

Self-assembly Coordination Compounds of Cu(II), Zn(II) and Ag(I) with btp Ligands (btp = 2,6-bis(N'-1,2,4-triazolyl)pyridine): Counteranion Effects

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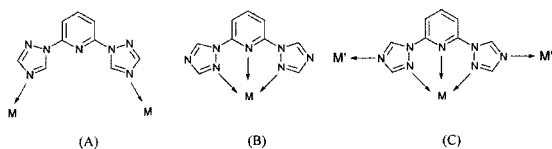
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Abstract

Five Cu(II) compounds were obtained from different copper salts with btp ligands, and their structures were determined by X-ray crystallography. The structure of coordination polymer **2** contains btp-bridged tetranuclear Cu(II) units weakly connected by nitrate ions, and the structure of a discrete Cu(II) molecule **1** contains acetates and btp ligands. With perchlorate anions, two btp ligands bridge Cu(II) ions to form a double zigzag chain **3**, while a single zigzag chain **4** is created with sulfate anions. The reaction of Cu(NO₃)₂ containing NH₄PF₆ with btp ligands also produced a polymeric compound **5** containing Cu(H₂O)₂²⁺ and Cu(NO₃)₂ units alternatively bridged by btp ligands with H-bonds between copper bonded water and nitrate oxygen atoms. Five Zn(II) compounds were obtained from different zinc salts with btp ligands, and the structures of polymeric compounds (**6**, **7** and **8**) and monomeric compounds (**9** and **10**) were determined by X-ray crystallography. With nitrate, chloride and bromide anions, btp ligands bridge Zn(II) ions to form polymeric compounds (**6**, **7** and **8**), but btp ligands coordinate to a Zn(II) ion to form monomeric complexes (**9** and **10**) with PF₆⁻ and perchlorate anions. Four silver salts and btp ligands produced two kinds of structures, dinuclear 20-membered rings and one-dimensional zigzag chain depending on different anions. For ClO₄⁻ and OTf anions, weak interactions between Ag(I) and anions make dinuclear 20-membered rings construct polymeric compounds (**11** and **13**). For PF₆⁻ anion, there are also weak interactions between Ag(I) and F(PF₆)⁻ (**12**), but they do not construct a polymeric compound. For O₂CCF₃⁻ anion, btp ligands bridge Ag(I) atoms to make one-dimensional zigzag chain (**14**), and there are also interactions between Ag(I) and anions.

1. Introduction

Self-assembly of organic ligands and inorganic metal ions is one of the most efficient and widely used approaches for the construction of supramolecular architectures.¹⁾ Owing to their potential as new functional solid materials such as gas or chemical absorption,²⁾ ion-exchange,³⁾ magnetism,⁴⁾ host-guest chemistry,⁵⁾ and catalysis,⁶⁾ interest in self-assembled coordination polymers with interesting physical properties has grown rapidly. In this field, the coordination chemistry of bidentate organodiamine ligands has been the main interest. So far, several types of bidentate rigid organodiamine ligands such as 4,4'-bipyridine,⁷⁾ 1,2-bis(4-pyridyl)ethene,⁸⁾ and 1,2-bis(4-pyridyl)ethyne,⁹⁾ and flexible organodiamine ligands



Scheme 1.

such as 1,2-bis(4-pyridyl)ethane¹⁰⁾ and 1,3-bis(4-pyridyl)propane,¹¹⁾ have been utilized. Consequently, a number of organic-inorganic coordination polymers based on those ligands have been successfully synthesized, including one-, two-, and three-dimensional motifs exhibiting honeycomb,¹²⁾ grid,¹³⁾ ladder,¹⁴⁾ brick,¹⁵⁾ bilayer,¹⁶⁾ and diamondoid,¹⁷⁾ but the possible network topologies for analogous metal complexes with angular bifunctional ligands are far less studied.^{18,19)}

The btp (2,6-bis(N'-1,2,4-triazolyl)pyridine) ligand^{6d,6e,20} has the potential to show various coordination modes (Scheme 1): bridging two metal centers (A), chelating a metal ion as a terdentate ligand (B) and functioning two cases simultaneously (C).

The different coordination possibilities of the btp ligand are similar to poly(triazolyl)- and -(tetrazolyl)borate anions that have produced both a chlate coordination and a bridge coordination to form a two-dimensional polymer.²¹ However, in our case, the potentially chelating mode has not been observed so far. The btp ligand acted as a bridging ligand to form a polymeric compound or a monodentate ligand to form a discrete molecule.^{20,22}

In our attempt to investigate the design and control of the self-assembly of coordination polymers with the angular bridging ligands, we initiated a synthetic program for the construction of various supramolecular complexes with interesting extended frameworks based on the angular btp ligand. As the metal coordination spheres we chose Cu(II), Zn(II), and Ag(I) salts, because the coordination spheres of the metal salts²³⁻²⁵ are very flexible and can adopt various coordination numbers between two and six and various geometries²⁶ from linear through trigonal to tetrahedral, trigonal pyramidal and octahedral.²⁷

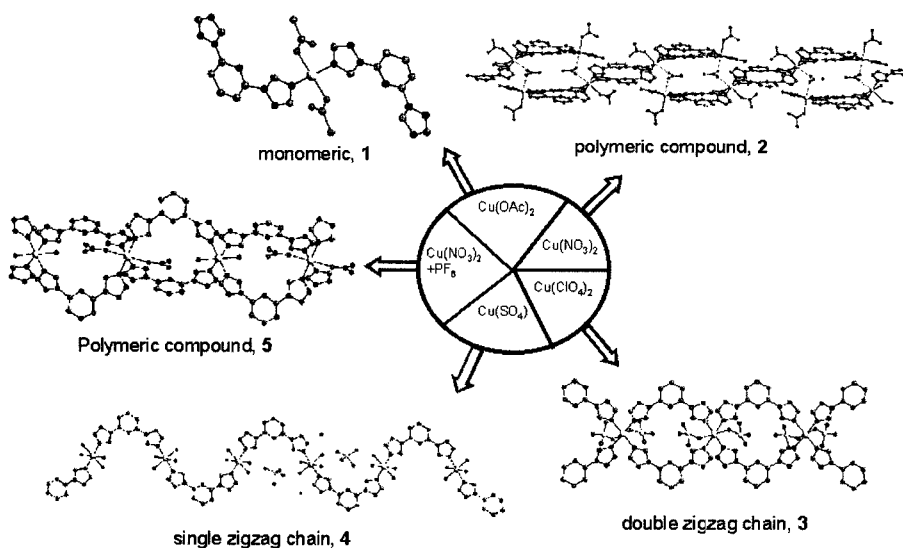
2. Result and Discussion

2-1. Crystal structures of Cu(II) complexes

The several polymeric compounds were obtained from different copper salts with btp ligands, and their structures were determined by X-ray crystallography. The structure of coordination polymer **2** contains btp-bridged tetranuclear Cu(II) units weakly connected by nitrate ions, and the structure of a discrete Cu(II) molecule **1** contains acetates and btp ligands. With perchlorate anions, two btp ligands bridge Cu(II) ions to form a double zigzag chain **3**, while a single zigzag chain **4** is created with sulfate anions. The reaction of Cu(NO₃)₂ containing NH₄PF₆ with btp ligands also produced a polymeric compound **5** containing Cu(H₂O)₂²⁺ and Cu(NO₃)₂ units alternatively bridged by btp ligands with H-bonds between copper bonded water and nitrate oxygen atoms. The structures of all five Cu(II) compounds containing btp ligands are shown in Scheme 2. The crystallographic data for Cu(II) compounds are listed in Table 1-1. The selected bond length and angles are listed in Table 1-2.

2-1-1. Monomeric compound, Cu(OAc)₂(btp)₂ (**1**)

Blue needle-type crystals were obtained by the slow evaporation of the mixture of a methanol solution of Cu(CH₃COO)₂ and a methanol solution of



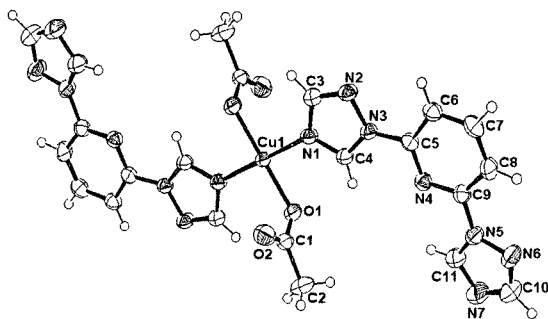
Scheme 2.

Table 1-1. Crystallographic data for compounds 1, 2, 3, 4 and 5

| | 1 | 2 | 3 | 4 | 5 |
|--|---|--|--|--|--|
| Empirical formula | C ₂₇ H ₂₁ Cu ₂ N ₂₅ O ₁₂ | C ₂₂ H ₂₄ CuN ₁₄ O ₆ | C ₁₈ H ₁₄ Cl ₂ CuN ₁₄ O ₈ | C ₉ H ₁₉ CuN ₇ O ₁₀ S | C ₃₆ H ₃₆ Cu ₂ F ₁₂ N ₃₀ O ₁₀ P ₂ |
| Formula weight | 1014.77 | 644.09 | 688.87 | 480.91 | 1465.97 |
| Temp. (K) | 150(1) K | 293(2) K | 293(2) | 293(2) | 150(1) K |
| Crystal system | Triclinic | Triclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | P-1 | P-1 | Cmma (no. 67) | C2/c (no. 15) | P2/n (no. 14) |
| a (Å) | 11.1473(3) | 6.867(3) | 17.375(2) | 16.752(4) | 11.6300(3) |
| b (Å) | 13.3356(3) | 9.304(2) | 19.743(2) | 14.445(4) | 12.8000(4) |
| c (Å) | 13.4689(3) | 10.935(4) | 7.126(2) | 7.370(3) | 19.2960(6) |
| α (°) | 78.475(2) | 93.40(2) | 90 | 90 | 90 |
| β (°) | 70.419(2) | 102.42(3) | 90 | 93.27(3) | 98.620(19) |
| γ (°) | 76.033(2) | 97.11(2) | 90 | 90 | 90 |
| Volume (Å ³) | 1815.12(8) | 674.3(4) | 2444.5(8) | 1780.4(10) | 2840.03(15) |
| Z | 2 | 1 | 4 | 4 | 2 |
| Absorption coefficient (mm ⁻¹) | 1.274 | 1.117 | 1.192 | 1.413 | 0.926 |
| No. of data collected | 23632 | 2882 | 2451 | 1800 | 20950 |
| No. of unique data | 23632 | 2882 | 1284 | 1742 | 6483 |
| R(int.) | 0.0352 | 0.0543 | 0.0275 | 0.0244 | 0.0547 |
| Final R indices [I>2σ(I)] | R ₁ ^a =0.0751, wR ₂ ^b =0.1947 | R ₁ ^a =0.0405, wR ₂ ^b =0.1026 | R ₁ ^a =0.0393, wR ₂ ^b =0.1073 | R ₁ ^a =0.0620, wR ₂ ^b =0.1698 | R ₁ ^a =0.0629, wR ₂ ^b =0.1614 |
| Final R indices (all data) | R ₁ ^a =0.1003, wR ₂ ^b =0.2211 | R ₁ ^a =0.0596, wR ₂ ^b =0.1091 | R ₁ ^a =0.0489, wR ₂ ^b =0.1129 | R ₁ ^a =0.0832, wR ₂ ^b =0.1857 | R ₁ ^a =0.1094, wR ₂ ^b =0.1805 |

