含N, N′-二-(4-吡啶)-乙二醯二胺配位基配位高分化合物合成與結構之研究

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Abstract

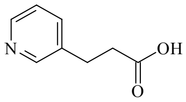
The syntheses and crystal structures of three new coordination polymers of the types $[Ag(PPIA) \cdot H_2O]_n$ (PPIA = 3-Pyridinepropionic acid), **1**, $[Cu(PPIA)_2 \cdot 2H_2O]_n$, **2** and $[Zn(PPIA)_2(H_2O)_2]_n$, **3**, are reported. The reactions of 3-Pyridinepropionic acid with $AgNO_3$, $Cu(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ in MeOH afforded complexes **1** ~ **3**, respectively. Single-crystal X-ray crystallography structure determinations show that complexes **1, 2** and **3** crystallize in the space groups P1, Pbca and $P2_1/n$, respectively. The Ag(I) centers in **1** adopt a slightly distorted T-sharped geometry, while the Cu(II) centers in **2** exhibit a distorted square planer coordination geometry and the Cu(II) centers in **3** adopt a distorted square planer coordination geometry. The metal centers in **1** - **3** coordinate to both the pyridyl and carboxylate groups to form one-dimensional polymeric chains and two-dimensional framework structures, respectively. Intrestingly, the one-dimensional chain complex of **1** or the two-dimensional frameworks of **2** and **3** are also linked to form three-dimensional networks through hydrogen bonds.

Keyword: Coordination polymer; 3-Pyridinepropionic acid; framework; Chain; Silver; Copper; Zinc.

1. Introduction

Much effort has been devoted to the self-assembly of inorganic molecules during recent years [1], because it extends the range of designing new solids with desired physical and chemical properties. Bidentate ligands are commonly used for building up coordination polymers, which give rise to different types of polymeric structures, including 1-D [2], 2-D [3] and 3-D [4] network. The range and variety of self-assembled inorganic structures that can be constructed relies on the suitable use of metal-ligand interactions and weak interactions such as hydrogen bondings and π-π interactions [5 - 6]. The metal centers as well as organic building blocks play a key role in molecular recognition process. It has been noticed from our recent studies [7] and other reports [8 - 9] that polydentate ligands, such as PPz (PPz = piperazine), bpp (bpp = 1, 3-bis(4-pyridyl)propane), bpa (bpa = 1, 2-bis(4-pyridyl)ethane), bpen (bpen = *trans*-bis(4-pyridyl)ethene), and nic (nic = nicotinate) are able to generate polymetallic coordination networks with interesting supramolecular solid-state architectures.

The multidentate ligand, **PPIA (PPIA =** 3-Pyridinepropionic acid)**,** containing two functional groups, which are pyridyl nitrogen atom and two oxygen atoms of carboxylic groups. The ligand of **PPIA** can acts as good polydentate ligands as chelate, bridging and chelate/bridging ligands through their pyridine and/or carboxylate ends. During our investigation on the reactions of transition metal complexes with nicotinic acid, we have obtained three complexes which show 1-D and 2-D polymeric structures, and found that the weak interactions and hydrogen bonds, such as Ag···Ag, Ag···O, Cu···O, C-H···π and C-H---O, play important roles in linking the structures to form 3-D supramolecular structures. The syntheses and crystal structures of $[Ag(PPIA) \cdot H_2O]_n$ (PPIA = 3-Pyridinepropionic acid), **1**, $[Cu(PPIA)_2 \cdot 2H_2O]_n$, **2,** and $[Zn(PPIA)_2(H_2O)_2]_n$, **3**, for the subject of this report.



PPIA

2. Experimental

2.1. General procedures

The IR spectra were recorded on a Bio-Rad FTs-7 spectrometer. Thermogravimetric analysis (TGA) were conducted on a SDT 2960 using a heating rate of 10°C/min. Differential scanning calorimetry (DSC) measurements were carried on a Dupon DSC Q-10.

2.2. Starting Material

The complexes $AgNO_3$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}6H_2O$ were used as obtained from commercial sources without further purification. The reagent PPIA (PPIA = 3-Pyridinepropionic acid) was purchased from Aldrich.

2.3. Preparation of $[Ag(PPIA) \cdot H_2O]_n$, 1

$AgNO_3$ (0.17 g, 1.0 mmol) and PPIA (0.15 g, 1.0 mmol) were placed in a flask containing 15 mL CH_3OH. The mixture was stirred at room temperature for 20 h to yield a white precipitate. The solid was filtered out, washed with diethyl ether (2 × 10ml) and dried under vaccum to give a white powder. Yield: 0.21g , (76.1 %) Anal. Calcd. for $C_8H_{10}AgNO_3$ (MW = 276.04): C, 34.81; H, 3.65; N, 5.07. Found: C, 34.69; H, 3.46; N, 5.28. IR (KBr disk, cm^{-1}): 3409(br), 3034(m), 2921(m), 2406(m), 1972(m), 1715(m), 1567(m), 1482(m), 1419(m), 1333(s), 1310(m), 1222(m), 1125(m), 1068(m), 1008(m), 909(m), 810(m), 699(m), 652(m), 634(m).

2.4. Preparation of $[Cu(PPIA)_2 \cdot 2H_2O]_n$, 2

$Cu(NO_3)_2{\cdot}6H_2O$ (0.30 g, 1.0 mmol) was added to a MeOH solution (20 mL) containing 3-Pyridinepropionic acid (0.30 g, 2.0 mmol). The mixture was then refluxed for 20 hr to afford a light blue solution and a blue solid. The precipitate was filtered and washed by ether (3 × 10ml) and then dried under reduced pressure to give a blue solid. Yield: 0.45 g (56.3 %). Calcd. For $C_{16}H_{20}CuN_2O_6$ (MW = 399.88), C, 48.06%; H, 5.04%; N, 7.01%; Found: C, 47.74%; H, 5.03%; N, 6.67%. IR (KBr disk, cm^{-1}):3469(br), 3043(m), 2921(m), 2406 (m), 1972(m), 1718(m), 1609(m), 1549(m), 1469(m), 1437(s), 1305(m), 1225(m), 1045(m), 1030(m), 771(m), 677(m). Blue crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a MeOH solution of **2**.

