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Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: [www.elsevier.com/locate/jssc](http://www.elsevier.com/locate/jssc)

# Syntheses, structures and photoluminescent properties of three $d^{10}$ coordination architectures based on *in-situ* 1,3,5-triazine derivatives

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## ARTICLE INFO

## Article history:

Received 8 July 2013

Received in revised form

29 September 2013

Accepted 6 October 2013

Available online 12 October 2013

## Keywords:

Coordination polymers

Topology

Photoluminescent property

## ABSTRACT

In the presence of aromatic carboxylic acids, three new  $d^{10}$  transition metal coordination polymers,  $[\text{Ag}(\text{PAHT})]_n$  (**1**),  $[\text{Ag}_2(\text{HCA})]_n$  (**2**) and  $[\text{Cu}_6(\text{CA})_2(\text{H}_2\text{O})]_n$  (**3**) (HPAHT = 2-phenyl-4-amino-6-hydroxy-1,3,5-triazine,  $\text{H}_3\text{CA}$  = cyanuric acid) have been synthesized based on *in-situ* 1,3,5-triazine derivatives resulting from 2,4-diamino-6-phenyl-1,3,5-triazine, 2-chloro-4,6-diamino-1,3,5-triazine and melamine under hydrothermal conditions. Complexes **1–3** have been characterized by single-crystal X-ray diffraction, IR spectra, elemental analysis and thermogravimetric analysis (TGA). The compound **1** exhibits a uninodal three-connected 3D network with a rare **lig LiGe** type topology, which contains right-handed and left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chains. For compound **2**, the 3D network is comprised of 2D sheet by strongly Ag–O and weakly Ag(I)⋯Ag(I) interactions. In compound **3**, it is infrequently observed that dodecanuclear copper(I) units as secondary building units (SBUs) construct 3D network by the ligands  $\text{CA}^{3-}$  with a rare uninodal 10-connected **bct** topology ( $3^{12}.4^{28}.5^5$ ). The photoluminescent properties of three compounds have also been measured.

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## 1. Introduction

In recent years, the design and controlled assembly of coordination polymers, especially 2D and 3D metal–organic frameworks based on metal centers and multifunctional bridging ligands are of great interests, not only owing to their versatile intriguing architectures and topologies but also for their potential applications in a variety of areas, including catalysis [1,2], gas storage [3,4], separations [5,6], fluorescent sensing [7,8], nonlinear optics [9,10], electronic and magnetic devices [11,12]. Meanwhile, it is well known that  $d^{10}$  coordination polymers such as Ag(I) and Cu(I) complexes, have already aroused chemists' wide attention because Ag(I) or Cu(I) have high affinity for N or O donors, variable coordination geometries, greater tendency to form polymeric species and are extensively used as metallic node to construct novel structural topologies. Furthermore, the researches on Ag(I) or Cu(I) coordination polymers are motivated by several recent reports about highly efficient organic light-emitting devices [13–15].

The aim of obtaining the desirable architectures of Ag(I) or Cu(I) coordination polymers with 2D and 3D networks is still a long-term challenge to chemists. Because crystallization is a very complicated process, some factors such as assistant ligands, pH

value, the reaction temperature and time, and metal-to-ligand ratio, can have unpredictable impacts on the composition and structure of the resultant complexes. However, the smart selection of metal ions and organic ligands still plays a decisive role in the construction of desirable coordination polymers. The meaningful use of *N*-heterocyclic ligand is an effective method for designing and constructing Ag(I) or Cu(I) coordination complexes, owing to the fact that they can satisfy and even mediate the coordination needs of the metal center. The ligands of 1,3,5-triazine (trz) and its derivatives, which has three coordinating N-atoms with  $120^\circ$  angles and may act as three-connected node, as well as can form  $\pi\cdots\pi$  stacking interactions between the triazine rings, have received considerable attention on the assembly process and been extensively used in the construction of coordination polymers with different metal ions [16–19]. Although fascinating architectures and properties of Ag(I) or Cu(I) coordination polymers with carboxylic acid ligands/1,3,5-triazine ligands have been widely investigated [20–23], to the best of our knowledge, only limited compounds containing metal-1,3,5-triazine have been documented to date [24,25].

Herein, in the presence of aromatic carboxylic acids, three 3D compounds  $[\text{Ag}(\text{PAHT})]_n$  (**1**),  $[\text{Ag}_2(\text{HCA})]_n$  (**2**) and  $[\text{Cu}_6(\text{CA})_2(\text{H}_2\text{O})]_n$  (**3**) (HPAHT = 2-phenyl-4-amino-6-hydroxy-1,3,5-triazine,  $\text{H}_3\text{CA}$  = cyanuric acid) were *in situ* synthesized under hydrothermal reactions of 1,3,5-triazine derivatives with  $\text{AgNO}_3$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . Compound **1** shows a uninodal three-connected 3D network with right-handed and left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chains, whose

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feature is a rare topology with **lig LiGe** type [26–28]. Compound **2** is composed of 2D sheets which are entangled through strongly Ag–O and weakly Ag(I)...Ag(I) interactions to generate a 3D network. The feature of compound **3** is that it is an unusual sign of dodecanuclear copper(I) units as secondary building units (SBUs) to construct 3D network by the ligands  $CA^{3-}$  with a rare uninodal 10-connected **bct** topology ( $3^{12} \cdot 4^{28} \cdot 5^5$ ). In addition, complexes **1–3** were found to exhibit photoluminescent properties in the solid state.

## 2. Experimental

### 2.1. Materials and methods

All materials were commercially available and used as received. Infrared spectra were recorded on a Nicolet magna 750 FT-IR spectrophotometer using KBr pellets in the range of 400–4000  $cm^{-1}$ . Elemental analyses were performed via Vario EL III Etro Elemental Analyzer. Thermogravimetric analyses (TGA) were performed under atmosphere with a heating rate of 10 °C/min using TGA/SDTA851e. Photoluminescence spectra were measured on a Hitachi Fluorescence spectrophotometer –luores.

### 2.2. Synthesis of the complexes

#### 2.2.1. Syntheses of $[Ag(PAHT)]_n$ (**1**)

2,4-Diamino-6-phenyl-1,3,5-triazine (0.094 g, 0.5 mmol), 3-nitrophthalic acid (0.106 g, 0.5 mmol) and  $AgNO_3$  (0.171 g, 1 mmol) in 10 mL  $H_2O$  were stirred for 20 min at room temperature, and the mixture was sealed in a 25 mL Teflon-lined reactor, which was heated to 180 °C for 3 days. After the autoclave had been cooled to room temperature over 6–7 h, yellow rod-like crystals of **1** were obtained, and washed by  $H_2O$  (Yield: 0.062 g, 42.0% based on 2,4-diamino-6-phenyl-1,3,5-triazine). Anal. Calc. for (%):  $C_9H_7AgN_4O$ : C 36.64, H 2.39, N 18.99; Found: C 36.84, H 2.45, N 19.26. IR (KBr pellet,  $cm^{-1}$ ): 3459, 1649, 1590, 1542, 1490, 1442, 1400, 1160, 1115, 1056, 1000, 818, 787, 701.