Table 1-2. Selected bond lengths and angles for compounds 1, 2, 3, 4, and 5

| | 1 | 2 | 3 | 4 | 5 |
|--------------------|---------------------------|---|-------------|-------------|--|
| Cu-N(btp) | 1.986(2) Å | 1.978(3)-2.061(3) Å | 2.021(2) Å | 1.990(4) Å | 2.007(3)-2.041(3) Å |
| Cu-L(axial ligand) | Cu-O(OAc) 1.9433(19) Å | Cu-O(monodentate nitrate) 2.359(2), 2.275(2) Å Cu-O(bridging nitrate) 2.482(2), 2.420(2) Å | 2.398(17) Å | 2.469(16) Å | Cu-O(water) 2.360(3) Å Cu-O(nitrate) 2.399(3) Å |
| Cu...Cu | - | 9.659(7), 10.014(7) Å | 9.871(1) Å | 9.341(9) Å | 8.647(1) Å |
| N-Cu-N | 180.0° | 130.62(11)° | 106.4(3)° | 180.0° | 180.0° |

**Fig. 1. ORTEP drawing of compound 1.**

btp ligand. The asymmetric unit cell of mononuclear Cu(II) complex **1** contains half molecule and a water molecule. A crystallographic center of inversion is located on the Cu atom, and complete molecule is shown in Fig. 1. In the case of using Cu(CH₃COO)₂ for a reaction with btp ligands, btp ligand does not bridge Cu atoms. Two acetate ions and two btp ligands are coordinated to Cu(II) ion with O-Cu-O and N-Cu-N angles of 180.0°. Therefore, the geometry of Cu(II) ion is essentially square planar.

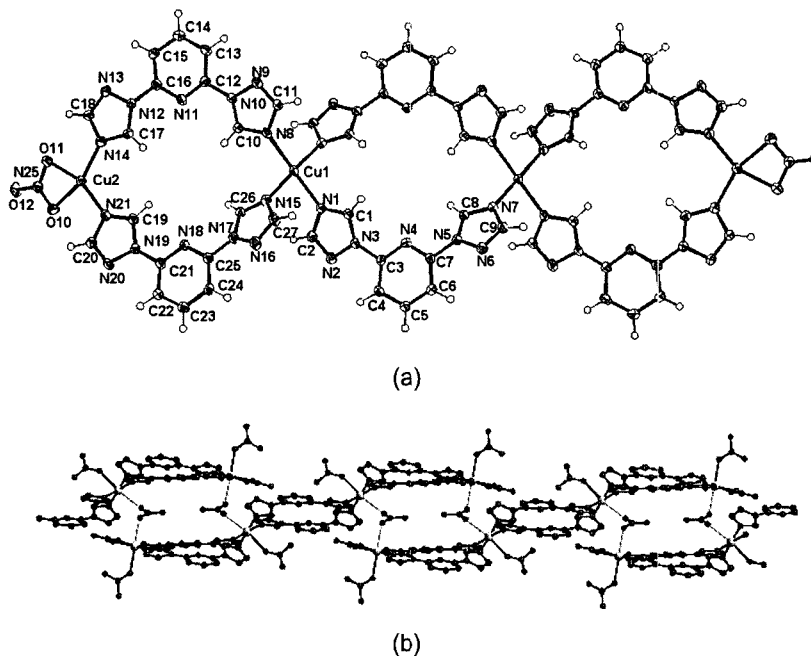


Fig. 2. (a) ORTEP drawing of the tetranuclear compound containing Cu(II) ions, btp ligands and nitrates. Axial nitrate anions are omitted for clarity. (b) Nitrate bridged polymeric structure.

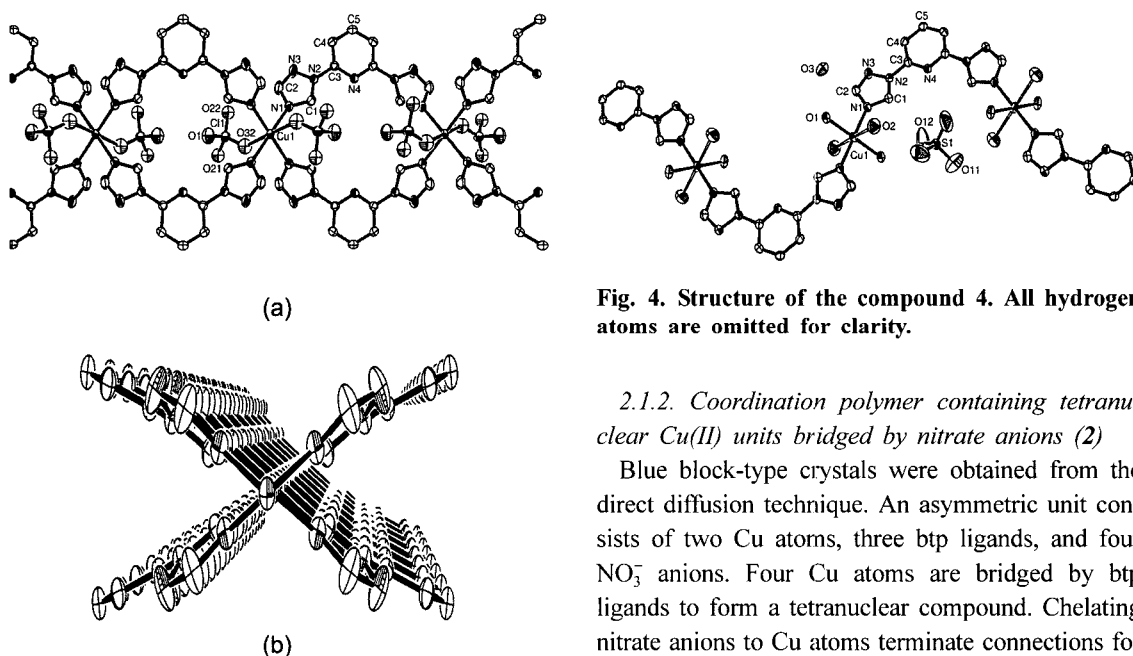


Fig. 3. (a) Structure of the double zigzag chain containing Cu(I) and btp ligand. All hydrogen atoms are omitted for clarity. (b) Drawing of a chain of compound 3 along b axis.

Fig. 4. Structure of the compound 4. All hydrogen atoms are omitted for clarity.

2.1.2. Coordination polymer containing tetranuclear Cu(II) units bridged by nitrate anions (2)

Blue block-type crystals were obtained from the direct diffusion technique. An asymmetric unit consists of two Cu atoms, three btp ligands, and four NO_3^- anions. Four Cu atoms are bridged by btp ligands to form a tetranuclear compound. Chelating nitrate anions to Cu atoms terminate connections for polymerization. The terminal Cu2 atoms have a monodentate nitrate anion, a chelating bidentate nitrate anion, and two btp ligands, and inner Cu1 atoms have four btp ligands and a monodentate nitrate

anion. There is a crystallographic center of inversion at the mid-point of the compound. Fig. 2(a) shows the complete structure of a tetranuclear compound containing three bridged rings. Cu1 and Cu2

atoms are also weakly bridged by nitrate anions (Cu-O(bridging nitrate) 2.482(2) and 2.420(2) Å). The nitrate bridged polymeric structure is shown in Fig. 2(b). If the weak coordination of nitrate is con-

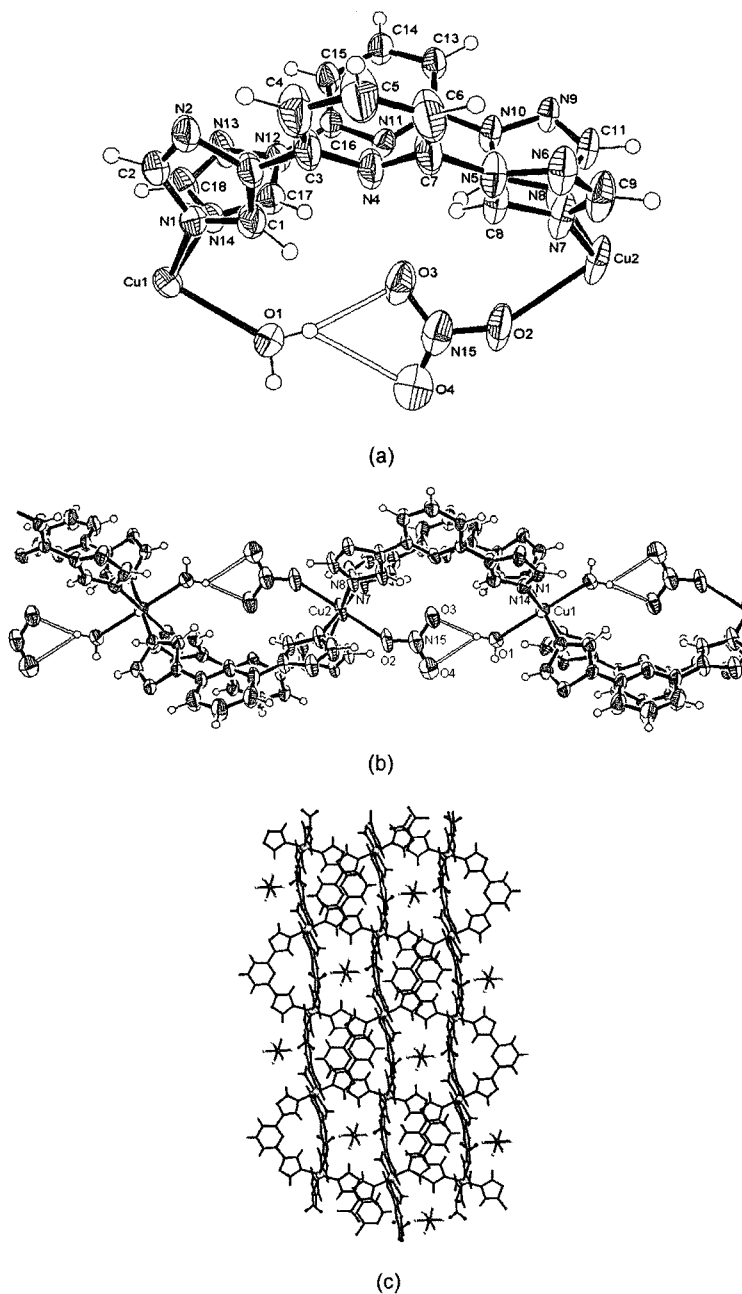


Fig. 5. (a) Asymmetric unit for the polymeric compound 5 with labeling atoms. (b) One-dimensional structure with strong H-bonds between copper bonded water and nitrate oxygen atoms. PF_6^- anions were omitted for clarity. (c) Two-dimensional structure with noncovalent C-H...F interactions.