2.5. Preparation of $[Zn(PPIA)_2(H_2O)_2]_n$, 3

$Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1.0 mmol) and PPIA (0.30 g, 2.0 mmol) were placed in a flask containing 15 mL CH_3OH. The mixture was stirred at room temperature for 20 h to yield a white precipitate. The solid was filtered out, washed with diethyl ether (2 × 10ml) and dried under vaccum to give a white powder. Yield: 0.49 g (61.0 %). Anal. Calcd. for $C_{16}H_{20}ZnN_2O_6$ (MW = 401.71): C, 47.84; H, 5.02; N, 6.97 %. Found: C, 47.48 ; H, 4.96 ; N, 7.02 %. IR (KBr disk): 3571(br), 3068(m), 2933(m), 2000(m), 1906(m), 1722(m), 1611(m), 1564(m), 1470(m), 1445(m), 1399(m), 1338(m), 1310(s), 1270(m), 1257(m), 1223(m), 1181(m), 1112(m), 1046(m), 981(m), 957(m), 836(m), 740(m), 676(m), 585(m). Colorless crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a MeOH solution of **3** over 3 days.

3. X-ray Crystallography

The diffraction data of 1 - 3 were collected on a Siemens CCD diffractometer, which was equipped with graphite-monochromated Mo-K_α (K_α = 0.71073 Å) radiation. Data reduction was carried by standard methods with use of well-established computational procedures [10]. A colorless crystal of 1 was mounted on the top of a glass fiber with epoxy cement. The hemisphere data collection method was used to scan the data points at $5.28 < 2\theta < 50.02°$. The structure factors were obtained after Lorentz and polarization correction. The positions of some of the heavier atoms, including the Silver atom, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements [11]. The final residuals of the final refinement were R1 = 0.0220, wR2 = 0.0493. The crystallographic procedures for 2 and 3 were similar to those for 1. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

4. Results and discussion

4.1. Synthesis and spectroscopic studies

The reactions of 3-Pyridinepropionic acid with $AgNO_3$, $Cu(NO_3)_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ in MeOH/H_2O afforded complexes $[Ag(PPIA) \cdot H_2O]_n$ (PPIA = 3-Pyridinepropionic acid), **1**, $[Cu(PPIA)_2 \cdot 2H_2O]_n$, **2,** $[Zn(PPIA)_2(H_2O)_2]_n$, **3**, respectively. The complexes **1-3** and PPIA ligand, the broad band centered at ca. 3400-3500 cm^{-1} indinicates the O-H stretching of the carboxylic group or water molecules. The IR spectrum of PPIA ligands suggests that the characteristic absorption bands of the COOH group occur in 1715 and 1482 cm^{-1}. The complexes **1-3**, the peaks at 1567, 1609 and 1611 cm^{-1}, respectively, are attributed to the antisymmetric stretching vibrations, and 1419, 1399 and 1399 cm^{-1} to the symmetric vibrations of the carboxylic groups. Furthermore, the values of the carboxlate groups are 148, 210 and 212 cm^{-1} for **1-3**, respectively, agreeing with their solid structural features [12].

4.2. Structure of $[Ag(PPIA) \cdot H_2O]_n$, 1

Complex 1 crystallizes in the triclinic space group P1. The asymmetric unit of 1, Figure 1(a), contains one Ag atom, one PPIA group and one included water molecular. The structure of complex 1, emphasizing the environment around the silver, is shown in Figure 1(b). Each Ag(I) center lies in a distorted T-sharped coordination environment $\{AgNO_2\}$ consisting of one pyridyl nitrogen donor from one PPIA ligand (Ag(1)-N(1B) = 2.366(3) Å), two oxygen atoms from different bridging carboxylate groups (Ag(1)-O(1) = 2.245(2) and Ag(1)-O(2A) = 2.216(2) Å). It is interesting that the tridentate PPIA ligand is coordinated to the silver center by the Ag-N bonds to link $\{Ag_2(PPIA)_2\}$ building blocks to form a one-dimensional polymeric chain

(Figure 1(b)). The Ag---Ag separation distance in the {Ag(PPIA)}$_2$ building block is 2.9203(7) Å, and the Ag---Ag separation distance in the 1-D polymeric chain by the bridging PPIA ligand is 9.622 Å. The carboxylate groups of PPIA ligand bridging silver centers formed the 8-member ring {$Ag_2O_4C_2$}, while the 16-member ring {$Ag_2O_2N_2C_{10}$} was formed by two silver atoms bonded to the pyridyl nitrogen donors and the carboxylate oxygen atoms of two bridging PPIA ligands in 1-D chains.

The chains are further linked through extensive Ag···Ag and Ag···O weak interactions (Fig. 2(a)). The Ag···Ag distance is 3.539 Å, while the Ag···O distance is 2.977 Å with Ag(I) atom linking with the oxygen atom of carboxylate. The type of C-H···π interactions that is from the methylene hydrogen atoms of the PPIA ligand to the to the center of the pyridyl ring of the other chain (H···π = 2.995 Å, ∠C-H···π = 145.8^o), Fig. 2(b), were found in the structure. The hydrogen atoms of the water molecules also interact with the carboxylate oxygen atoms (H···O = 2.050 Å, ∠O-H···O = 168.7^o) of the adjacent chains to form a 3-D supramolecular structure. (Fig. 2(c)).