**Table 1**  
Crystallographic data for compounds **1–3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$C_9H_7AgN_4O$	$C_3HA_2N_3O_3$	$C_6H_2Cu_6N_6O_7$
Formula mass	295.06	342.81	651.38
Crystal size [mm]	$0.40 \times 0.15 \times 0.11$	$0.48 \times 0.34 \times 0.19$	$0.36 \times 0.14 \times 0.10$
Space group	$I-42d$	$C2/c$	$P2(1)/n$
<i>a</i> [Å]	15.778(4)	12.7126(13)	11.6878(17)
<i>b</i> [Å]	15.778(4)	13.0461(13)	7.1569(11)
<i>c</i> [Å]	7.256(4)	6.6202(7)	14.279(2)
$\alpha$ [°]	90	90	90
$\beta$ [°]	90	97.296(2)	97.245(3)
$\gamma$ [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	1806.4(11)	1089.07(19)	1184.9(3)
<i>Z</i>	8	8	4
$\mu$ [mm <sup>-1</sup> ]	2.205	7.134	10.632
$\rho$ calcd. [g/cm <sup>-3</sup> ]	2.170	4.182	3.651
$\theta$ limits [°]	2.58 to 28.30	2.25 to 25.00	2.12 to 28.44
<i>h, k, l</i> limits	$-11 \leq h \leq 20, -20 \leq k \leq 19, -9 \leq l \leq 9$	$-11 \leq h \leq 15, -15 \leq k \leq 11, -7 \leq l \leq 4$	$-15 \leq h \leq 14, -9 \leq k \leq 8, -18 \leq l \leq 16$
Collected reflections	4515	2219	7123
<i>R</i> <sub>int</sub>	0.0425	0.0175	0.0290
<i>R</i> index [ $I > 2\sigma(I)$ ]	$R_1 = 0.0385$ $wR_2 = 0.0918$	$R_1 = 0.0341$ $wR_2 = 0.0862$	$R_1 = 0.0313$ $wR_2 = 0.0820$
<i>R</i> (all data)	$R_1 = 0.0457$ $wR_2 = 0.0944$	$R_1 = 0.0364$ $wR_2 = 0.0874$	$R_1 = 0.0463$ $wR_2 = 0.0867$
GOOF	1.035	1.314	1.060
$\Delta\rho_{min}$ [eÅ <sup>-3</sup> ]	-0.789	-1.350	-1.027
$\Delta\rho_{max}$ [eÅ <sup>-3</sup> ]	0.530	0.271	0.721

<sup>a</sup> $R = \sum(|F_o| - |F_c|) / \sum |F_o|$ , <sup>b</sup> $Rw = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$ ,  $w = 1 / [ \sigma^2(F_o^2) + (aP)^2 + bP ]$ ,  $P = (F_o^2 + 2F_c^2) / 3$ . **1**,  $a = 0.0475$ ,  $b = 2.9313$ ; **2**,  $a = 0.0439$ ,  $b = 23.0849$ ; **3**,  $a = 0.0411$ ,  $b = 1.5541$ .

#### 2.2.2. Syntheses of $[Ag_2(HCA)]_n$ (**2**)

Replacement of 2,4-diamino-6-phenyl-1,3,5-triazine, and 3-nitrophthalic acid of **1** by 2-chloro-4,6-diamino-1,3,5-triazine (0.073 g, 0.5 mmol) and phthalic acid (0.083 g, 0.5 mmol), colorless block crystals of **2** were obtained (Yield 0.037 g, 21.6% based on 2-chloro-4,6-diamino-1,3,5-triazine). Anal. Calc. for (%):  $C_3HA_2N_3O_3$ : C 10.51, H 0.29, N 12.26; Found: C 10.59, H 0.34, N 12.38. IR (KBr pellet,  $cm^{-1}$ ): 3404, 3126, 2950, 1685, 1655, 1598, 1485, 1421, 1387, 1021, 782, 770, 598.

#### 2.2.3. Syntheses of $[Cu_6(CA)_2(H_2O)]_n$ (**3**)

Replacement of 2,4-diamino-6-phenyl-1,3,5-triazine, 3-nitrophthalic acid and  $AgNO_3$  of **1** by melamine (0.063 g, 0.5 mmol), 2,2'-dithiodibenzoic acid (0.153 g, 1 mmol) and  $Cu(NO_3)_2 \cdot 3H_2O$  (0.241 g, 1 mmol), violet block crystals of **3** were obtained (Yield 0.176 g, 54.1% based on melamine). Anal. Calc. for (%):  $C_6H_2Cu_6N_6O_7$ : C 11.12, H 0.31, N 12.97; Found: C 11.38, H 0.78, N 12.94. IR (KBr pellet,  $cm^{-1}$ ): 1689, 1649, 1608, 1472, 1413, 1392, 1091, 851, 771, 711, 613, 564.

### 2.3. Crystallographic data collection and refinement

X-ray single crystal data of the compounds **1–3** were collected at 296(**2**) K on a Bruker Apex-II CCD area detector diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction and absorption correction were made with empirical methods. These structures were solved by direct methods using SHELXS-97 [29] and refined by full matrix least-squares methods using SHELXL-97 [30]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. And all hydrogen atoms bonding to carbon and nitrogen atoms were added in the riding model without refinement. Due to high symmetry, one nitrogen atom and one oxygen atom from HPAHT ligand were treated as two positions with occupancy of 1/2 each in complex **1**. The crystal data and refinement details for three complexes are listed in Table 1.

The selected bond lengths and angles of compounds **1–3** are listed in Table S1 (seeing in Supporting information).

### 3. Results and discussion

#### 3.1. Synthesis and IR spectroscopy

Three 3D compounds  $[\text{Ag}(\text{PAHT})]_n$  (**1**),  $[\text{Ag}_2(\text{HCA})]_n$  (**2**) and  $[\text{Cu}_6(\text{CA})_2(\text{H}_2\text{O})]_n$  (**3**) have been obtained with *in situ* synthesized ligands (HPAHT or  $\text{H}_3\text{CA}$ ) by the hydrothermal reactions of 1,3,5-triazine, different metal salts and aromatic carboxylic acids at 180 °C for 3 days. Though the aromatic carboxylic acids do not participate in coordinating to metal ion, it has been proved that the  $\text{NH}_2^-$  and/or  $\text{Cl}^-$  of triazines part or all have high hydrolysis and can be replaced by  $\text{OH}^-$  groups in the carboxylic acidic conditions, giving the ligands  $\text{PAHT}^-$ ,  $\text{HCA}^{2-}$  and  $\text{CA}^{3-}$  [31–33]. The results from elemental analyses also demonstrated them. It is inferred that divalent copper atom takes a reduction reaction into monovalent copper to maintain the balance of charge while negative divalent sulfur change into the elemental sulfur along with the cleavage of S–S bond of 2,2'-dithiodibenzoic acid. Compounds **1–3** are air and moisture-stable. Compounds **1–3** are all insoluble in DMF, DMSO and the common solvents such as methanol and  $\text{CH}_2\text{Cl}_2$ . The peak at  $3459\text{ cm}^{-1}$  for **1** ( $3404\text{ cm}^{-1}$  for **2**) should be ascribed to N–H stretching vibrations. In addition, the peaks at about  $1680\text{--}1100\text{ cm}^{-1}$  are attributed to the 1,3,5-triazine ring stretching vibrations.