sidered, the geometry of each Cu atom is tetragonally elongated octahedral. The Cu1...Cu2 and Cu1...Cu1' distances are 9.659(7) and 10.014(7) Å, respectively.

2.1.3 Double zigzag chain, $[Cu(ClO_4)_2(btp)_2] (3)$

The asymmetric unit consists of a quarter of copper(II) ion, half of a btp ligand, and half of a perchlorate anion. The complete polymeric compound is generated by symmetry operations $(-x, y, z)$, $(x, -y+1, -z)$, $(-x, -y+1, -z)$, and $(x, -y+1/2, -z)$ as shown in Fig. 3(a). Two btp ligands bridge two Cu(II) ions to form a double zigzag chain. The N(btp)-Cu-N(btp) angles are $92.61(14)^\circ$ and $87.39(14)^\circ$ as shown in Fig. 3(b). The Cu-N(btp) distance is 2.021(2) Å, and the perchlorate anions are axially coordinated to Cu(II) ions with Cu(II)-O(ClO₄) distances of 2.398(17) Å. The coordination of Cu(II) ion has D_{2h} symmetry. The Cu...Cu distance is 9.871(1) Å.

2.1.4 Single zigzag chain, $[Cu(btp)(H_2O)_4](SO_4) \cdot 2H_2O (4)$

The asymmetric unit consists of a Cu atom, half of a btp ligand, two water ligands, a sulfate anion, and a water solvent molecule. Mirror planes are located in the pyridyl ring of the btp ligand. The complete compound structure is generated by the symmetry operations $(-x+1/2, -y+3/2, -z)$ and $(-x, y, -z+1/2)$ as shown in Fig. 4. Cu(II) ions are bridged by btp ligands to form a single zigzag chain. Two water molecules are coordinated to a Cu(II) atom with the distance of 1.956(4) Å, and other two water molecules are weakly bonded to a Cu(II) atom with the distance 2.469(16) Å. The sulfate anions are located inside the zigzag chain, and the water solvent molecules are located between the zigzag chains. The coordination of Cu(II) ion has D_{2h} symmetry. The Cu...Cu distance is 9.341(9) Å.

2.1.5 Polymeric compound, $[Cu(H_2O)_2(btp)_2 Cu(NO_3)_2](PF_6)_2 (5)$

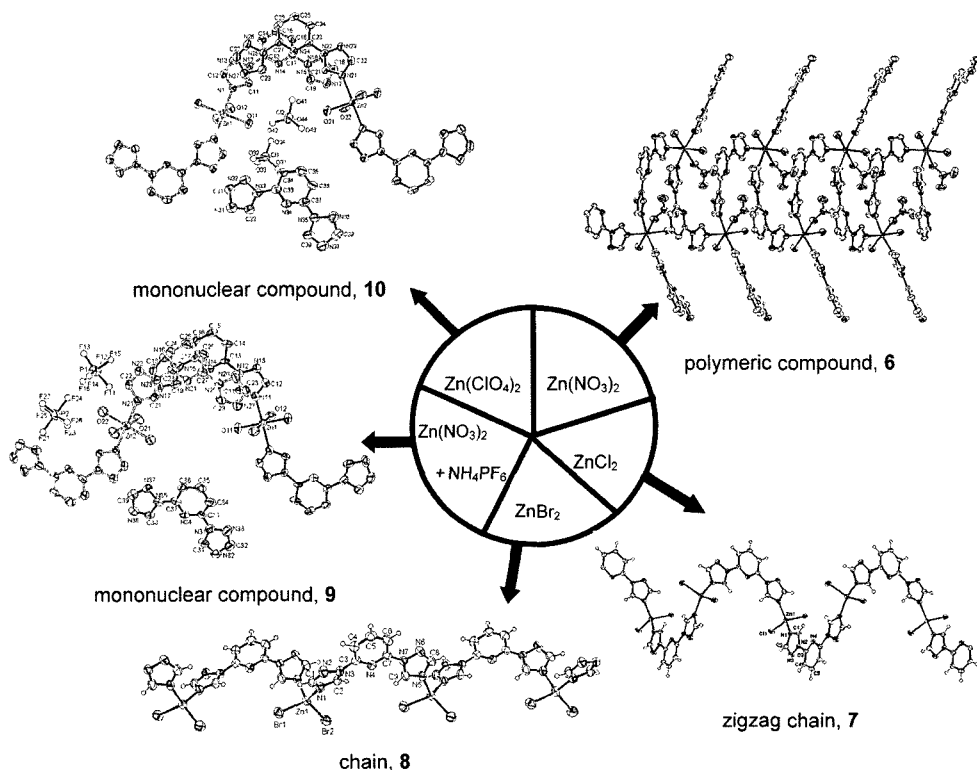
Asymmetric unit without PF₆⁻ anions is shown in Fig. 5(a). The complete compound structure is generated by the symmetry operations, $(-x+1, -y, -z+1)$, $(-x, -y+1, -z+1)$ and $(-x+1, -y+1, -z+1)$ as shown in Fig. 5(b). Two btp ligands bridge Cu(NO₃)₂ units and Cu(H₂O)₂ alternatively to form an one-dimensional coordination polymer with H-bonds between copper bonded water and nitrate oxygen atoms

(O1(water)-H...O3(nitrate) and O1(water)-H...O4(nitrate) distances of 2.886(1) and 3.126(2) Å, respectively). PF₆⁻ anions connect each one-dimensional polymer to form a two-dimensional compound with noncovalent interchain C-H...F interaction (C11-H11...F1 distance of 2.430(1) Å) and intrachain C-H...F interactions (C8-H8...F2 and C1-H1...F2 distances of 2.730(1) and 2.66(1) Å, respectively) (Fig. 5(c)). The Cu-N(btp) distances range from 2.007(3) to 2.041(3) Å. The Cu1-O1(water) distance is 2.360(3), and the Cu2-O(nitrate) distance is 2.399(3) Å. The O1(water)-Cu1-O1(water) and O2(nitrate)-Cu2-O2(nitrate) angles are 180°.

To see the anion effect for making polymeric structures of Cu(II), we have changed the counter anions such as CH₃COO⁻, NO₃⁻, ClO₄⁻, SO₄²⁻, and PF₆⁻. With ClO₄⁻ anions, two btp ligands bridge Cu(II) ions to form a double zigzag chain **3**, while a single zigzag chain **4** is created with SO₄²⁻ anions. In the compound **3**, ClO₄⁻ counter anions are weakly coordinated to the axial positions of Cu(II) ions, while the NO₃⁻ counter anions in the compound **2** are not only weakly coordinated to the axial positions of Cu(II) ions but also chelated to the terminal Cu(II) ions. The SO₄²⁻ anions in compound **4** are not coordinated to the Cu(II) ions, and btp ligand in compound **1** containing CH₃COO⁻ anions do not act as a bridging ligand but do as a monodentate ligand to form a discrete molecule. With PF₆⁻ anions, Cu(H₂O)₂²⁺ and Cu(NO₃)₂ units are alternatively bridged by btp ligands to form a polymeric compound **5** with H-bonds between copper bonded water and nitrate oxygen atoms. In all five compounds, the coordination of Cu(II) ion has D_{2h} symmetry. This result demonstrates that both the Jahn-Teller effect of the electronic configuration of Cu(II) and the counter anion effect are important for the construction of coordination polymers.

2-2. Crystal structures of Zn(II) complexes

Five new compounds **6**, **7**, **8**, **9** and **10** were obtained from different zinc salts with btp ligands as colorless crystals, and the structures of polymeric compounds (**6**, **7** and **8**) and monomeric compounds (**9** and **10**) were determined by X-ray crystallography. The btp ligands in **6**, **7** and **8** bridge Zn(II)



Scheme 3.

ions to form polymeric compounds, but btp ligands in **9** and **10** coordinate to a Zn(II) atom to form monomeric complexes. The structures of all five Zn(II) compounds containing btp ligands are shown in the Scheme 3. The crystallographic data for Zn(II) compounds are listed in Table 2-1. The selected bond length and angles are listed in Table 2-2.

2-2-1. Coordination polymer containing $[Zn(NO_3)(H_2O)_2(btp)_3]^{+}$ units bridged by btp ligands (**6**)

A zinc(II) coordination polymer is found in the cation in $[Zn(NO_3)(OH_2)_2(btp)_2]NO_3$. Each zinc(II) atom is coordinated by three N donor atoms from btp and three O donor atoms from a nitrate and two water molecules so that the coordination geometry is distorted octahedral; Fig. 6(a). Two btp ligands bridge two zinc(II) atoms to form a coordination polymer as shown in Fig. 6(b). A water molecule hydrogen bonds to an oxygen atom of a nitrate counteranion ($O6 \cdots O43$ 2.838(7) Å).