Complex 1 is in marked contrast to some Ag(I) complexes containing pyridine carboxylate ligands. The structure of {[Ag(Isonic)(HIsonic)]$_{0.5}$ · [Ag(Isonic)]}$_n$ (Isonic = the anion of isonicotinic acid) [13] consists two different of 1-D chains; the hydrogen bonded assembly [Ag(Isonic)(HIso)]$_{0.5}$ and a wavy [Ag(Isonic)] polymeric chain. The complex [Ag(nic)]$_n$ (nic = the anion of nicotinic acid), [14] shows 1-D zigzag chains of silver atoms, while each Ag atom is fivefold linked to two oxygen atoms of two different nicotinate ligands, to one nitrogen atom of a third nicotinate and to two other Ag atoms, having a dissymmetric trigonal bipyramid. Reaction of $AgBF_4$ with isonicotinic acid led to the polymeric structure {[Ag_3(Isonic)$_2$]BF_4}$_n$, [15] consisting of Ag_3 triangles linked together by two isonicotinate ligands. The structure of polymeric [Ag(nic)]$_n$ is based on a three-coordinate silver complex units to form the 1-D helical chain, while {NH_4[Ag(nic)$_2$] · H_2O}$_n$ shows the 1-D zigzag chains with Ag(I) center adopted distorted trigonal planer geometry. [16] The structure of H[Ag(nic)$_2$] can be described as 1-D polymeric chain consisting of [Ag(nic)$_2$]$^-$ monomers linked via O···H···O hydrogen bonds. [17]

4.3 Structure of [Cu(PPIA)$_2$ · 2H_2O]$_n$, 2

Complex **2** was solved in the orthorhombic space group Pbca. The asymmetric unit of **2** consists of one Cu(II) atom, two PPIA group and one free water molecule (Figure 3(a)). Each Cu(II) is in a distorted square planar geometry with the bond angles significantly deviate from 90 or 180^o (Table 2). In Figure 3(b), the equatorial basal plane is determined by two *trans* monodentate carboxylate groups from different PPIA ligands (Cu(1)-O(1A) = 1.9968(12) Å, O(1B)-Cu(1)-O(1A) = 180.0^o) and two *trans* pyridyl nitrogen atoms (Cu(1)-N(1) = 2.0254(14) Å, N(1C)-Cu(1)-N(1) = 180.0^o). The Cu(II) is coplanar with the mean plane of the five equatorial atoms, with a deviation of 0 °. PPIA acts as a bridging ligand, through its pyridyl nitrogen atom and monodentate carboxylate group, linking different Cu(II) centers.

Four PPIA with a head-to-tail aggregation link Cu(II) into a {Cu(PPIA)}$_4$ 32-member ring. In the {Cu(PPIA)}$_4$ ring, four Cu(II) ions and four PPIA are not coplanar, which may be due to the different arrangement of PPIA and the coordination geometry of the metal ion. The {Cu(PPIA)}$_4$ rings are further extended into a 2D layer by sharing Cu(II) joints and PPIA edges, Figure 3(c). The complex shows void space with a Cu---Cu separation of 8.648 Å. The layers are further linked through extensive O-H···O (H···O = 1.921 – 2.133 Å; ∠ O-H···O = 161.4 – 176.0°) and C-H···O (H···O = 2.027 Å; ∠ C-H···O = 175.3°) hydrogen bondings and the weak Cu---O interactions (Cu---O = 2.467 Å) among the layers, Figure 3(d).

The grids in complex **3** is in marked to those found in the complex $Cu(PPIA)_2(H_2O)_2$ which the flexibility in the aliphatic section of the ligand allows the copper centers to connected into buckled layers with coordinated water molecules between the layers. [18] The complex $[Cu_{1.5}(3\text{-PYD})_3(H_2O)]\cdot 1.5H_2O$ is a twofold interpenetrating 3-D framework based on {Cu(3-PYD)}$_6$ rings formed through head-to head and head-to-tail mixed arrangement of 3-PYD. [19] The multi-dimension Cu(II) coordination polymers $[Cu(Isonic)_2] \cdot EtOH$, $Cu(nic)_2$ [8(f)], $Cu(nic)_2$ [20], $\{[Cu_2(Isonic)_4\cdot 3H_2O]\cdot[Cu_2(Isonic)_4\cdot 2H_2O]\}\cdot 3H_2O$ [21] and $[Cu(Isonic)_2] \cdot 2H_2O$ [22] were synthesized by treating copper nitrate and copper chloride with isonicotinic acid and nicotinic acid under hydro(solvo)thermal conditions that show rhombic open channels, pleated sheets, perpendicular 24-member rings-like framework, mixed 2-D and 3-D open structure and chessboard tunnels, respectively.

4.3. Structure of $[Zn(PPIA)_2(H_2O)_2]_n$, 3

Single-crystal X-ray diffraction analysis reveals that **3** is similar to **2** showing a 2-D supramolecular network consisting of {Zn(PPIA)}$_4$ rings derived from head-to-tail arranged PPIA. Complex **3** was solved in the monoclinic space group $P2_1/n$. The asymmetric unit of **3**, Figure 4(a), contains one Zn atom, one PPIA group and one bonded water molecule. Figure 4(b) shows the coordination geometry about the Zn metal center. The zinc metal center adopts a distorted octahedral coordination geometry with the bond angles significantly deviate from 90 or 180° (Table 2). The Zn atom is bonded to two *trans* pyridyl nitrogen atoms (Zn(1)-N(1) = 2.164(2) Å, N(1)-Zn(1)-N(1A) = 180°) and two *trans* monodentate carboxylate groups (Zn(1)-O(1A) = 2.109(2) Å, O(1B)-Zn(1)-O(1A) = 180°) in the equatorial plane. The Zn atom is also bonded to two H_2O ligand (Zn-O = 2.150(2) Å, O(3)-Zn(1)-O(3A) = 180°) in the axial position to complete the distorted octahedral coordination geometry. Unlike complex **1**, PPIA ligand bridges Zn(II) through the pyridyl nitrogen atoms and the oxygen atoms of the monodentate carboxylate groups, generating a head-to-tail aggregated {Zn(PPIA)}$_4$ 32-member ring, Figure 4(c). In the {Zn(PPIA)}$_4$ ring, four Zn(II) ions and four PPIA are not coplanar, which may be due to the different arrangement of PPIA and the coordination geometry of the metal ion.

