary material

CCDC 819190 and 819191 contain the supplementary 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](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.008.

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