

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:22

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

### Synthesis and crystal structure of 2-D silver coordination polymers containing aminopyrazine

Hui-An Tsai<sup>a,d</sup>, Maw-Cherng Suen<sup>a</sup>, Pin-Ning Wang<sup>a</sup>, Yi-Fen Hsu<sup>b</sup> & Ju-Chun Wang<sup>c</sup>

<sup>a</sup> Department of Material and Fiber, Graduate School of Materials Applied Technology, Nanya Institute of Technology, Zhongli, Taiwan, ROC

<sup>b</sup> Department of Chemistry, Chung-Yuan University, Zhongli, Taiwan, ROC

<sup>c</sup> Department of Chemistry, Soochow University, Taipei, Taiwan, ROC

<sup>d</sup> R&D Center for Membrane Technology, Chung-Yuan Christian University, Zhongli, Taiwan, ROC

Published online: 28 Jul 2011.

To cite this article: Hui-An Tsai, Maw-Cherng Suen, Pin-Ning Wang, Yi-Fen Hsu & Ju-Chun Wang (2011) Synthesis and crystal structure of 2-D silver coordination polymers containing aminopyrazine, Journal of Coordination Chemistry, 64:15, 2658-2666, DOI: [10.1080/00958972.2011.605123](https://doi.org/10.1080/00958972.2011.605123)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.605123>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Synthesis and crystal structure of 2-D silver coordination polymers containing aminopyrazine

HUI-AN TSAI†¶, MAW-CHERNG SUEN\*†, PIN-NING WANG†, YI-FEN HSU‡  
and JU-CHUN WANG§

†Department of Material and Fiber, Graduate School of Materials Applied Technology,  
Nanya Institute of Technology, Zhongli, Taiwan, ROC

‡Department of Chemistry, Chung-Yuan University, Zhongli, Taiwan, ROC

§Department of Chemistry, Soochow University, Taipei, Taiwan, ROC

¶R&D Center for Membrane Technology, Chung-Yuan Christian University, Zhongli,  
Taiwan, ROC

(Received 6 August 2010; in final form 20 June 2011)

Two supramolecules of Ag(I),  $[\text{Ag}(\text{NO}_3)(\text{APZ})]_n$  (**1**) and  $\{[\text{Ag}(\text{APZ})_2][\text{CF}_3\text{COO}]\cdot\text{H}_2\text{O}\}_n$  (**2**) (APZ = aminopyrazine) have been prepared by self-assembly of Ag(I) salts with APZ in MeOH/H<sub>2</sub>O. EA, IR, and TGA spectra have been recorded and the complexes have been structurally characterized by X-ray crystallography, confirming that **1** and **2** are 2-D pleated rectangular grid coordination polymers. The NO<sub>3</sub><sup>-</sup> in **1** is coordinated to Ag<sup>+</sup>, bidentate, and  $\mu^2, \eta^1\text{-NO}_3^-$ , while CF<sub>3</sub>COO<sup>-</sup> in **2** is not coordinated. Ag...O interactions, hydrogen bonds, and  $\pi\cdots\pi$  stacking interactions support the supramolecular structures.

*Keywords:* Silver; Coordination polymer; Aminopyrazine

### 1. Introduction

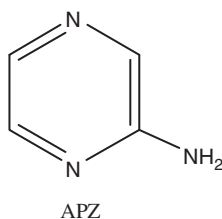
Self-assembly of supramolecular structures using metal coordination has become a focus of interest [1], largely due to the range of potential applications in electrical, magnetic, and optical devices [2] and porous zeolite mimics [3]. The specific properties of each coordination network are directly related to its structure, which is a function of both the ligand and the metal. There has been resurgent interest in extended organic or organometallic crystals based on hydrogen bonds and metal coordination bonds [4–6]. It is important to understand and control the interplay between coordination characteristics of the ligands and the metals and the ultimate shape of the self-assembled suprastructure.

Many studies have centered on the use of supramolecular contacts between suitable molecules to generate multidimensional arrays or networks. Through ligand design with various coordination characteristics of metal ion and lengths of the spacer, a variety of

\*Corresponding author. Email: sun@nanya.edu.tw

structural motifs have been created [7]. Many topologically promising architectures have been constructed for Ag(I) ion with bidentate building blocks containing nitrogen donors, including 1-D, 2-D, and 3-D network structures [8]. Despite some recent progress, the ability to predict and control the supramolecular assembly of molecules remains elusive, and much more work is required to understand the inter- and intramolecular forces that determine the patterns of molecular structure and crystal packing in the solid state. Various bipyridine-type and biphenyl cyanide-type ligands have been used as supramolecular building blocks [9–11].

Exploitation of the potentially tridentate aminopyrazine (APZ) has been unprecedented until recently. In this article, we report two supramolecular Ag(I) complexes,  $[\text{Ag}(\text{NO}_3)(\text{APZ})]_n$  (**1**) and  $\{[\text{Ag}(\text{APZ})_2][\text{CF}_3\text{COO}] \cdot \text{H}_2\text{O}\}_n$  (**2**).