#### 3.2. Crystal structure of complex 1

Single-crystal X-ray diffraction analysis reveals that the complex **1** crystallizes in tetragonal system group *I*-42d with 3D network consisting of right-handed and left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chains. As shown in Fig. 1, there exists one Ag(I) ion and a half  $\text{PAHT}^-$  ligand in the asymmetric unit of **1**. The Ag(I) forms a perfect trigonal planar geometries by being coordinated to three nitrogen atoms from three  $\text{PAHT}^-$  ligands without mean deviation. The distances of Ag–N ranging from 2.168(5) to 2.332(4) Å, with N–Ag–N of about 97.4(2) and 131.28(11)° (see Table S1), respectively, are corresponding to this type of coordination environment [34–36].

The most remarkable structure feature is that the compound **1** contains two kinds of single helical chains, which are respectively

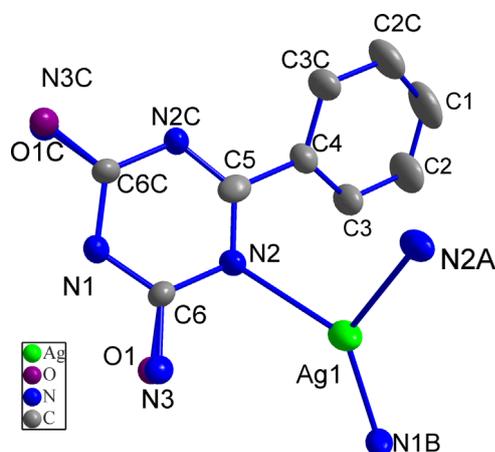


Fig. 1. The construction unit of **1** with thermal ellipsoid at 50% probability ignoring hydrogen atoms (symmetry codes: (A)  $x, 1.5 - y, 0.25 - z$ ; (B)  $1.5 - y, 0.5 + x, 0.5 - z$ ; (C)  $0.5 - x, y, 0.75 + z$ ).

right-handed and left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chains, similar to those of our reported compound  $[\text{Ag}_2(1,2\text{-bdc})(\text{phadt})]_n$  (1,2-bdc = phthalic acid dianion; phadt = 2,4-diamino-6-phenyl-1,3,5-triazine) [20]. As shown in Fig. 2, the ligands  $\text{PAHT}^-$  in bidentate mode join Ag(I) to form right-handed and left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chains, which spiral parallelly around a screw axis along the *c* axis with a pitch of 7.256(4) Å, where the nearest Ag(I) distance is 6.4414(15) Å. Two kinds of helical chains arrange alternately along *c* axis direction, which are further extended into 3D network in virtue of  $\text{Ag}_1\text{--N}_1$  contact ( $\text{Ag}_1\text{--N}_1$  2.168(5) Å, Fig. 2e). Each HPAHT lose one hydrogen proton forming  $\text{PAHT}^-$  ligand to balance the charge and the ligand  $\text{PAHT}^-$  adopts  $\mu_3:\eta^1:\eta^1:\eta^1$  coordination mode. In the ligand  $\text{PAHT}^-$ , the dihedral angle is 27.4° between the phenyl ring and the triazine ring. In addition, a kind of strong  $\pi\cdots\pi$  stacking interaction is observed from triazine ring and phenyl ring between the ligands of  $\text{PAHT}^-$  with the vertical plane–plane distance of 3.519 Å, the centroid–centroid distance of about 3.717 Å, which plays an important role in stabilizing the framework.

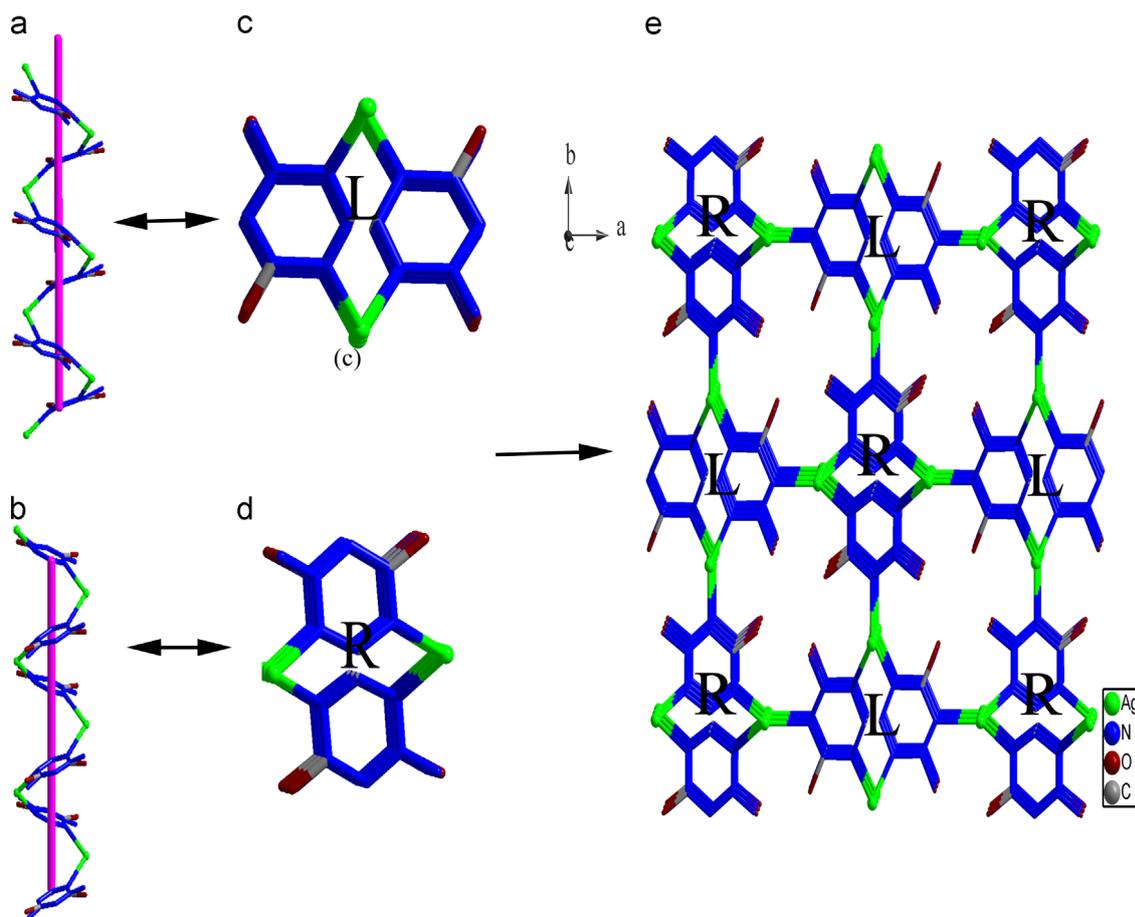
To better understand the structure of compound **1**, the topological analysis approach is employed. If each Ag(I) atom and each ligand  $\text{PAHT}^-$  was treated as one three-connected node, as a result, the 3D network can be described as uninodal three-connected with the Schläfli symbol of  $\{8^2.10\}$ , which is a rare topology with **lig LiGe** type (Fig. 3), resembling that of  $[\{\text{Ph}_3\text{PCH}_2\text{Ph}\}[\text{Cd}(\text{tp})\cdot\text{Cl}]\cdot 2\text{H}_2\text{O}]_n$  (tp = terephthalate) [26].