2-2-2. Zigzag chain, $[ZnCl_2 \cdot btp]$ (**7**)

The asymmetric unit consists of half of a zinc(II)

ion, half of a btp ligand, and a chloro anion. There are one 2-fold axis on Zn1 and another 2-fold axis through N4 and C5 atoms of the pyridyl ring. The complete zigzag chain is generated by symmetry operations $(-x+3/2, -y+1, z)$ and $(x, -y+1/2, -z+3/2)$ as shown in Fig. 7(a). The btp ligands bridge Zn(II) ions to form a zigzag chain. The bond angles of N(btp)-Zn-N(btp) and Cl-Zn-Cl are $130.62(11)^\circ$ and $116.46(4)^\circ$, respectively. The Zn-N(btp) distance is 2.0397(18) Å, and the Zn-Cl distance is 2.2467(7) Å. The geometry of Zn(II) ion is tetrahedral. The Zn \cdots Zn distance is 9.831(1) Å. The intrachain distance (C-H \cdots Cl) between triazolyl hydrogen and chloride ligand is 2.602(1) Å, and the interchain distance (C-H \cdots Cl(next chain)) between triazolyl hydrogen and chloride ligand of the next chain is 2.769(1) Å as shown in Fig. 7(b). The zigzag chains are face-to-face aligned, but there is no interaction with the interchain distance between btp ligands of 4.665 Å. These non-covalent interactions of C-H \cdots Cl and face-to-face stacking along with covalent coordination bonds

Table 2-1. Crystallographic data for compounds 6, 7, 8, 9 and 10

| | 6 | 7 | 8 | 9 | 10 |
|---|--|--|--|--|--|
| Empirical formula | C ₁₈ H ₁₈ N ₁₆ O ₈ Zn | C ₉ H ₇ Cl ₂ N ₇ Zn | C ₉ H ₇ Br ₂ N ₇ Zn | C ₂₇ H ₂₉ F ₁₂ N ₂₁ O ₄ P ₂ Zn | C ₂₇ H ₂₉ Cl ₂ N ₂₁ O ₁₂ Zn |
| Formula weight | 651.85 | 349.49 | 438.41 | 1067.02 | 975.98 |
| Temperature | 293(2) | 150(1) K | 293(2) K | 293(2) K | 293(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Space group | P2(1)/a | Pnna | P2 ₁ /n | P-1 | P-1 |
| a | 17.500(4) | 18.544(4) Å | 5.8120(10) Å | 10.860(1) Å | 10.620(1) Å |
| b | 7.399(4) | 14.408(3) Å | 15.091(2) Å | 10.908(1) Å | 10.902(1) Å |
| c | 19.485(4) | 4.6646(9) Å | 16.824(2) Å | 18.028(2) Å | 17.631(2) Å |
| α | 90 | 90.000° | 90.000° | 90.90(1)° | 92.28(2)° |
| β | 97.98(3) | 90.000° | 93.560(10)° | 90.99(1)° | 90.50(1)° |
| γ | 90 | 90.000° | 90.000° | 98.87(1)° | 100.99(2)° |
| Volume | 2498.4(16) | 1246.3(4) Å ³ | 1472.8(4) Å ³ | 2109.4(4) Å ³ | 2001.9(3) Å ³ |
| Z | 4 | 4 | 4 | 2 | 2 |
| Calculated density | 1.733 | 1.863 Mg/m ³ | 1.977 Mg/m ³ | 1.680 Mg/m ³ | 1.619 Mg/m ³ |
| Absorp.coefficient | 1.065 | 2.395 mm ⁻¹ | 7.090 mm ⁻¹ | 0.774 mm ⁻¹ | 0.834 mm ⁻¹ |
| F(000) | 1328 | 696 | 840 | 1076 | 996 |
| Crystal size | 0.45×0.354 ×0.30 | 0.16×0.16 ×0.12 mm ³ | 0.20×0.15 ×0.15 mm ³ | 0.25×0.20 ×0.15 mm | 0.20×0.15 ×0.15 mm |
| Data/restraints/ parameters | 4881/4/402 | 1424/0/89 | 2574/0/172 | 5523/32/626 | 7820/20/629 |
| Goodness-of-fit ^a on F ² | 1.033 | 1.072 | 1.107 | 1.005 | 1.194 |
| Final R indices [I>2σ(I)] | R ₁ ^b =0.549, wR ₂ ^c =0.1286 | R ₁ ^b =0.0317, wR ₂ ^c =0.0764 | R ₁ ^b =0.0664, wR ₂ ^c =0.1622 | R ₁ ^b =0.0833, wR ₂ ^c =0.2075 | R ₁ ^b =0.0566, wR ₂ ^c =0.1976 |
| R indices (all data) | R ₁ ^b =0.1351, wR ₂ ^c =0.1604 | R ₁ ^b =0.0443, wR ₂ ^c =0.0836 | R ₁ ^b =0.0901, wR ₂ ^c =0.1858 | R ₁ ^b =0.2161, wR ₂ ^c =0.2693 | R ₁ ^b =0.0886, wR ₂ ^c =0.2682 |
| Largest diff. peak and hole | 0.519 and -0.524 | 0.534 and -0.525 eÅ ⁻³ | 1.418 and -1.237 eÅ ⁻³ | 1.019 and -0.627 eÅ ⁻³ | 0.926 and -0.931 eÅ ⁻³ |

Table 2-2. Selected bond lengths and angles for compounds 6, 7, 8, 9, and 10

| | 6 | 7 | 8 | 9 | 10 |
|--------------------------------------|---|----------------------|--|--|--|
| Zn-N(btp) | 2.124(4) Å, 2.103(4) Å, 2.125(4) Å | 2.0397(18) Å | 2.020(7) Å, 2.044(8) Å | 2.121(9) Å, 2.143(8) Å | 2.130(4) Å, 2.115(3) Å |
| Zn-L | Zn-O(water) 2.033(4) Å, 2.141(5) Å Zn-O(nitrate) 2.231(4) Å | Zn-Cl 2.2467(7) Å | Zn-Br 2.3553(15) Å, 2.3625(14) Å | Zn-O(water) 2.090(7) Å, 2.120(8) Å, 2.078(6) Å, 2.117(9) Å | Zn-O(water) 2.069(4) Å, 2.110(3) Å, 2.064(4) Å, 2.133(3) Å |
| Zn···Zn (in a polymeric compound) | 9.192(5) Å | 9.831(1) Å | 9.0585(27) Å | | |
| N-Zn-N | 171.77(18)° | 130.62(11)° | 106.4(3)° | 180.0° | 180.0° |

are motifs to build the crystal structure of compound 7.

2-2-3. Chain compound, [ZnBr₂-btp] (8)

The asymmetric unit consists of a zinc(II) ion, a btp ligand, and two bromo anions. The complete chain is generated by symmetry operations (x+1/2,

-y+3/2, z-1/2) and (x-1/2, -y+3/2, z+1/2) as shown in Fig. 8(a). The btp ligands bridge Zn(II) ions to form a chain. The bond angles of N(btp)-Zn-N(btp) and Br-Zn-Br are 106.4(3)° and 118.22(6)°, respectively. The Zn-N(btp) distances are 2.020(7) and

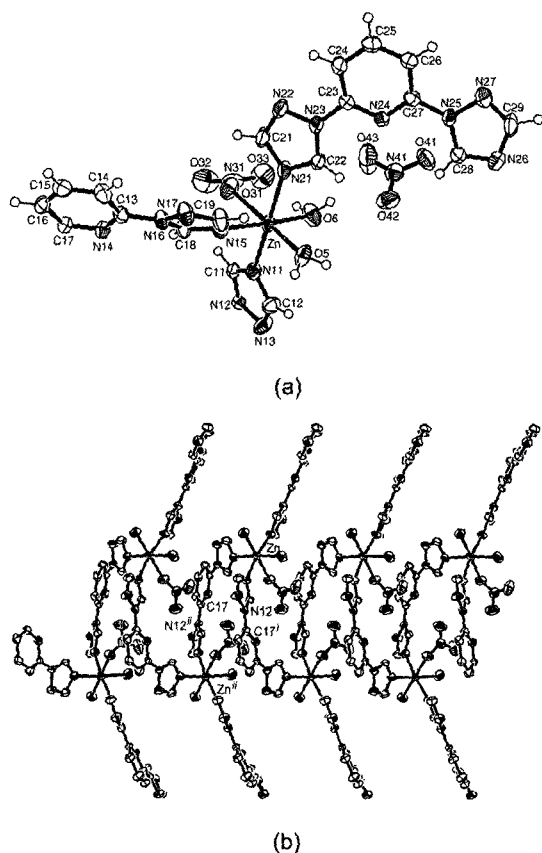


Fig. 6. (a) The asymmetric unit of $[Zn(NO_3)(H_2O)_2(btp)_2]NO_3$. (b) The structure of a coordination polymer with hydrogen atoms omitted for clarity.

2.044(8) Å, and the Zn-Br distances are 2.3553(15) and 2.3625(14) Å. The geometry of Zn(II) ion is tetrahedral. The Zn...Zn distance is 9.0585(27) Å. The chains are face-to-face aligned with interchain distance between btp ligands of 5.812 Å. The intrachain distances (C-H...Br) between triazolyl hydrogen atoms and bromide ligand range from 2.975(1) Å to 3.230(3) Å, and the interchain distances (C-H...Br (next chain)) between triazolyl hydrogen atoms and bromide ligand of the next chain range from 2.979(9) Å to 3.253(1) Å as shown in Fig. 8(b). These C-H...Br non-covalent interactions and face-to-face stacking along with covalent coordination bonds are motifs to build the crystal structure of compound **8**.