## 2. Experimental

### 2.1. General procedures

All manipulations were carried out under dry, oxygen-free nitrogen by Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over appropriate reagents before use. IR spectra were recorded on a Jasco FT/IR-460 plus spectrometer. Elemental analyses were conducted with a PE 2400 series II CHNS/O analyzer.

### 2.2. Starting materials

$\text{AgNO}_3$ ,  $\text{AgCF}_3\text{COO}$ , and APZ were purchased from Aldrich Chemical Co. and used as received.

### 2.3. Preparation of $[\text{Ag}(\text{NO}_3)(\text{APZ})]_n$ (**1**)

APZ (0.025 g, 0.10 mmol) in 5 mL MeOH was layered onto a solution of  $\text{AgNO}_3$  (0.019 g, 0.10 mmol) in 5 mL  $\text{H}_2\text{O}$ . The resulting solution was slowly diffused for several weeks to generate colorless crystals. The yield was 0.017 g (65%). The calculated composition for  $\text{C}_4\text{H}_5\text{AgN}_4\text{O}_3$  is C, 18.13; H, 1.90; N, 21.14, while the experimentally found composition is C, 18.03; H, 1.91; N, 21.14. IR(KBr disc,  $\text{cm}^{-1}$ ): 3337(br), 3153(m), 2714(m), 1659(m), 1586(m), 1532(m), 1482(m), 1429(m), 1383(m), 1317(m), 1236(m), 1208(m), 1059(m), 1004(m), 888(m), 825(m), 812(m), 589(m), 546(m).

#### 2.4. Preparation of $\{[Ag(APZ)_2][CF_3COO] \cdot H_2O\}_n$ (**2**)

APZ (0.025 g, 0.10 mmol) in 5 mL MeOH was layered onto a solution of  $Ag[CF_3COO]$  (0.022 g, 0.10 mmol) in 5 mL  $H_2O$ . The resulting solution was slowly diffused for several weeks to generate colorless crystals. The yield was 0.049 g (76%). The calculated composition for  $C_{12}H_{12}Ag_2F_6N_6O_5$  is C, 22.15; H, 1.84; N, 12.92, while the experimentally found composition is C, 22.05; H, 1.83; N, 12.95. IR (KBr disc,  $cm^{-1}$ ): 3330(m), 3168(m), 2974(m), 2359(m), 1652(m), 1602(m), 1541(m), 1450(m), 1429(m), 1359(m), 1326(m), 1190(m), 1134(m), 1069(m), 1020(m), 893(m), 839(m), 821(m), 797(m), 667(m).

#### 2.5. X-ray crystallography

Diffraction data for **1** and **2** were collected at 25°C on a Siemens P4 diffractometer equipped with graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Data reduction was carried out by standard methods using well-established computational procedures [12]. The structure factors were obtained after Lorentz and polarization correction. The positions of some heavier atoms, including silver atom, were measured by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements [13]. The residuals of the final refinement were  $R_1 = 0.0692$ ,  $wR_2 = 0.1376$  for **1**. The crystallographic procedures for **2** were similar to those for **1** and the residuals of the final refinement were  $R_1 = 0.0288$ ,  $wR_2 = 0.0913$  for **2**. Basic information pertaining to crystal parameters and structure refinement is summarized in table 1.

### 3. Results and discussion

#### 3.1. Syntheses

$[Ag(NO_3)(APZ)]_n$  (**1**) and  $\{[Ag(APZ)_2][CF_3COO] \cdot H_2O\}_n$  (**2**) were prepared by reacting  $AgX$  ( $X = NO_3^-$ , **1** and  $CF_3COO^-$ , **2**) with APZ in MeOH/ $H_2O$ . These complexes were structurally characterized by X-ray crystallography. Complexes **1** and **2** were insoluble in most organic solvents; suitable crystals for X-ray diffraction were obtained from layering APZ in methanol solution onto a solution of  $AgX$  ( $X = NO_3^-$ , **1** and  $CF_3COO^-$ , **2**) in  $H_2O$ .

#### 3.2. Structure of complexes

The crystal structure of **1** belongs to the space group P2. Representative asymmetric units and ORTEP diagrams showing the geometry of Ag in **1** are depicted in figure 1(a). Table 2 lists the bond distances and angles around Ag (1) and Ag (2) for **1**. Ag (1) is coordinated with two nitrogens [ $Ag-N = 2.187(8) \text{ \AA}$ ] from two different APZ ligands and two oxygens [ $Ag-O = 2.482(12) \text{ \AA}$ ] from two different  $NO_3^-$  anions to generate a distorted tetrahedral geometry. Ag (2) is coordinated with two pyridyl nitrogens [ $Ag-N = 2.227(9) \text{ \AA}$ ] of different APZ ligands and two oxygens [ $Ag-O = 2.583(9) \text{ \AA}$ ] of  $NO_3^-$ . Adjacent Ag's are bridged with APZ and  $NO_3^-$  to form 24-membered macrocyclic