#### 3.3. Crystal structure of complex 2

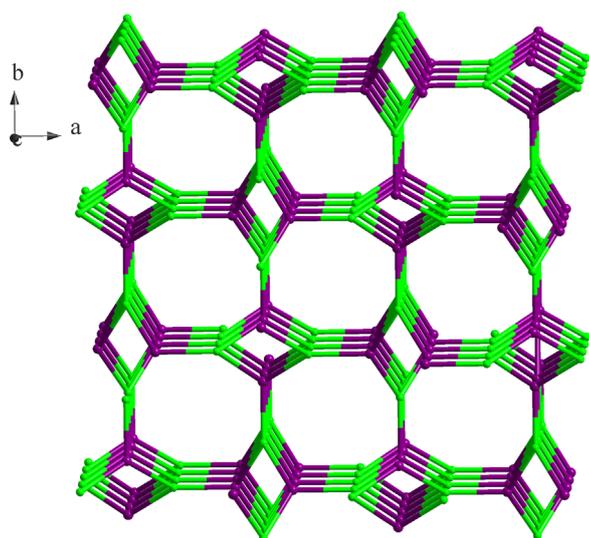
Replacement of 2,4-diamino-6-phenyl-1,3,5-triazine, and 3-nitrophthalic acid of **1** by 2-chloro-4,6-diamino-1,3,5-triazine and phthalic acid, the complex **2** was obtained. The compound **2** crystallizes in monoclinic space group *C*2/c and shows 3D network through 2D sheets connected by strongly Ag–O and weakly Ag(I)...Ag(I) interactions. In the asymmetric unit, there are three crystallographically unique Ag(I) atoms surrounded by one coordinating  $\text{HCA}^{2-}$  ligand.

As shown in Fig. 4, the  $\text{Ag}_1$  atom is coordinated to two oxygen atoms and one nitrogen atom from three ligands  $\text{HCA}^{2-}$ , resulting in three-coordinated trigonal planar geometries, mean deviation from planarity of 0.0345 Å. In the dimeric  $\text{Ag}_2\cdots\text{Ag}_3$  unit, the  $\text{Ag}_2$  atom bears perfect linear geometry by being coordinated to two nitrogen atoms from two ligands  $\text{HCA}^{2-}$  with  $\text{N}_3(\text{A})\text{--Ag}_2\text{--N}_3(\text{B})$  (A:  $1 - x, y, 1.5 - z$ ; B:  $x, -y, 0.5 + z$ ) of 180.0°, while  $\text{Ag}_3$  atom is coordinated to two oxygen atoms from two ligands  $\text{HCA}^{2-}$  with  $\text{O}_1\text{--Ag}_3\text{--O}_1(\text{A})$  of about 156.8(3)°. The Ag–N and Ag–O lengths ranging from 2.078(6) to 2.151(6) Å, and 2.218(6) and 2.492(5) Å, respectively, are in agreement with the distances reported earlier of this type of coordination environment [24,25]. The dimeric  $\text{Ag}_2\cdots\text{Ag}_3$  interaction with Ag–Ag of 2.9204(7) Å are found, significantly shorter than the van der Waals contact distance (3.44 Å), and longer than the Ag...Ag contact distance in metallic silver (2.88 Å), indicating the existence of argentophilicity can promote the aggregation of silver center [37–39].

Each  $\text{H}_3\text{CA}$  lose two hydrogen protons, and remanent hydrogen atom bonding to oxygen transfers into nitrogen atom of triazine ring forming  $\text{HCA}^{2-}$  ligand. Then the  $\text{HCA}^{2-}$  ligand adopts  $\mu_4:\eta^1:\eta^1:\eta^1$  coordination mode to construct 2D sheets (Fig. 5). Furthermore, along *b*-axis direction, the compound **2** shows 3D network by strongly Ag–O and weakly Ag(I)...Ag(I) interactions ( $\text{Ag}_3\text{--O}_1$  2.387 Å Fig. 6). In addition, a kind of  $\pi\cdots\pi$  stacking interaction is observed among triazine rings with the vertical plane–plane distance of 3.144 Å, the centroid–centroid distance of about 3.3403 Å, which plays an important role in stabilizing the framework.



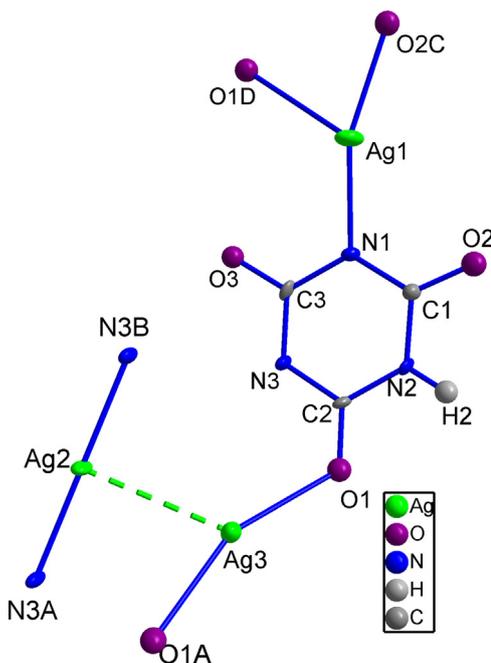
**Fig. 2.** (a) The left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chain viewed perpendicular to the  $c$  axis; (b) the right-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chain viewed perpendicular to the  $c$  axis; (c) the left-handed  $[\text{Ag}(\text{PAHT})]_n$  single helical chain screw along the  $c$  axis; (d) the right-handed  $[\text{Ag}(\text{PAHT})]_n$  chain screw along the  $c$  axis; (e): the interconnection of the helices in the compound **1** viewed along the  $c$  axis ( $R$  represents right-handed and  $L$  represents left-handed, phenyl rings are omitted for clarity).



**Fig. 3.** A uninodal three-connected 3D networks with point symbol of  $\{8^2.10\}$  net, which is a **lig LiGe** topological net.