2-2-4. Monomeric compounds $[Zn(H_2O)_4(btp)_2](PF_6)_2$ (**9**) and $[Zn(H_2O)_4(btp)_2](ClO_4)_2$ (**10**)

The asymmetric units of both **9** and **10** consist of

two different half of a Zn atom, two coordinated btp ligands, a free btp ligand, two anions (PF_6^- for **9** and ClO_4^- for **10**), and four water molecules. The complete compound structure of **9** is generated by the symmetry operations $(-x+1, -y+1, -z+1)$ and $(-x, -y+1, -z)$ as shown in Fig. 9(a). The complete compound structure of **10** is generated by the symmetry operations $(-x+1, -y, -z+1)$ and $(-x, -y, -z)$ as shown in Fig. 10(a). Both structures of compounds **9** and **10** are very similar. Two btp ligands and four water molecules are coordinated to Zn(II) ions to form a mononuclear complex. The N(btp)-Zn-N(btp) angle is exactly 180° since there is an inversion center on a Zn atom. In compound **9**, the Zn-N distances are 2.121(9) and 2.143(8) Å, and the Zn-O(water) distances range from 2.078(6) Å to 2.120(8) Å. In compound **10**, the Zn-N distances are 2.130(3) and 2.115(3) Å, and the Zn-O(water) distances range from 2.064(4) and 2.133(3) Å. The left btp wing of Zn1 and the right btp wing of Zn2 were stacked with face-to-face π - π interactions between btp wings. The distances between left wing of Zn1 and right wing of Zn2 are typical π - π interaction distances as presented in Fig. 9(b) for **9** and Fig. 10(b) for **10**. The free btp ligands are located between π - π coupled wings, and they align slipped to the coupled wings in both compounds **9** and **10** as shown in Fig. 9(b) and 10(b), respectively. In compound **9**, there are H-bonds between hydrogen atoms of water ligands and fluorine atoms of PF_6^- anions with O...F distances of 2.842~3.566 Å. In compound **10**, there are also H-bonds between hydrogen atoms of water ligands and oxygen atoms of ClO_4^- anions with O...O(ClO_4^-) distances of 2.717~3.420 Å. These H-bonds and non-covalent π - π interactions along with covalent coordination bonds are motifs to build the crystal structures of both compounds **9** and **10**. The geometry of Zn(II) ions of both compounds **9** and **10** is almost perfect octahedral.

To study main roles for the construction of crystal structures in different metal cations containing btp ligands, Zn(II) salts with different anions such as nitrate, chloride, bromide, PF_6^- , and ClO_4^- have been chosen. Coordinating nitrate, chloride and bromide anions produce polymeric Zn(II) compounds, while

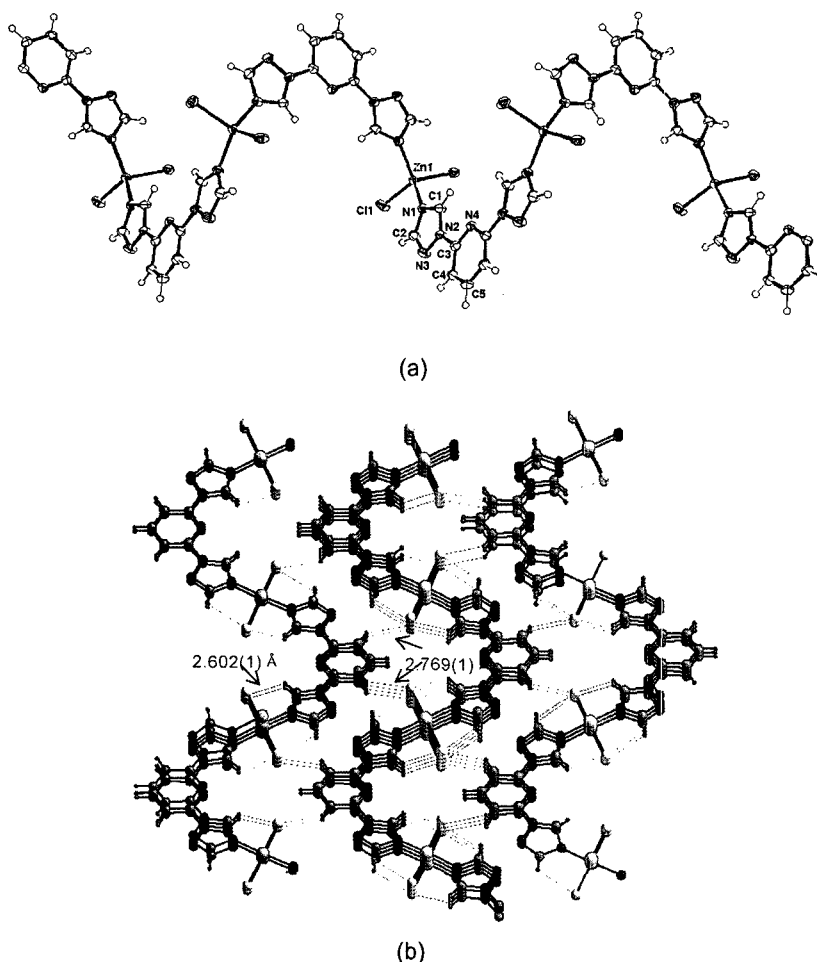


Fig. 7. (a) Structure of the zigzag chain of compound 7. (b) Packing diagram of compound 7. Gray-colored dashed lines show C-H...Cl interactions.

non-coordinating ClO_4^- and PF_6^- anions produce Zn(II) monomeric compounds. With coordinating nitrate anions, $[\text{Zn}(\text{NO}_3)(\text{H}_2\text{O})_2(\text{btp})_2]^+$ units are bridged by btp ligands to form a polymeric compound. With coordinating halide (chloride and bromide) anions, Zn(II) produces one-dimensional chains **7** and **8** that are face-to-face aligned, and their C-H...X(Cl or Br) inter- and intra-chain interactions make crystal structures. Differences between chain **7** and **8** indicate that a little variation of counter anions can produce structural effect. With non-coordinating ClO_4^- and PF_6^- anions, Zn(II) produces monomeric compounds **9** and **10** that are stacked with face-to-face π - π interactions, and their H-bonds between anions

and water ligands make crystal structures. These results demonstrate that both non-covalent C-H...X(Cl or Br) interactions and π - π interactions as well as covalent coordination bonds are important roles for building crystal structures of those Zn(II) complexes with btp ligands.

2-3. Crystal structures of Ag(I) complexes

Direct diffusion technique with silver salts (AgClO_4 , AgPF_6 , AgOTf , and $\text{Ag}(\text{O}_2\text{CCF}_3)$) and btp ligands produced two kinds of structures, dinuclear 20-membered rings and one-dimensional zigzag chain depending on different anions. For ClO_4^- and OTf^- anions, weak interactions between Ag(I) and anions make dinuclear 20-membered rings construct poly-

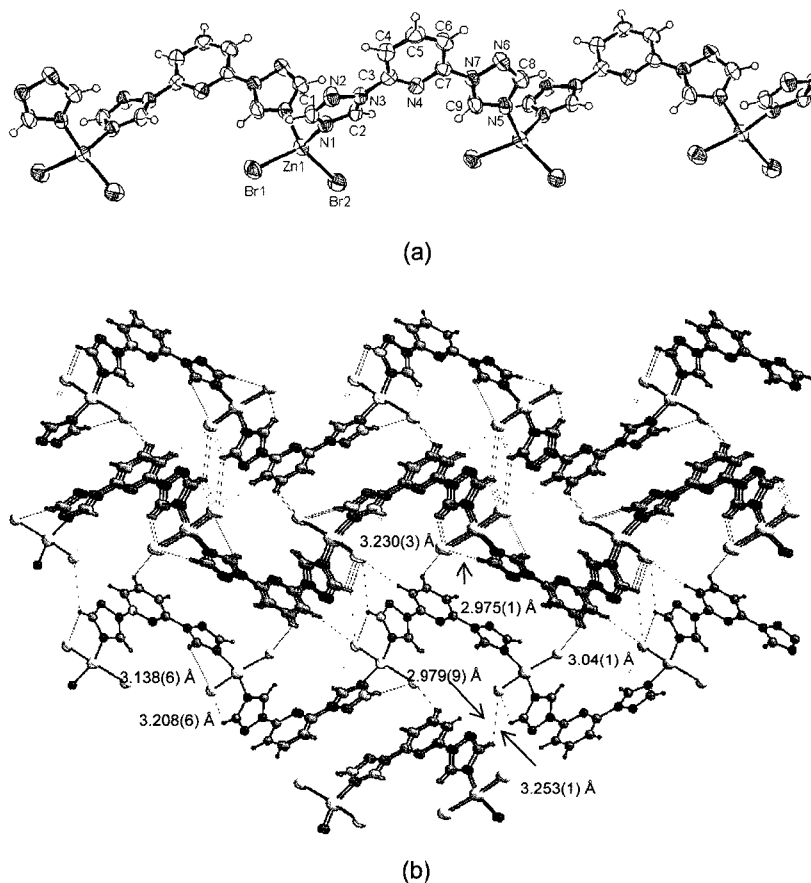


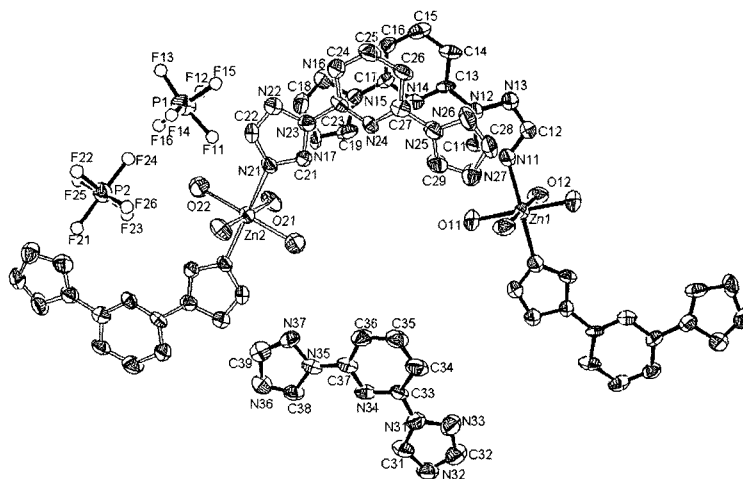
Fig. 8. (a) Structure of the chain compound **8**. (b) Packing diagram of compound **8**. Gray-colored dashed lines show C-H...Br interactions.

meric compounds. For PF_6^- anion, there are also weak interactions between Ag(I) and $\text{F}(\text{PF}_6^-)$, but they do not construct a polymeric compound. For O_2CCF_3^- anion, btp ligands bridge Ag(I) atoms to make one-dimensional zigzag chain, and there are also interactions between Ag(I) and anions. The structures of all four Ag(I) compounds containing btp ligands are shown in the Scheme 4. The crystallographic data for Ag(I) compounds are listed in Table 3-1. The selected bond length and angles are listed in Table 3-2.