The {Zn(PPIA)}$_4$ rings are further extended into a 2D wave-like layer by sharing Zn(II) joints and PPIA edges, Figure 5(a).The complex shows void space with a Zn---Zn separation of 8.850 Å. The layers are further linked through extensive C-H···O (H···O = 2.369 – 2.441 Å; ∠ C-H···O = 150.7 – 171.5°) and O-H···O (H···O = 2.027 Å; ∠ O-H···O = 175.3°) hydrogen bondings, Figure 5(b).

The nets in complex **3** is different from the chiral complex $Zn(nic)_2$ where the pyridine rings of the nicotinate groups intrude into the square cavities to result in interdigitation of the 2-D square networks. [23] The non-centrosymmetric $[Zn(pecm)_2(H_2O)]_2\cdot CH_3CN\cdot 3H_2O$ (pecm = 4-[2-(4-pyridyl)ethenyl]cinnamate) adopts a caterpillar 1-D chain structure [24] and the complex [Zn(3-PYD)$_2$(H$_2$O)$_2$] (3-PYD = 3-(3-pyridyl)acrylic acid) shows a 3-D supramolecular frameworks constructed by 1-D {Zn(3-PYD)} chains through hydrogen-bonding interactions. [19] The complexes Zn(nic)$_2$ [25] and Zn(Isonic)$_2$ [26] were prepared by hydro(solvo)thermal reactions with 3-cyanopyridine or 4-cyanopyridine and Zn(ClO$_4$)$_2$ · 6H$_2$O, which exhibit complicated 2-D grids with the *exo*-tridentate nicotinate groups and 3-D diamond-like networks.

5. Conclusion

Reactions of PPIA with different metal ions have afforded four coordination polymers based on {Ag(PPIA)}$_2$ and {M(PPIA)}$_4$ (M = Cu and Zn) rings or metal-carboxylate chains, respectively. It may be conceivable to design and synthesize desired metal-organic frameworks when using the selected organic ligands with special conformations.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 275207-275209. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]

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References

1. (a) R. Robson, B. E. Abrahams, S. R. batten, R. W. Gable, B. F. Hoskins, J. Lieu, *Supramolecular Architecture*, ACS publications, Washington, DC, 1992. (b) H. Gudbjartson, K. Biradha, K. M. Poirier, M. J. Zaworotko, *J. Am. Chem. Soc.* 121 (1999) 2599. (c) S.-I. Noro, R. Kitauta, M. Kondo, S. Kitagawa, T. Ishii, H. Matauzaka, M. Yamashita, *J. Am. Chem. Soc.* 124 (2002) 2568. (d) C. Janiak, *J. Chem. Soc. Dalton Trans.* (2003**)** 2781. (e) S. Kitagawa, S. Masaoka, *Coord. Chem. Rev.* 246 (2003) 73. (f) S. R. Batten, K. S. Murray, *Coord. Chem. Rev.* 246 (2003) 103. (g) S. L. James, *Chem. Soc. Rev.* 32 (2003) 276.
2. (a) E. Bakalbassis, C. Tsipis, A. Bozopoulos, W. Dreissig, H. Hartl, J. Mrozinski, *Inorg. Chim. Acta* 186 (1991) 113. (b) J. Cano, G. D. Munno, J. L. Sanz, R. Ruiz, F. Lioret, J. Faus, M. Julve, *J. Chem. Soc. Dalton Trans.* (1994**)** 3465. (c) R. H. Groeneman, L. R. Macgillvrey, J. L. Atwood, *Inorg. Chem.* 38 (1999) 208. (d) L. Deakin, A. M. Arif, J. S. Miller, *Inorg. Chem.*, 38 (1999) 5272. (e) Y. Suenaga, T. Kuroda-Sowa, M. Maekawa, M. Munakata, *Polyhedron* 18 (1998) 191. (f) M.-L. Tong, X.-M. Chen, S. W. Ng, *Inorg. Chem. Commun.* 3 (2000) 436. (g) C. Richardson, P. J. Steel, *Inorg. Chem. Commun.* 1 (1998) 260. (h) M.-L. Tong, X.-M. Chen, B.-H. Ye, S. W. Na, *Inorg. Chem.* 37 (1998) 5278.
3. (a) E. Bakalbassis, P. Bergerat, O. Kahn, S. Jeannin, Y. Jeannin, Y. Dromzee, M. Guillot, *Inorg. Chem.* 31 (1992) 625. (b) C. S. Hong, Y. Do, *Inorg. Chem.* 36 (1997) 5684. (c) G. K. H. Shimizu, G. D. Enright, C. I. Ratciffe, J. A. Ripmeester, *Chem. Commun.* (1999) 461. (d) L. Carlucci, G. Ciani, D. M. Proserpio, *Chem. Commun.* (1999) 449.