### 3.4. Crystal structure of complex **3**

The complex **3** crystallizes in monoclinic groups  $P2(1)/n$  and shows the 3D network consisting of dodecanuclear copper(I) units



**Fig. 4.** The asymmetric unit of compound **2** with thermal ellipsoid at 50% probability ignoring hydrogen atoms (symmetry codes: (A)  $1-x, -y, 1.5-z$ ; (B)  $x, -y, 0.5+z$ ; (C)  $-x, -y, -z$ ; (D)  $0.5-x, -0.5+y, 0.5-z$ ).

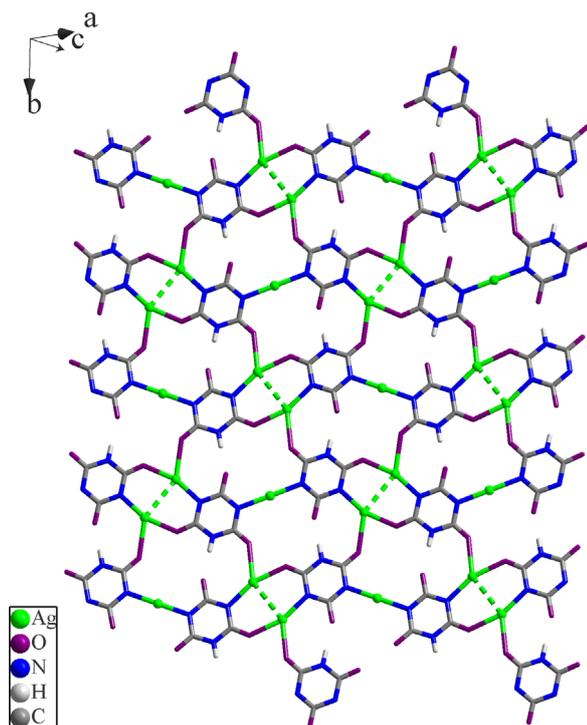


Fig. 5. The two-dimensional sheet of **2**.

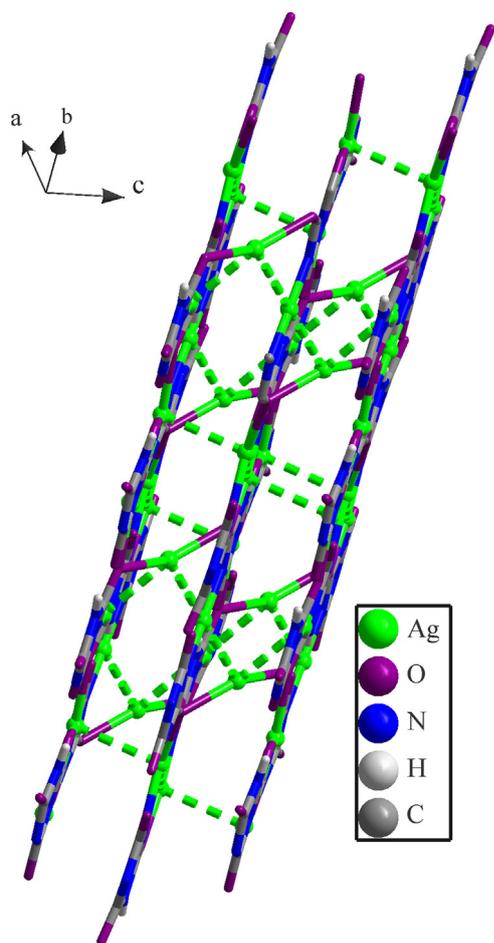


Fig. 6. The 3D network of **2** constructed by Ag–O and Ag...Ag interactions (Ag...Ag indicated as dashed lines).

as SBUs connected by the ligands  $CA^{3-}$ . As is shown in Fig. 7, there are six crystallographically unique copper(I) atoms, two  $CA^{3-}$  ligands and one water molecule in the asymmetric unit. Each Cu1, Cu2, Cu3 and Cu5 atoms is coordinated by N/O atoms from two  $CA^{3-}$  ligands locating in a two-coordinated linear geometry in which the angle N–Cu–O/N is in the range of  $164.08(16)$ – $175.28(16)^\circ$ . The Cu<sub>1</sub> and Cu<sub>2</sub> atoms are bridged by two  $CA^{3-}$  ligands and almost coplanar with 1,3,5-triazine rings with mean deviation from planarity of about  $0.0565 \text{ \AA}$ . The Cu<sub>1</sub>–Cu<sub>2</sub> distance is  $2.5719(10) \text{ \AA}$  similar to  $2.56 \text{ \AA}$  in copper metal [40,41], significantly shorter than the Cu(I)...Cu(I) distances from the documents [42–44], and are in fact shorter than the van der Waals contact distance ( $2.80 \text{ \AA}$ ) [45,46], which points to a pronounced effect of cuprophilicity. The Cu<sub>4</sub> and Cu<sub>6</sub> atoms are coordinated to two oxygen atoms and one nitrogen atom from three ligands  $CA^{3-}$ , three oxygen atoms from two ligands  $CA^{3-}$  and one water molecule, respectively, giving rise to the three-coordinated trigonal planar geometries mean deviation from planarity of about  $0.0224$ ,  $0.0461 \text{ \AA}$ , respectively. The Cu–N and Cu–O distances ranging  $1.867(4)$ – $1.900(4) \text{ \AA}$  and  $1.850(3)$ – $2.386(3) \text{ \AA}$  (see Table S1), respectively, are in agreement with distances reported earlier for similar coordination environment [47,48]. The Cu<sub>1</sub> to Cu<sub>6</sub> atoms are interconnected to form Cu<sub>6</sub> units through  $CA^{3-}$  ligands, which further link its symmetric part via the symmetric center between the Cu<sub>5</sub>...Cu<sub>5</sub>C (C:  $1-x, 1-y, 1-z$ ) to construct Cu<sub>12</sub> units, respectively. In the dodecanuclear copper(I) unit, many kinds of weakly Cu...Cu interactions are observed except above strongly interaction (Cu<sub>3</sub>...Cu<sub>4</sub>  $2.9230 \text{ \AA}$ ; Cu<sub>4</sub>...Cu<sub>6</sub>C  $2.9393(10) \text{ \AA}$ ; Cu<sub>5</sub>...Cu<sub>5</sub>C  $2.7843 \text{ \AA}$ ; Cu<sub>2</sub>...Cu<sub>6</sub>C  $3.076 \text{ \AA}$ ). In addition, many kinds of  $\pi$ ... $\pi$  stacking interaction are observed between triazine rings with the vertical plane–plane distance of  $3.161$ – $3.295 \text{ \AA}$ , the centroid–centroid