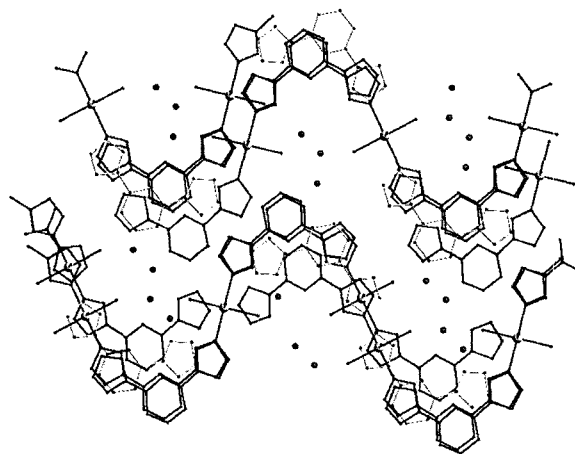
2-3-1. Dinuclear silver ring $[\text{Ag}_2(\text{btp})_2](\text{ClO}_4)_2$ (**11**)

The structure of dinuclear silver ring **11** is shown in Fig. 11(a). The asymmetric unit contains an Ag, a half of btp ligand, and a half of ClO_4^- anion in monoclinic cell with $Z = 2$. The complete structure is generated by the symmetry operations $(x, -y+1, z)$,

$(-x+1, -y+1, -z+1)$, and $(-x+1, y, -z)$. Two btp ligands bridge two Ag(I) atoms to make a 20-membered ring with Ag...Ag distance of 8.37(7) Å. There are weak interactions between Ag(I) and anions with Ag(I)-O(ClO_4^-) distance of 2.79(5) and 2.80(2) Å (shown in Fig. 11(b)). These interactions make another 8 member-rings consisting of two Ag(I) atoms, four oxygen atoms, and two chlorine atoms. The Ag...Ag distance in a 8-membered ring is 5.34(5) Å. As one can see in Fig. 1(b), 20-membered rings and 8-membered rings are connected alternatively to construct an one-dimensional chain. In addition, there are interchain-interactions as shown in Fig. 1(c) with interchain Ag...Ag bond distance of 3.19(5) Å to form two-dimensional sheets. These two-dimensional sheets are packed through π - π interactions between btp ligands from each sheet with



(a)



| | | | | | | | |
|---------|-------------|---------|-------------|---------|-------------|---------|-------------|
| C11-C29 | 3.469(12) Å | N11-N27 | 3.492(13) Å | C12-C28 | 3.683(13) Å | N12-N25 | 3.691(13) Å |
| N13-N26 | 3.797(14) Å | C13-C27 | 3.730(12) Å | C14-C26 | 3.822(13) Å | C15-C25 | 3.871(13) Å |
| C16-C24 | 3.789(12) Å | C17-C23 | 3.655(11) Å | N14-N24 | 3.596(11) Å | C18-C22 | 3.621(10) Å |
| N15-N23 | 3.606(11) Å | C19-C21 | 3.467(1) Å | N16-N22 | 3.685(1) Å | N17-N21 | 3.468(1) Å |

(b)

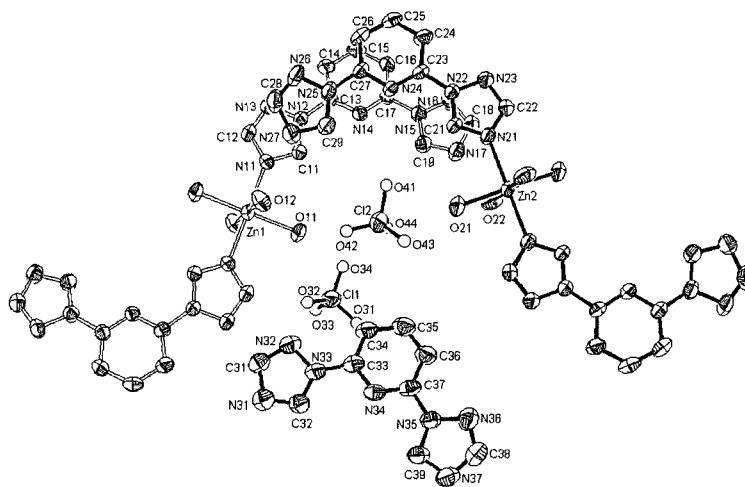
Fig. 9. (a) Structure of the compound 9. One of disordered fluorine sets of PF_6^- anion is not shown, and all fluorine atoms are shown as circles. All hydrogen atoms are omitted for clarity. (b) Packing diagram of compound 9. All fluorine and hydrogen atoms are omitted for clarity.

the shortest distance of 3.37(5) Å. The N-Ag(I)-N angle is 148.23(1)°.

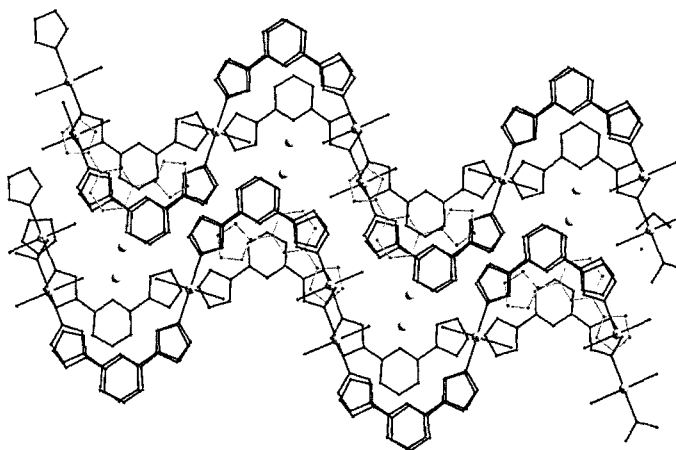
2-3-2. Dinuclear silver ring $[Ag_2(btp)_2](PF_6)_2$ (**12**)

The structure of dinuclear silver ring **12** is shown in Fig. 12(a). The asymmetric unit contains an Ag, a half of btp ligand, and a half of PF_6^- anion in monoclinic cell with $Z = 2$. The complete structure is

generated by the symmetry operations $(x, -y+1, z)$ and $(-x+1, y, -z+1)$. Similar to **11**, two btp ligands bridge two Ag(I) atoms to make a 20-membered ring with Ag...Ag distance of 8.221(6) Å. There are weak interactions between Ag(I) and anions with Ag(I)-F(PF_6^-) distance of 2.834(2) Å. As shown in Fig. 12(b), interactions between Ag(I) and anions



(a)



| | | | | | | | |
|---------|-------------|---------|-------------|---------|-------------|---------|-------------|
| C11-C29 | 3.455(18) Å | N12-N25 | 3.526(18) Å | N13-N26 | 3.583(17) Å | C12-C28 | 3.545(16) Å |
| N11-N27 | 3.437(17) Å | C13-C27 | 3.601(19) Å | C14-C28 | 3.714(20) Å | C15-C25 | 3.815(21) Å |
| C16-C24 | 3.766(22) Å | C17-C23 | 3.649(22) Å | N14-N24 | 3.564(20) Å | C18-C22 | 3.619(24) Å |
| N17-N21 | 3.414(23) Å | C19-C21 | 3.420(22) Å | N15-N22 | 3.626(22) Å | N16-N23 | 3.751(24) Å |

(b)

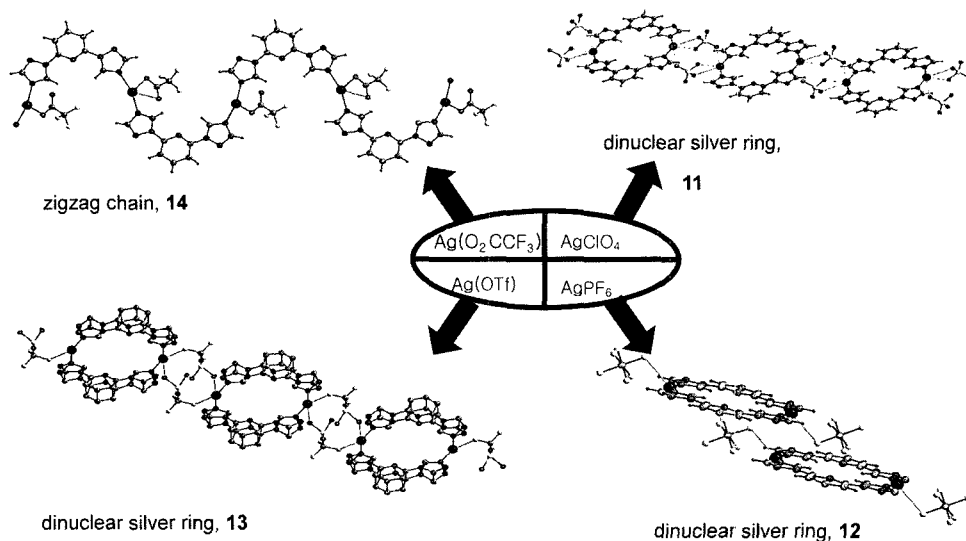
Fig. 10. (a) Structure of the compound 10. One of disordered oxygen sets of ClO_4^- anion is not shown, and all oxygen atoms of ClO_4^- are shown as circle. All hydrogen atoms are omitted for clarity. (b) Packing diagram of compound 10. All oxygen atoms of ClO_4^- anion and hydrogen atoms are omitted for clarity.

do not make a polymeric compound in contrast to **11**. There are interactions between Ag atoms from each chain with the interchain distance of 3.593(4) Å, and dinuclear silver rings are stacked through π - π interactions between *btP* ligands from each rings with the shortest distance of 3.549(4) Å as shown in

Fig. 2(c). The N-Ag(I)-N angle is 153.03(11)°.

2-3-3. Dinuclear silver ring [$\text{Ag}_2(\text{btP})_2(\text{OTf})_2$] (**13**)

The asymmetric unit contains an Ag, a half of *btP* ligand, and a half of O_3SCF_3^- (OTf^-) anion in monoclinic cell with $Z = 2$. The complete structure is generated by the symmetry operations ($x, -y, z$),



Scheme 4.

$(-x, -y, -z+1)$, and $(-x, y, -z+2)$. The structure of the disordered dinuclear silver ring **13** is shown in Fig. 13(a). The btp ligands and OTf^- anions are highly disordered even though compound **13** has the same space group ($C2/m$) as those of compounds **11** and **12**. That is why compound **13** has a little higher R value than those in compounds **11** and **12**. Similar to **11**, two btp ligands bridge two Ag(I) atoms to make a 20-membered ring, and weak interactions between Ag(I) and anions (Ag(I)-F and Ag(I)-O distances of 2.656(1) Å and 2.469(1) Å, respectively) make another 10-membered rings consisting of two Ag(I) atoms, two fluorine atoms, two oxygen atoms, two sulfur atoms, and two carbon atoms. As shown in Fig. 13(b), 20-membered rings and 10-membered rings are connected alternatively to construct an one-dimensional chain. There are interactions between Ag atoms from each chain with the interchain distance of 3.359(2) Å, and there are also π - π interactions (the shortest distance of 3.549(4) Å) between btp ligands from each rings for construction of a crystal structure as shown in Fig. 3(c). The N-Ag(I)-N angle is 152.2(8)°.