4. (a) H. J. Choi, M. P. Suh, *Inorg. Chem.* 38 (1999) 6309. (b) H.-K. Fun, S. S. S. Raj, R.-G. Xiong, J.-L. Zuo, Z. Yu, X.-Z. You, *J. Chem. Soc. Dalton Trans.* (1999**)** 1915. (c) Y. Suenaga, T. Kamiya, T. Kuroda-Sowa, M. Maekawa, M. Munakata, *Inorg. Chim. Acta* 308 (2000) 17. (e) W.-M. Bu, L. Ye, Y.-G. Fan, *Inorg. Chem. Commun.* 3 (2000) 194. (f) X.-H. Bu, K. Biradha, T. Yamaguchi, M. Nishimura, T. Ito, K. Tanaka, M. Shionoya, *Chem. Commun.* (2000**)** 1953. (g) L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Angew. Chem. Int. Ed. Engl.* 34(1995) 1895.
5. (a) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* 183 (1999) 117; (b) S. Muthu, J. H. K. Yip, J. J. Vittal, *Dalton Trans.* (2002) 4561; (c) C.-W. Yeh, Y.-S. Yen, W.-B. Lin, C.-W. Su, J.-D. Chen, Ju-Chun Wang, *Struct. Chem.* 16 (2005) 141; (d) H.-L. Hu, C.-W. Yeh, J.-D. Chen, *Eur. J. Inorg. Chem.* (2004) 4696.
6. (a) C.-W. Su, C.-P. Wu, J.-D. Chen, L.-S. Liou, J.-C. Wang, *Inorg. Chem. Commun.* 5 (2002) 215; (b) S.-H. Liu, J.-D. Chen, L.-S. Liou, J.-C. Wang, *Inorg. Chem.* 40 (2001) 6499; (c) Y.-F. Hsu, J.-D. Chen, *Eur. J. Inorg. Chem.* (2004) 1488; (d) C.-W.Yeh, H.-L. Hu, R.-H. Liang, K.-M. Wang, T.-Y. Yen, J.-D. Chen, J.-C. Wang, *Polyhedron,* 24 (2005) 539.
7. (a) M.-C. Suen, Y.-Y. Wu, G.-C. Dong, J.-D. Chen, T.-C. Keng, J.-C. Wang, *J. Chin. Chem. Soc.* 49 (2002) 331; (b) M.-C. Suen, T.-C. Keng, J.-C. Wang, *Polyhedron,* 21 (2002) 2705; (c) M.-C. Suen, Y.-H. Wang, J.-C. Wang, *J. Chin. Chem. Soc.* 51 (2004) 43; (d) C.-W.Yeh, M.-C. Suen, H.-L. Hu, J.-D. Chen, J.-C. Wang, *Polyhedron,* 23 (2004) 1947. (e) H.-L. Hu, M.-C. Suen, C.-W.Yeh, J.-D. Chen, *Polyhedron,* 23 (2005) 1497.
8. (a) D. Visinescu, G. I. Pascu, M. Andruh, J. Magull, H. W. Roesky, *Inorg. Chim. Acta.* 340 (2002) 201. (b) S. Sain, T. K. Maji, G. Mostafa, T.-H. Lu, N. R. Chaudhuri, *New J. Chem.* 27 (2003) 185. (c) L. Carlucci, G. Ciani, D. M. Proserpio, S. Rizzato, *Chem. Commun.* (2001) 1198. (d) H.-X. Zhang, B.-S. Kang, Z.-Y. Zhou, A. S. C., Chan, Z.-N. Chen, C. Ren, *Dalton Trans.* (2001) 1664. (e) P. Ayyappan, O. R. Evans, W. Lin, *Inorg. Chem.* 40 (2001) 4627; (f) M. E. Chapman, P. Ayyappan, B. M. Foxman, G. T. Yee, W. Lin, *Cryst. Grow. Des.* 1 (2001) 159; (g) D. Visinescu, M. Andruh, A. Müller, M. Schmidtmann, Y. Journaux, *Inorg. Chem. Commun.* 5 (2002) 42.
9. (a) S. R. Batten, B. F. Hoskins, R. Robson, *Chem. Eur. J.* 6 (2000) 156. (b) D. J. Chesnut, D. Plewak, J. Zubieta, *Dalton Trans.* (2001) 2567. (c) S. R. Batten, A. R. Harris, P. Jensen, K. S. Murray, A. Ziebell, *Dalton Trans.* (2000) 3829. (d) J. M. Knaust, S. W. Keller, *Inorg. Chem.* 41 (2002) 5650. (e) J. Y. Lu, A. M. Babb, *Inorg. Chem.* 40 (2001) 3261. (f) J. M. Knaust, S. Lopez, S. W. Keller, *Inorg. Chim. Acta* 324 (2001) 81.
10. (a) XSCANS, Release, 2.1, Siemens Energy & Automation, Inc, Madison, Wisconsin, USA, 1995. SMART/SAINT/ASTRO, Release 4.03, Siemens Energy & Automation, Inc., Madison, Wisconsin, USA, 1995.
11. SHELXTL 5.10. Bruker Analytical X–ray Instruments Inc., Karlsruche, Germany, 1997.
12. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds; Wiley: New York, 1986
13. B. Cova, A. Briceño, R. Atencio, *New J. Chem.*, 25 (2001) 1516.
14. F. Jaber, F. Charbonnier, R. Faure, M. Petit-Ramel, *Zeits. Fur Krist.* 209 (1994) 536.

15. A. D. Burrows, M. F. Mahon, M. T. Palmer, *J. Chem. Soc., Dalton Trans.*, (1998) 1941.
16. G. Smith, A. N. Reddy, K. A. Byriel, C. H. Kennard, *Polyhedron*, 13 (1994) 2425.
17. P.-O. Käll, J. Grin, M. Fahlman, F. Söderlind, *Polyhedron*, 20 (2001) 2747.
18. L. A. Brokowski, C. L. Cahill, *Acta Cryst. Sect. E,* E59 (2003) m1127.
19. X. Li, R. Cao, Y. Sun, W. Bi, X. Li, Y. Wang, *Eur. J. Inorg. Chem.* (2005) 321.
20. J. Y. Lu, A. M. Babb, *Inorg. Chem. Commun.*, 4 (2001) 716.
21. J. Y. Lu, A. M. Babb, *Chem. Commun.*, (2001) 821.
22. Y.-H. Liu, Y.-L. Lu, H.-L. Tsai, J.-C. Wang, K.-L. Lu, *J. Solid State Chem.* 158 (2001) 315.
23. J. Y. Lu, E. E. Kohler, *Inorg. Chem. Commun.*, 5 (2002) 600.
24. P. Ayyappan, G. Sirokman, O. R. Evans, T. H. Warren, W. Lin, *Inorg. Chim. Acta,* 357 (2004) 3999.
25. O. R. Evans, R.-G. Xiong, W. Lin, Z. Wang, *J. Am. Chem. Soc.*, 120 (1998) 13272.
26. O. R. Evans, R.-G. Xiong, W. Lin, Z. Wang, G. K. Wong, *Angew. Chem. Int. Ed.*, 38 (1999) 536.