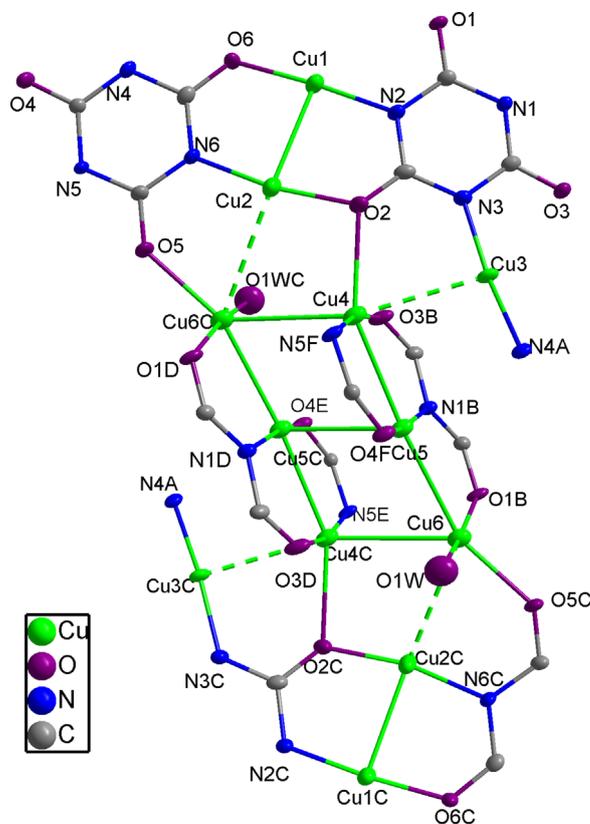
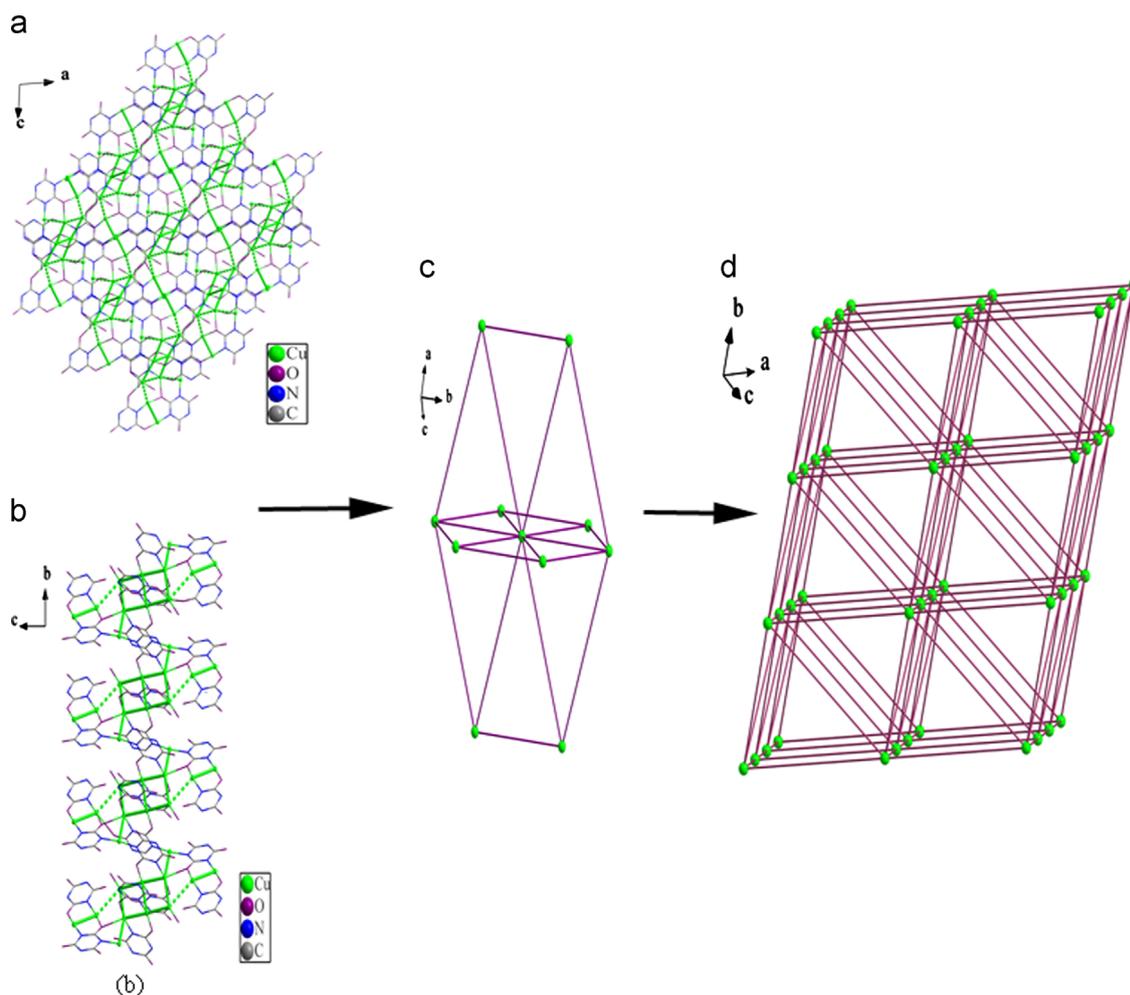


Fig. 7. The dodecanuclear copper(I) unit of **3** with thermal ellipsoid at 50% probability ignoring hydrogen atoms (symmetry codes: (A)  $0.5+x, 0.5-y, -0.5+z$ ; (B)  $1.5-x, 0.5+y, 1.5-z$ ; (C)  $1-x, 1-y, 1-z$ ; (D)  $-0.5+x, 0.5-y, 0.5+z$ ; (E)  $0.5+x, 1.5-y, -0.5+z$ ; (F)  $0.5-x, -0.5+y, 1.5-z$ ).



**Fig. 8.** For compound **3**, (a) each  $\text{Cu}_{12}$  unit is surrounded by eight  $\text{Cu}_{12}$  units viewed perpendicular to the  $b$  axis; (b) Along  $b$  axis direction, the  $\text{Cu}_{12}$  units are connected by two  $\text{Cu}_{12}$  units via three kind of Cu–O/N interactions to form a linear chain; (c) the surrounding of the  $\text{Cu}_{12}$  units; (d) a uninodal 10-connected **bct** type 3D framework omitting the  $\text{CA}^{3-}$  ligands for clarity.

distance of about 3.2056–3.7959 Å, which play an important role in stabilizing the framework.

Analogous to forming  $\text{HCA}^{2-}$  ligands, each  $\text{H}_3\text{CA}$  loses three hydrogen protons forming  $\text{CA}^{3-}$  ligand, and these  $\text{CA}^{3-}$  ligands adopt  $\mu_6:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$  and  $\mu_7:\eta^2:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$  coordination modes. As shown in Fig. 8a, each dodecanuclear copper(I) unit is surrounded by eight dodecanuclear copper(I) unit viewed perpendicular to the  $b$  axis. Along  $b$  axis direction, dodecanuclear copper(I) units are connected by two dodecanuclear copper(I) units via three kind of Cu–O/N interactions to form a linear chain (Fig. 8b). Thus, each  $\text{Cu}_{12}$  unit is surrounded by ten  $\text{Cu}_{12}$  units, which can be understood by the topological analysis approach. Each SBU was treated as one ten-connected node, and the resulting structure of complex **3** is an uninodal 10-connected **bct** type 3D framework (Fig. 8d) with the Schläfli symbol  $(3^{12}.4^{28}.5^5)$  analysis by TOPOS [49–51]. To the best of knowledge, several coordination polymers with **bct** type have been discussed in the literature, however, most of them contain coordinating carboxylic acids. For example, in the compound  $[\text{SmCo}(\mu_5\text{-PyIDC})(\mu_2\text{-INIC})(\mu_3\text{-INIC})] \cdot 3\text{H}_2\text{O}$  (HINIC = isonicotinic acid;  $\text{H}_3\text{PyIDC}$  = 2-(pyridine-3-yl)-1H-4,5-imidazolecarboxylic acid), the planer hexanuclear heterometallic  $[\text{Sm}_2\text{Co}_4(\mu_5\text{-PyIDC})_2]$  secondary building units are considered as 10-connected nodes, which obtained the rare 3D lanthanide-transition heterometal-organic coordination polymers with 10-connected **bct** type.