2-3-4. Zigzag chain ($\text{Ag}(\text{btp})(\text{O}_2\text{CCF}_3)_n$) (**14**)

The Structure of a zigzag chain **14** is shown in Fig. 14(a). A symmetric unit contains two Ag(I) atoms, two btp ligands, and two O_2CCF_3^- anions.

The btp ligands bridge Ag(I) atoms to make an one-dimensional zigzag chain. The anions are bonded to Ag(I) atoms with Ag(I)-O distances of 2.518(4) Å and 2.460(3) Å. All anions are oriented to the one side of the one-dimensional chain, and two chains are fit each other like a toothed wheel as shown in Fig. 14(b). There are interactions between Ag atoms from each chain with $\text{Ag}\cdots\text{Ag}$ interchain distances of 3.163(1) and 3.434(1) Å, and there are also π - π interactions between btp ligands from each chain with the shortest interchain distance of 3.341(3) Å in a toothed wheel. The N-Ag(I)-N angles are 150.11(15)° and 154.91(15)°.

In our efforts to systematically investigate the influences of terminal groups and counteranions on the coordination polymer formations of the Ag(I) complexes with the angular btp ligand, the coordination chemistry of the angular ligand btp with inorganic Ag(I) salts has been studied. The btp ligands with silver salts produce three different modes of structures, dinuclear silver rings **12**, dinuclear units linked by anions to form an one-dimensional polymers **11** and **13**, and one-dimensional zigzag chains **14**. The ClO_4^- and PF_6^- are known as noncoordinating anions, and the coordinating ability of the OTf^- anion is between the coordinating and noncoordinating anions. Those ClO_4^- , PF_6^- and OTf^- anions

Table 3-1. Crystallographic data for compounds 11, 12, 13, and 14

| | Ag(ClO ₄)-btp 11 | Ag(PF ₆)-btp 12 | Ag(OTf)-btp 13 | Ag(O ₂ CCF ₃)-btp 14 |
|-----------------------------------|--|--|--|---|
| Empirical formula | C ₁₈ H ₁₄ Ag ₂ Cl ₂ N ₁₄ O ₈ | C ₁₈ H ₁₄ Ag ₂ F ₁₂ N ₁₄ P ₂ | C ₂₀ H ₁₄ Ag ₂ F ₆ N ₁₄ O ₆ S ₂ | C ₂₂ H ₁₄ Ag ₂ F ₆ N ₁₄ O ₄ |
| Formula weight | 841.07 | 932.11 | 940.31 | 868.21 |
| Temperature | 150(1) K | 150(1) K | 293(2) K | 150(1) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Space group | C 2/m | C 2/m | C 2/m | P 2 ₁ /c |
| a | 7.6348(15) Å | 8.0230(4) Å | 8.8252(7) Å | 7.9520(3) Å |
| b | 18.806(4) Å | 19.6090(6) Å | 19.5911(14) Å | 23.0200(7) Å |
| c | 9.1269(18) Å | 8.7750(4) Å | 8.8075(6) Å | 15.1000(6) Å |
| α | 90° | 90° | 90° | 90° |
| β | 101.14(3)° | 101.474(2)° | 99.260(1)° | 92.9520(18)° |
| γ | 90° | 90° | 90° | 90° |
| Volume | 1285.7(5) Å ³ | 1352.9(1) Å ³ | 1502.93(19) | 2760.46(17) Å ³ |
| Z | 2 | 2 | 2 | 4 |
| Density (calc.) | 2.172 Mg/m ³ | 2.288 Mg/m ³ | 2.078 Mg/m ³ | 2.089 Mg/m ³ |
| Absorption coeff. | 1.808 mm ⁻¹ | 1.692 mm ⁻¹ | 1.544 mm ⁻¹ | 1.521 mm ⁻¹ |
| F(000) | 824 | 904 | 920 | 1696 |
| Crystal size | 0.36×0.26×0.16 mm ³ | 0.10×0.10×0.04 mm ³ | 0.15×0.10×0.10 mm ³ | 0.12×0.10×0.08 mm ³ |
| Reflections collected | 6105 | 6252 | 8374 | 16115 |
| Independent reflections | 1510[R(int)=0.0543] | 1603[R(int)=0.0381] | 1783[R(int)=0.0485] | 16141[R(int)=0.0890] |
| Data/restraints/parameters | 1510/0/108 | 1603/0/121 | 1783/10/163 | 16141/0/435 |
| Goodness-of-fit on F ² | 1.025 | 1.114 | 1.211 | 1.058 |
| Final R indices [I>2σ(I)] | R ₁ =0.0342, wR ₂ =0.0808 | R ₁ =0.0281, wR ₂ =0.0666 | R ₁ =0.1192*, wR ₂ =0.3568* | R ₁ =0.0615, wR ₂ =0.1321 |
| R indices (all data) | R ₁ =0.0461, wR ₂ =0.0888 | R ₁ =0.0334, wR ₂ =0.0694 | R ₁ =0.1225*, wR ₂ =0.3588* | R ₁ =0.0945, wR ₂ =0.1485 |
| Largest diff. peak and hole | 1.144 and -1.068 eÅ ⁻³ | 0.760 and -0.678 eÅ ⁻³ | 2.27 and -1.756 eÅ ⁻³ | 1.485 and -1.477 eÅ ⁻³ |

*The R value is a little high since whole molecule is highly disordered, and atoms of OTf⁻ anion except a sulfur atom were refined isotropically. It was the best crystal for data collection.

Table 3-2. Selected bond lengths and angles for compounds 11, 12, 13, and 14

| | 11 | 12 | 13 | 14 |
|----------------------------------|--|--------------------------------------|--|---|
| Ag-N(btp) | 2.160(2) Å | 2.161(2) Å | 2.160(14) Å | 2.190(4) Å, 2.210(4) Å, 2.165(4) Å, 2.172(4) Å |
| Ag-L(anion) | Ag-O(ClO ₄) 2.794(46) Å, 2.801(17) Å | Ag-F(PF ₆) 2.834(2) Å | Ag-O(OTf) 2.469(1) Å Ag-F(OTf) 2.656(1) Å | Ag-O(O ₂ CCF ₃) 2.518(4) Å, 2.460(3) Å |
| Ag...Ag (in a 20 membered ring) | 8.37(7) Å | 8.221(6) Å | 8.253(3) Å | 8.751(6) Å, 8.853(6) Å |
| Ag...Ag (interchain interaction) | 3.19(5) Å | 3.593(4) Å | 3.359(2) Å | 3.163(1) Å, 3.434(1) Å |
| N-Ag-N | 148.23(1)° | 153.03(11)° | 148.23(15)° | 150.11(15)°, 154.91(15)° |

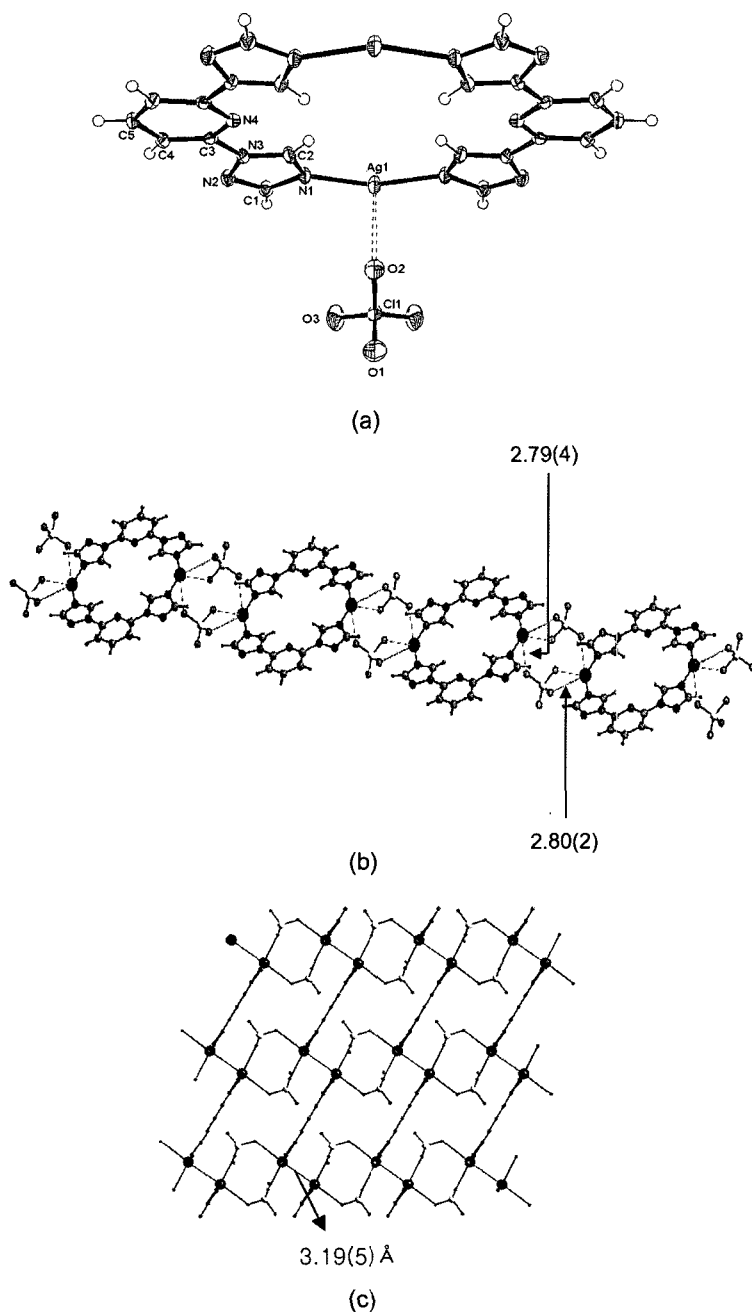
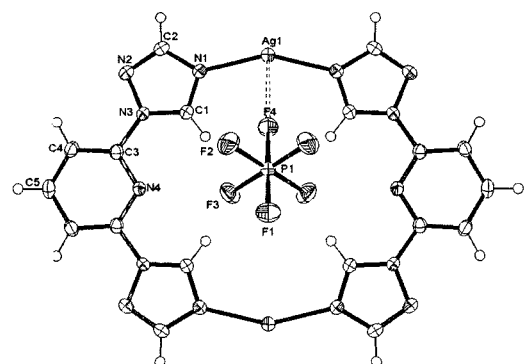