Table 1 Crystal data for **1-3**

Formula	$C_8H_{10}AgNO_3$	$C_{16}H_{20}CuN_2O_6$	$C_{16}H_{20}ZnN_2O_6$
Fw	276.04	399.88	401.71
crystal system	Triclinic	Orthorhombic	Monoclinic
space group	P1	Pbca	$P2_1/n$
a, Å	4.8828(11)	9.0572(7)	9.5055(9)
b, Å	8.2018(18)	11.195(3)	8.7994(6)
c, Å	11.813(3)	31.898(2)	9.9916(12)
α,°	100.548(4)	90	90
β,°	98.494(3)	90	103.905(7)
γ,°	104.797(4)	90	90
V, $Å^3$	440.19(17)	3234.3(8)	811.23(14)
Z	2	8	2
d_{calc},g/cm^3	2.083	1.757	1.645
cryst size, mm	0.35 × 0.35 × 0.72	1.00 × 0.40 × 0.30	0.80 × 0.80 × 0.20
μ(Mo Kα),mm^{-1}	2.261	1.611	1.551
range(2θ) for data collection,deg	$5.28 \leq 2\theta \leq 50.02$	$5.10 \leq 2\theta \leq 49.98$	$5.32 \leq 2\theta \leq 48.98$
temp.°C	25	25	25
limiting indices	$-5 \leq h \leq 5$, $-9 \leq k \leq 8$, $-11 \leq l \leq 14$	$0 \leq h \leq 10$, $0 \leq k \leq 13$, $0 \leq l \leq 37$	$0 \leq h \leq 11$, $0 \leq k \leq 10$, $-11 \leq l \leq 11$
independent reflections	1544 [R(int) = 0.0225]	2810 [R(int) = 0.0000]	1448 [R(int) = 0.0350]
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data / restraints / parameters	1514/ 0 / 151	2810/ 0 / 199	1373/ 0 / 155
quality-of-fit indicator [c]	1.008	1.232	1.030
final R indices [I > 2σ(I)] [a,b]	R1 = 0.0220, wR2 = 0.0493	R1 = 0.0489, wR2 = 0.1101	R1 = 0.0313, wR2 = 0.0661
R indices (all data)	R1 = 0.0232, wR2 = 0.0500	R1 = 0.0646, wR2 = 0.1201	R1 = 0.0395, wR2 = 0.0700
largest diff. peak and hole,e/$Å^3$	0.689 and –0.423	1.147and –0.560	0.327 and –0.654

[a] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.　$w = 1 / [\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)] / 3$. a = 0.0000, b = 1.1818. for **1**; a = 0.0000, b = 28.8445. for **2**; a = 0.0000, b = 1.7549 for **3**.

[c] quality-of-fit = $[\Sigma w(|F_o^2| - |F_c^2|)^2 / N_{observed} - N_{parameters}]]^{1/2}$.

Table 2 Selected Bond Distances (Å) and Angles (°) for **1**-**3**

1

Distances

Ag(1)-O(2A)	2.216(2)	Ag(1)-O(1)	2.245(2)
Ag(1)-N(1B)	2.366(3)	N(1)-Ag(1B)	2.366(3)
O(2)-Ag(1A)	2.216(2)	Ag(1)---Ag(1A)	2.9203(7)

Angles

O(2A)-Ag(1)-O(1)	161.93(8)	O(2A)-Ag(1)-N(1B)	108.92(9)
O(1)-Ag(1)-N(1B)	88.85(9)	O(2A)-Ag(1)-Ag(1A)	87.68(6)
O(1)-Ag(1)-Ag(1A)	74.25(6)	N(1A)-Ag(1)-Ag(1A)	160.43(7)

2

Distances

Cu(1)-O(1A)	1.9968(12)	Cu(1)-O(1B)	1.9968(12)
Cu(1)-N(1)	2.0254(14)	Cu(1)-N(1C)	2.0254(14)
O(1)-Cu(1D)	1.9968(12)		

Angles

O(1A)-Cu(1)-O(1B)	180.0	O(1A)-Cu(1)-N(1)	90.14(5)
O(1B)-Cu(1)-N(1)	89.86(5)	O(1A)-Cu(1)-N(1C)	89.86(5)
O(1B)-Cu(1)-N(1C)	90.14(5)	N(1)-Cu(1)-N(1C)	180.0