According to our survey, though several cases involving in dodecanuclear copper(I) compound have been reported [52–55],

all compounds exhibit only discrete clusters. For example, in the dodecanuclear cluster  $[\text{Cu}_2\text{PPh} \cdot \text{PPh}_3]_6$ , the twelve Cu atoms occupy the corners of a compressed cuboctahedron and the six PPh groups cap the  $\text{Cu}_4$  rings of the  $\text{Cu}_{12}$  polyhedron [52]. However, the compound **3** is different from that of the above compound, in that twelve copper atoms in the middle form almost planer configuration.

### 3.5. Fluorescence of **1–3**

The  $d^{10}$  (Ag(I) or Cu(I)) coordination complexes with  $N$ -heterocyclic ligands have received much attention for the development of photoluminescent materials. Then, the solid-state photoluminescent properties of compounds **1–3** were shown in Fig. 9. Intense emissions are observed at 472 and 580 nm for **1** ( $\lambda_{\text{ex}} = 364$  nm), 339 nm for **2** ( $\lambda_{\text{ex}} = 287$  nm), 412 nm for **3** ( $\lambda_{\text{ex}} = 300$  nm), respectively. It can be inferred that those broad peaks (472 nm of **1**, 339 nm of **2**, 412 nm of **3**) originate from the  $\pi^* \rightarrow \pi$  transition [22,56,57]. The peak 580 nm of **1** may be assigned to the ligand-to-metal charge-transfer (LMCT) [21,58].

## 4. Conclusions

Based on *in-situ* synthesized 1,3,5-triazine derivatives, we have prepared and structurally characterized three new coordination complexes. The feature of compound **1** is that it exhibits 3D

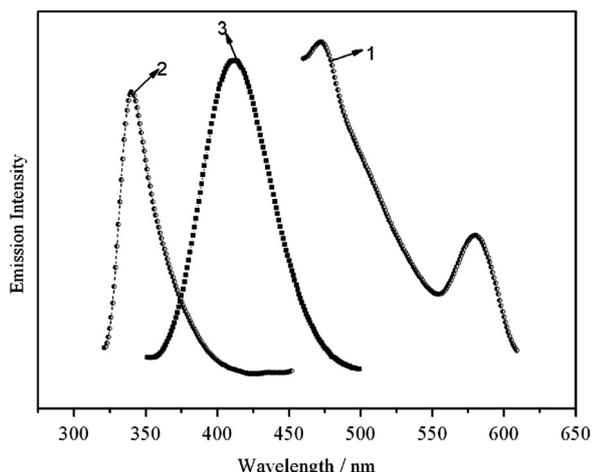


Fig. 9. Emission spectrum for solid compounds 1–3 at room temperature.

network consisting of right-handed and left-handed  $[\text{Ag}(\text{PAHT})]_n$  helical chains with a rare three-connected uninodal **lig LiGe** type topology. Compound **2** exhibits a 3D network composed of 2D sheet through strongly Ag–O and weakly Ag...Ag interactions. In compound **3**, twelve nuclear copper(I) units as SBUs was unusual observed to construct 3D network by ligands  $\text{CA}^{3-}$  with a rare uninodal 10-connected **bct** topology. In addition, compounds **1–3** display solid-state emissions.

### Acknowledgments

This research is supported by the National Science Foundation of China (21271025), the National Science Foundation of the Education Department of Henan Province (2011A150004, 12B150004), the Department of Science and Technology of Henan Province (122102210174), the State Key Laboratory of Structural Chemistry (20110008).

### Appendix A. Supplementary material

CCDC numbers 946265, 946266 and 946267 for compounds **1–3**, respectively. These crystallographic data for this paper can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jssc.2013.10.004>.