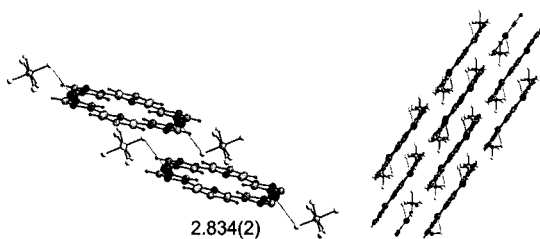
Fig. 11. (a) ORTEP drawing of $[\text{Ag}_2(\text{btp})_2](\text{ClO}_4)_2$, **11**. (b) Polymeric structure containing Ag-O(perchlorate) interactions. (c) Drawing of polymeric Ag compound **11** along *b* axis with interchain-interactions.

produce dinuclear silver rings with the same space group ($C2/m$). The dinuclear units of **11** and **13** are further linked by anions to form one-dimensional polymers, while the dinuclear silver rings of **12** are

weakly interacted with F atoms of PF_6^- anions. All three compounds **11**, **12**, and **13** show Ag \cdots Ag interchain interactions, and are packed through π - π interactions between btp ligands from each chain or



(a)



(b)



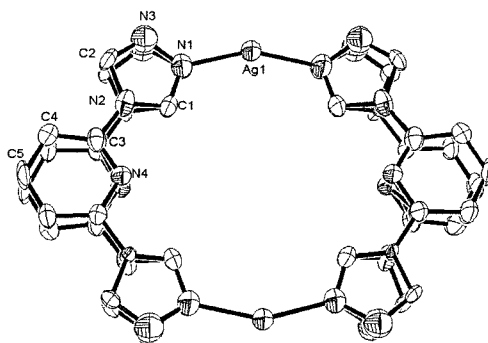
(c)

Fig. 12. (a) ORTEP drawing of $[\text{Ag}_2(\text{btp})_2](\text{PF}_6)_2$, 12. (b) Drawing of 12 with Ag-F(PF_6) interactions. (c) Packing diagram of compound 2 with π - π interactions between btp ligands from each rings.

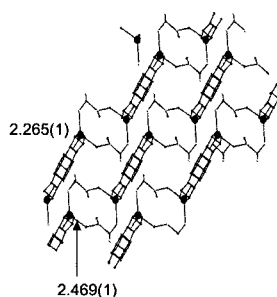
ring to form a higher dimensional polymeric compound. The coordinating O_2CCF_3^- anions are bonded to Ag(I), and btp ligands bridge Ag(I) atoms to construct an one-dimensional zigzag chain. Chelating bonds between Ag(I) and O_2CCF_3^- anions and their orientations may prevent making dinuclear silver rings. These results demonstrate that the structural differences between 11, 12, 13, and 14 show the influences of the counteranions on the structures of the complexes, and that π - π interactions between btp ligands from each chain or ring are also important roles for construction of crystal structures.

3. Crystallography

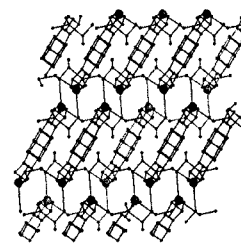
The X-ray diffraction data for compounds 1, 3, 4, 6, 9 and 10 were collected on an Enraf-Nonius CAD-4 Mach3 diffractometer equipped with a monochromator in the Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) incident beam. The crystal was mounted on a glass



(a)



(b)



(c)

Fig. 13. (a) ORTEP drawing of $[\text{Ag}_2(\text{btp})_2]^{2+}$, 13. All hydrogen atoms are omitted, and disordered OTf^- anions are shown for clarity. (b) Polymeric structure containing Ag-F(OTf^-) and Ag-O(OTf^-) interactions. (c) Packing diagram of compound 13 with π - π interactions between btp ligands from each ring.

fiber. A description of the data collection techniques for this diffractometer has been given before.²⁸ The final cell parameters were obtained from least squares fit to 25 reflections in the range $11.11 \leq \theta \leq 12.71^\circ$ for 1, $8.87 \leq \theta \leq 12.31^\circ$ for 3, $8.39 \leq \theta \leq 13.63^\circ$ for 4, $9.41 \leq \theta \leq 11.04^\circ$ for 6, $7.83 \leq \theta \leq 13.55^\circ$ for 9 and $9.89 \leq \theta \leq 12.32^\circ$ for 10. Intensities were corrected for Lorentz and polarization effects but not for absorption. The crystal structure was determined by the direct method and Fourier techniques. All the calculations were performed on IBM Pentium computer using SHELXS-97²⁹) and SHELXL-97³⁰) and atomic scattering factors for all non-hydrogen atoms were supplied by SHELXS-97. All non-hydrogen atoms except disordered oxygen atoms of the perchlorate anion were refined anisotropically

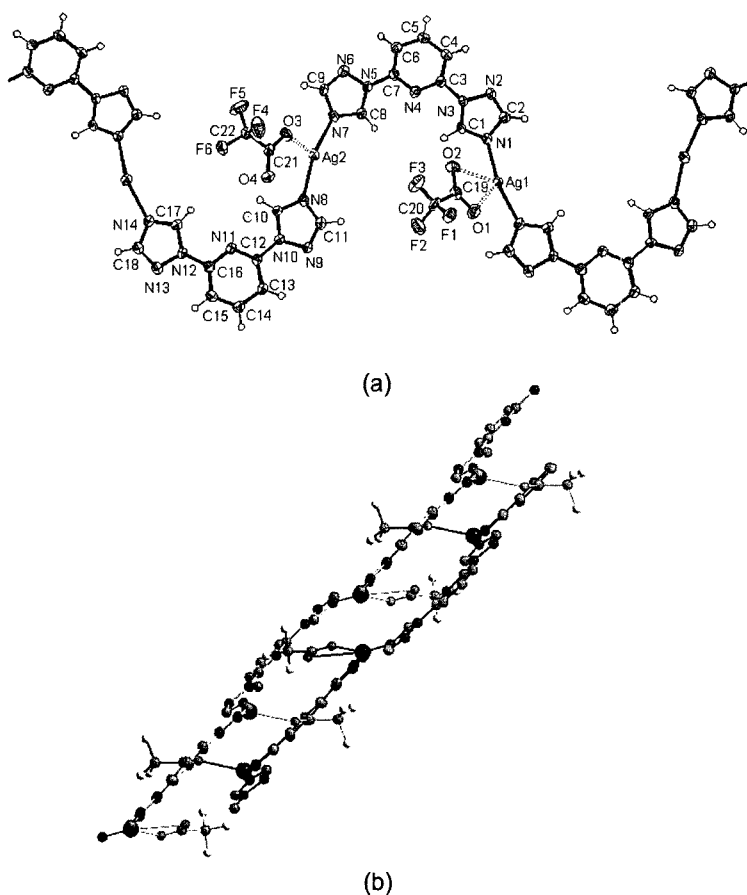


Fig. 14. (a) ORTEP drawing of zigzag chain $[\text{Ag}(\text{O}_2\text{CCF}_3)(\text{btp})]_n$, 14. (b) Drawing of zigzag chains which are fit like a toothed wheel. The black bonds represent one chain, and the green bonds represent the other chain.

for **3**. One of PF_6^- anion in **9** has two sets of fluorine atoms with 58.5% and 41.2% occupancies, and the F-P-F angles were fixed and refined isotropically. One of ClO_4^- anion in **10** has two sets of oxygen atoms with 56% and 44% occupancies, and the O-Cl-O angles were fixed. The wR_2 value of **9** is a little high since there are many inconsistent equivalent reflections, and one of PF_6^- anions is disordered, and data was used up to 45° of θ value. All hydrogen atoms except hydrogen atoms of water molecules were located in the calculated positions.

The diffraction data for **5**, **7**, **11**, **12**, and **14** were collected on a Nonius Kappa-CCD diffractometer using Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$).³¹⁾ The crystal was mounted on a glass fiber under epoxy resin. The

CCD data were integrated and scaled using the DENZO-SMN software package,³²⁾ and the structures were solved by direct method and refined by using SHEXTL/PC V5.1.³³⁾ During the refinement it was noticed the one of the PF_6^- anions was highly disordered over several sites and attempts to model the anion were unsuccessful. In addition, what appeared to be, a water molecule was also grossly disordered. Ultimately, the contributions from these species were removed using the SQUEEZE option in PLATON.³⁴⁾ This procedure did not affect the geometry of the rest of the structure but did improve the precision of the geometric parameters. The contributions of the removed species are included in the empirical formula. All hydrogen atoms were placed

in the calculated positions.

The diffraction data for compound **8** were collected on a STOE STADI4 4-circle-diffractometer D093 using Mo K α ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was determined by the direct method and Fourier techniques. All the calculations were performed on IBM Pentium computer using SHELXS-97 and SHELXL-97 and atomic scattering factors for all non-hydrogen atoms were supplied by SHELXS-97. All hydrogen atoms except hydrogen atoms of water molecules were located in the calculated positions.

The X-ray diffraction data for compound **13** was collected on a Bruker SMART APX diffractometer equipped with a monochromator in the Mo K α ($\lambda = 0.71073 \text{ \AA}$) incident beam.³⁵ The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-S SAINT software package, and the crystal structure was determined by the direct method and refined by using SHEXTL/PC V5.1.³³ Whole molecule is highly disordered, and atoms of the OTf⁻ anion except a sulfur atom were refined isotropically. All hydrogen atoms were located in the calculated positions. The molecular structure was drawn by the Ortep-3 for Windows program.³⁶

CCDC-196739 for **1**, CCDC-196738 for **2**, CCDC-218107 for **3**, CCDC 218108 for **4**, CCDC-266142 for **5**, CCDC-208842 for **6**, CCDC-240609 for **7**, CCDC-240610 for **8**, CCDC-240611 for **9**, CCDC-240612 for **10**, CCDC-259827 for **11**, CCDC-259828 for **12**, CCDC-259829 for **13**, and CCDC-259830 for **14** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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