3

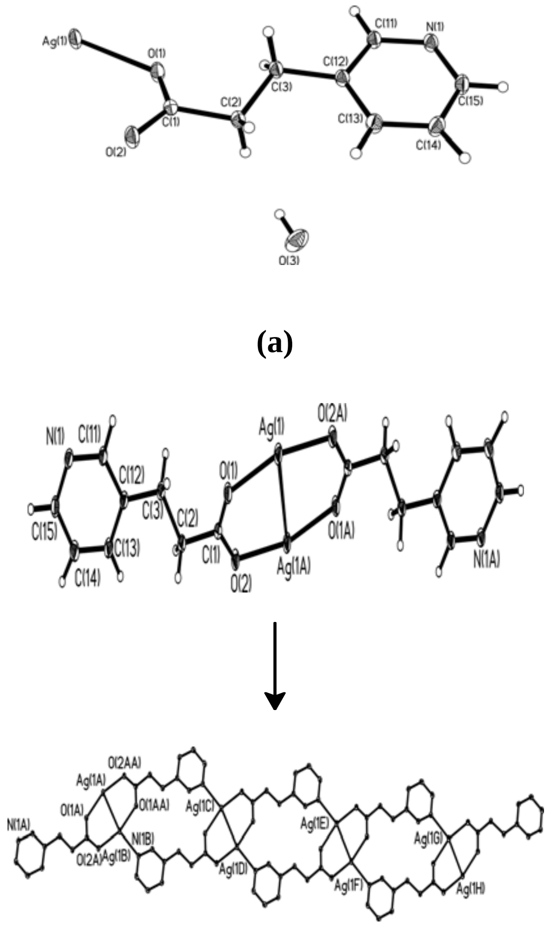
Distances

Zn(1)-O(1A)	2.109(2)	Zn(1)-O(1B)	2.109(2)
Zn(1)-O(3C)	2.150(2)	Zn(1)-O(3)	2.150(2)
Zn(1)-N(1)	2.164(2)	Zn(1)-N(1C)	2.164(2)
O(1)-Zn(1D)	2.109(2)		

Angles

O(1A)-Zn(1)-O(1B)	180.0	O(1A)-Zn(1)-O(3C)	86.74(9)
O(1B)-Zn(1)-O(3C)	93.26(9)	O(1A)-Zn(1)-O(3)	93.26(9)
O(1B)-Zn(1)-O(3)	86.74(9)	O(3C)-Zn(1)-O(3)	180.0
O(1A)-Zn(1)-N(1)	90.71(9)	O(1B)-Zn(1)-N(1)	89.29(9)
O(3C)-Zn(1)-N(1)	91.55(9)	O(3)-Zn(1)-N(1)	88.45(9)
O(1A)-Zn(1)-N(1C)	89.29(9)	O(1B)-Zn(1)-N(1C)	90.71(9)
O(3C)-Zn(1)-N(1C)	88.45(9)	O(3)-Zn(1)-N(1C)	91.55(9)
N(1)-Zn(1)-N(1C)	180.0		

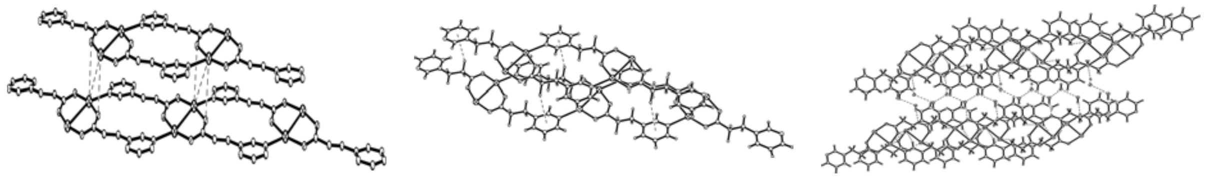
Symmetry transformations used to generate equivalent atoms:
1: (A): -x+2, -y+2, -z, (B): -x, -y+1, -z; **2**: (A): x+1/2, -y+1/2, z-1/2, (B): -x+1/2, y-1/2, -z+5/2, (C): -x+1, -y, -z+2, (D): -x+1/2, y+1/2, -z+5/2.**3**: (A): x-1/2, -y+1/2, z+1/2, (B): -x+5/2, y-1/2, -z+3/2, (C): -x+2, -y, -z+2, (D): -x+5/2,y+1/2,-z+3/2.



(a)

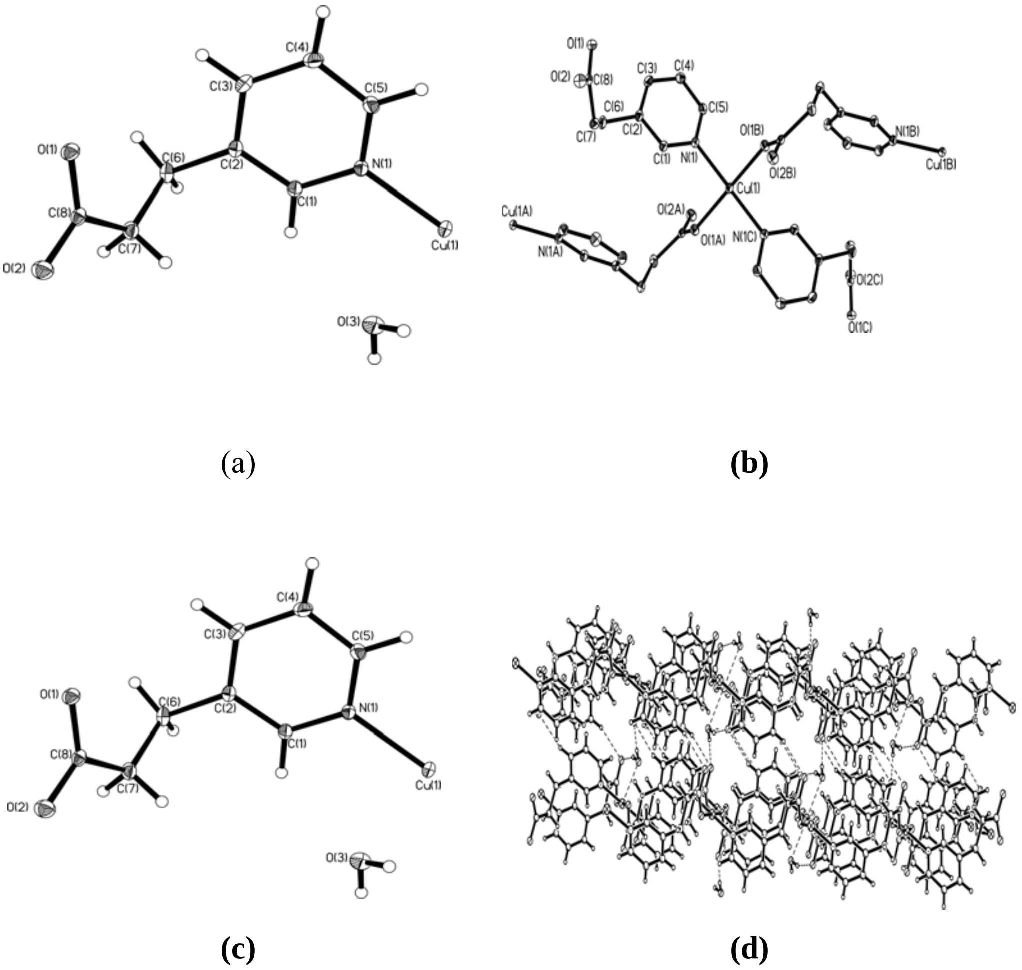
(b)