### References

- [1] A. Corma, U. Díaz, T. García, G. Sastre, A. Velty, *J. Am. Chem. Soc.* 132 (2010) 15011–15021.
- [2] D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* 48 (2009) 7502–7513.
- [3] A.U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* 38 (2009) 1284–1293.
- [4] C. Yang, X.P. Wang, M.A. Omary, *Angew. Chem. Int. Ed.* 48 (2009) 2500–2505.
- [5] M.J. Zaworotko, *Nature* 451 (2008) 410–411.
- [6] E.B. Rusanov, V.V. Ponomarova, V.V. Komarchuk, H. Stoeckli-Evans, E. Fernandez-Ibañez, F. Stoeckli, J. Sieler, K.V. Domasevitch, *Angew. Chem. Int. Ed.* 42 (2003) 2499–2501.
- [7] W.L. Leong, J.J. Vittal, *Chem. Rev.* 111 (2011) 688–764.
- [8] J. Rocha, L.D. Carlos, F.A.A. Paz, D. Ananias, *Chem. Soc. Rev.* 40 (2011) 926–940.
- [9] Y.L. Wang, J.H. Fu, J.J. Wei, X. Xu, X.F. Li, Q.Y. Liu, *Cryst. Growth Des.* 12 (2012) 4663–4668.
- [10] J.Y. Seo, S.H. Lee, M. Jazbinsek, H. Yun, J.T. Kim, Y.S. Lee, I.H. Baek, F. Rotermund, O.P. Kwon, *Cryst. Growth Des.* 12 (2012) 313–319.
- [11] M. Kurmoo, *Chem. Soc. Rev.* 38 (2009) 1353–1379.
- [12] J.C. Tan, A.K. Cheetham, *Chem. Soc. Rev.* 40 (2011) 1059–1080.
- [13] C.W. Hsu, C.C. Lin, M.W. Chung, Y. Chi, G.H. Lee, P.T. Chou, C.H. Chang, P.Y. Chen, *J. Am. Chem. Soc.* 133 (2011) 12085–12099.
- [14] E. Wong, J. Li, C. Seward, S. Wang, *Dalton Trans.* (2009) 1776–1785.
- [15] D.Z. Wang, C.S. Liu, J.R. Li, L. Li, Y.F. Zeng, X.H. Bu, *CrystEngComm* 9 (2007) 289–297.
- [16] M. Bertelli, L. Carlucci, C. Ciani, D.M. Proserpio, A. Sironi, *J. Mater. Chem.* 7 (1997) 1271–1276.
- [17] R. Wietzke, M. Mazzanti, J.M. Latour, J. Pécaut, *Inorg. Chem.* 38 (1999) 3581–3585.
- [18] R.D. Pike, B.D. Borne, J.T. Maeyer, A.L. Rheingold, *Inorg. Chem.* 41 (2002) 631–633.
- [19] M.X. Li, Z.X. Miao, M. Shao, S.W. Liang, S.R. Zhu, *Inorg. Chem.* 47 (2008) 4481–4489.
- [20] Y.M. Li, C.Y. Xiao, S. Li, Q. Chen, B.B. Li, Q. Liao, J.Y. Niu, *J. Solid State Chem.* 200 (2013) 251–257.
- [21] B.R. Manzano, F.A. Jalón, M.L. Soriano, M. Carrión, M.P. Carranza, K. Mereiter, A.M. Rodriguez, A. de la Hoz, A. Sáchez-Migallón, *Inorg. Chem.* 47 (2008) 8957–8971.
- [22] D. Sun, H.J. Hao, F.J. Liu, H.F. Su, R.B. Huang, L.S. Zheng, *CrystEngComm* 14 (2012) 480–487.
- [23] D. Sun, Y.H. Li, H.J. Hao, F.J. Liu, Y. Zhao, R.B. Huang, L.S. Zheng, *CrystEngComm* 13 (2011) 6431–6441.
- [24] M. Munakata, M. Wen, Y. Suenaga, T. Kuroda-Sowa, M. Maekawa, M. Anahata, *Polyhedron* 20 (2001) 2037–2043.
- [25] M. Munakata, M. Wen, Y. Suenaga, T. Kuroda-Sowa, M. Maekawa, M. Anahata, *Polyhedron* 20 (2001) 2321–2327.
- [26] J.C. Dai, X.T. Wu, Z.Y. Fu, S.M. Hu, W.X. Du, C.P. Cui, L.M. Wu, H.H. Zhang, R.Q. Sun, *Chem. Commun.* (2002) 12–13.
- [27] N.L. Rosi, J. Kim, M. Eddaoudi, B.L. Chen, M. O'keeffe, O.M. Yaghi, *J. Am. Chem. Soc.* 127 (2005) 1504–1518.
- [28] V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, *CrystEngComm* 6 (2004) 377–395.
- [29] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
- [30] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [31] H.P. Jia, W. Li, Z.F. Ju, J. Zhang, *Chem. Commun.* (2008) 371–373.
- [32] A. Kreutzberger, R. September, *J. Am. Chem. Soc.* 79 (1957) 2629–2633.
- [33] R.W. Mason, T.C. Parker, Purification of Cyanuric Acid, US, 4963674, 1990.
- [34] M. Zhu, J. Peng, H.J. Pang, P.P. Zhang, Y. Chen, D.D. Wang, M.G. Liu, Y.H. Wang, *J. Solid State Chem.* 184 (2011) 1070–1078.
- [35] J. Hamblin, A. Jackson, N.W. Alcock, M.J. Hammon, *J. Chem. Soc., Dalton Trans.* (2002) 1635–1641.
- [36] D.L. Reger, R.F. Semeniuc, M.P. Smith, *Eur. J. Inorg. Chem.* (2003) 3480–3494.
- [37] S. Sculfort, P. Braunstein, *Chem. Sov. Rev.* 40 (2011) 2741–2760.
- [38] P. Nockemann, B. Thijs, K.V. Hecke, L.V. Meervelt, K. Binnemans, *Cryst. Growth Des.* 8 (2008) 1353–1363.
- [39] D. Sun, G.G. Luo, N. Zhang, R.B. Huang, L.S. Zheng, *Chem. Commun.* 47 (2011) 1461–1463.
- [40] T.A. Tronic, K.E. de Krafft, M.J. Lim, A.N. Ley, R.D. Pike, *Inorg. Chem.* 46 (2007) 8897–8912.
- [41] P. Pykkö, *Chem. Rev.* 97 (1997) 597–636.
- [42] H. Chen, Y. Chen, M. Dai, C.N. Lü, H.F. Wang, Z.G. Ren, Z.J. Huang, C.Y. Ni, J.P. Lang, *CrystEngComm* 14 (2012) 466–473.
- [43] X.J. Yang, H.X. Li, Z.L. Xu, H.Y. Li, Z.G. Ren, J.P. Lang, *CrystEngComm* 14 (2012) 1641–1652.
- [44] G.A. Bowmaker, S.E. Boyd, J.V. Hanna, R.D. Hart, P.C. Healy, B.P. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (2002) 2722–2730.
- [45] J. Ni, K.J. Wei, Y.Z. Min, Y.W. Chen, S.Z. Zhan, D. Li, Y.Z. Liu, *Dalton Trans.* 41 (2012) 5280–5293.
- [46] A. Bondi, *J. Phys. Chem.* 68 (1964) 441–451.
- [47] J.Q. Sha, J. Peng, A.X. Tian, H.S. Liu, J. Chen, P.P. Zhang, Z.M. Su, *Cryst. Growth Des.* 7 (2007) 2535–2541.
- [48] J.P. Costes, C. Duhayon, L. Vendier, E. Colacio, A.J.M. Avila, J.S. Varela, *Inorg. Chem.* 51 (2012) 1011–1019.
- [49] S.L. Cai, S.R. Zheng, Z.Z. Wen, J. Fan, W.G. Zhang, *Cryst. Growth Des.* 12 (2012) 5737–5745.
- [50] W.C. Song, Q.H. Pan, P.C. Song, Q. Zhao, Y.F. Zeng, T.L. Hu, X.H. Bu, *Chem. Commun.* 46 (2010) 4890–4892.
- [51] O. Bon, I. Senkowska, I.A. Baburin, S. Kaskel, *Cryst. Growth Des.* 13 (2013) 1231–1237.
- [52] N. Wiberg, A. Wörner, D. Fenske, H. Nöth, J. Knizek, K. Polborn, *Angew. Chem. Int. Ed.* 39 (2000) 1838–1842.
- [53] M.W. Degroot, M.W. Cockburn, M.S. Workentin, J.F. Corrigan, *Inorg. Chem.* 40 (2001) 4678–4685.
- [54] C. Xu, J.J. Zhang, Q. Chen, T. Duan, W.H. Leung, Q.F. Zhang, *Inorg. Chem. Commun.* 21 (2012) 1–3.
- [55] J.F. Corrigan, D. Fenske, *Angew. Chem. Int. Ed.* 36 (1997) 1981–1983.
- [56] V.W.W. Yam, K.K.W. Lo, *Chem. Soc. Rev.* 28 (1999) 323–334.
- [57] H.J. Hao, D. Sun, F.J. Liu, R.B. Huang, L.S. Zheng, *J. Mol. Struct.* 1011 (2012) 105–110.
- [58] H.J. Hao, D. Sun, Y.H. Li, F.J. Liu, R.B. Huang, L.S. Zheng, *Cryst. Growth Des.* 11 (2011) 3564–3578.