Figure 1 (a) ORTEP drawing of the asymmetric unit of complex **1**. (b) ORTEP drawing shows the coordination geometry of silver metal center and the $Ag_2(PPIA)_2$ building blocks bound together by Ag-N bond into a one-dimensional chain in **1**. Ellipsoids are scaled to enclose 20% of the electron density.



(a)　**(b)**　**(c)**

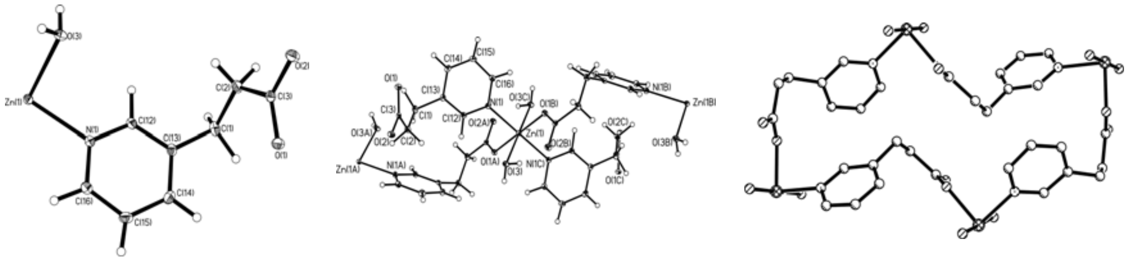
Figure 2 (a) An ORTEP diagram showing the 1-D chains penetrating to each other through Ag---Ag and Ag---O interactions in **1**. (b) An ORTEP diagram showing the set of one-dimensional chains stacking together through interchain C-H···π interactions in **1**. (c) An ORTEP diagram showing the 1-D chains penetrating to each other through O-H---O interactions, forming 3-D supramolecular structure that are occupied by the water molecules in **1**.



(a)　(b)

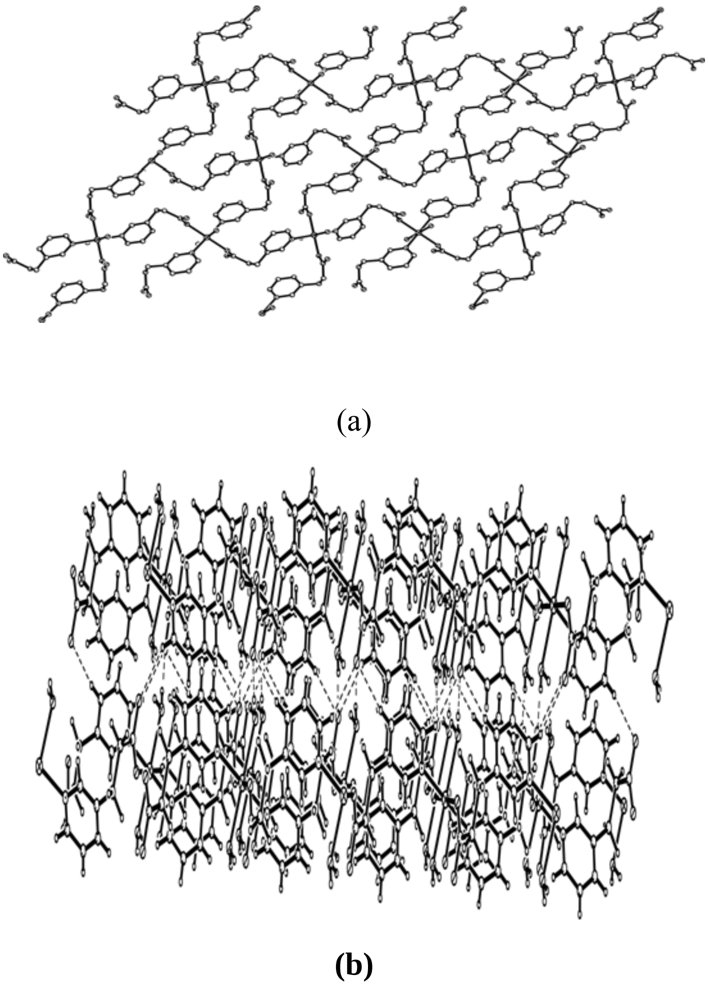
(c)　(d)

Figure 3 (a) ORTEP drawing of the asymmetric unit of complex **2**. (b) ORTEP drawing shows the coordination geometry of copper metal center in **2**. (c) A 2-D wave-like in **2** along the *c* axis. (d) Packing structure of **2** along the *b* axis showing the X-H---O (X = C or O) hydrogen bondings among the layers.



(a)　(b)　(c)

Figure 4 (a) ORTEP drawing of the asymmetric unit of complex **3**. (b) ORTEP drawing shows the coordination geometry of zinc metal center in **3**. (c) {Zn(PPIA)}$_4$ rings from head-to-tail arrangement of PPIA ligands. Ellipsoids are scaled to enclose 20% of the electron density.



(a)

(b)

Figure 5 (a) A 2-D wave-like in **3** along the *c* axis. (b) Packing structure of **3** along the *b* axis showing the X-H---O (X = C or O) hydrogen bondings among the sheets