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

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>4</sub> H <sub>5</sub> AgN <sub>4</sub> O <sub>3</sub>	C <sub>12</sub> H <sub>12</sub> Ag <sub>2</sub> F <sub>6</sub> N <sub>6</sub> O <sub>5</sub>
Formula weight	264.99	650.02
Crystal system	Monoclinic	Monoclinic
Space group	P2	C2/c
Unit cell dimensions (Å, °)		
<i>a</i>	3.6333(6)	19.5083(18)
<i>b</i>	7.7301(10)	6.9148(7)
<i>c</i>	12.7965(16)	14.0530(14)
$\beta$	95.651(12)	101.784(2)
Volume (Å <sup>3</sup> ), <i>Z</i>	357.65(9), 2	1855.7(3), 4
Calculated density (Mg cm <sup>-3</sup> )	2.461	2.327
<i>F</i> (000)	256	1256
Absorption coefficient (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	2.788	2.210
Radiation monochromated in incident beam ( $\lambda$ (Mo-K $\alpha$ ), Å)	0.71073	0.71073
2 $\theta$ range for data collection (°)	3.20 $\leq$ 2 $\theta$ $\leq$ 60.00	5.92 $\leq$ 2 $\theta$ $\leq$ 52.04
Limiting indices	-5 $\leq$ <i>h</i> $\leq$ 5; -10 $\leq$ <i>k</i> $\leq$ 10; -17 $\leq$ <i>l</i> $\leq$ 17	-17 $\leq$ <i>h</i> $\leq$ 24; -8 $\leq$ <i>k</i> $\leq$ 7; -17 $\leq$ <i>l</i> $\leq$ 16
Reflections collected	2483	4940
Independent reflections	2067 [ <i>R</i> (int) = 0.0362]	1830 [ <i>R</i> (int) = 0.0198]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2067/1/112	1830/0/172
Quality-of-fit indicator <sup>a</sup>	1.127	1.127
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b,c</sup>	<i>R</i> <sub>1</sub> = 0.0692, <i>wR</i> <sub>2</sub> = 0.1376	<i>R</i> <sub>1</sub> = 0.0288, <i>wR</i> <sub>2</sub> = 0.0913
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0899, <i>wR</i> <sub>2</sub> = 0.1469	<i>R</i> <sub>1</sub> = 0.0297, <i>wR</i> <sub>2</sub> = 0.0928
Largest difference peak and hole (e Å <sup>-3</sup> )	1.958 and -0.863	0.408 and -1.220

<sup>a</sup>Quality-of-fit =  $[\sum w(|F_o^2| - |F_c^2|)^2 / N_{\text{observed}} - N_{\text{parameters}}]^{1/2}$ . <sup>b</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$ ,  $p = [\max(F_o^2 \text{ or } 0) + 2(F_o^2)]/3$ .  $a = 0.0000$ ,  $b = 4.2565$  for **1**;  $a = 0.0750$ ,  $b = 0.0000$  for **2**.

building units. The 22-membered {Ag<sub>6</sub>N<sub>8</sub>O<sub>2</sub>C<sub>8</sub>} metallocycles in **1** have the size 3.633  $\times$  13.642 Å<sup>2</sup>. The nitrates have  $\mu^2, \eta^1\text{-NO}_3^-$  coordination mode with Ag (1) and bidentate coordination with Ag (2), interlinking the metallocycles into 2-D pleated rectangular grids that are formed between adjacent chains, as shown in figure 1(b). The nitrates in Ag<sub>2</sub>(2,3-diphenylquinoxaline)(NO<sub>3</sub>)<sub>2</sub>(X)<sub>2</sub> (X = DMF, H<sub>2</sub>O and CH<sub>3</sub>CN) show several bonding modes, including unidentate,  $\mu^2, \eta^1\text{-NO}_3^-$ , bidentate and  $\mu^2, \eta^1, \eta^1\text{-NO}_3^-$  coordination mode [14]. The formation of different bonding modes for NO<sub>3</sub><sup>-</sup> is presumably due to the different coordination abilities of the solvents, resulting in different structural types. The Ag distances are 3.63 and 7.12 Å in the macrocyclic building units. Complex **1** forms 3-D supramolecular structures that are interlinked by NO<sub>3</sub><sup>-</sup> through Ag...O [Ag...O = 3.522 Å] interaction and C-H...O [H...O = 2.354 Å and 2.560 Å,  $\angle\text{C-H}\cdots\text{O} = 138.0^\circ$  and  $128.5^\circ$ ] hydrogen bonds, as shown in figure 1(c). The phenyls in the macrocyclic building units interact through  $\pi$ - $\pi$  stacking [15], and the distance between the centers of the rings is 3.633 Å for **1**, as shown in figure 1(d).

The structure of **2** was solved in the space group C2/c. Representative asymmetric units and ORTEP diagrams showing the geometry of Ag in **2** are depicted in figure 2(a). Table 2 lists the bond distances and angles around Ag for **2**. The structure shows a coordination polymer consisting of silver ions, APZ ligands, CF<sub>3</sub>COO<sup>-</sup> and H<sub>2</sub>O. Figure 2(b) shows that **2** is a coordination polymer of [Ag(APZ)]<sub>n</sub><sup>+</sup>, forming 2-D sheets. The Ag coordinated with the two nitrogens [Ag-N = 2.200(2) and 2.216(2) Å] from two

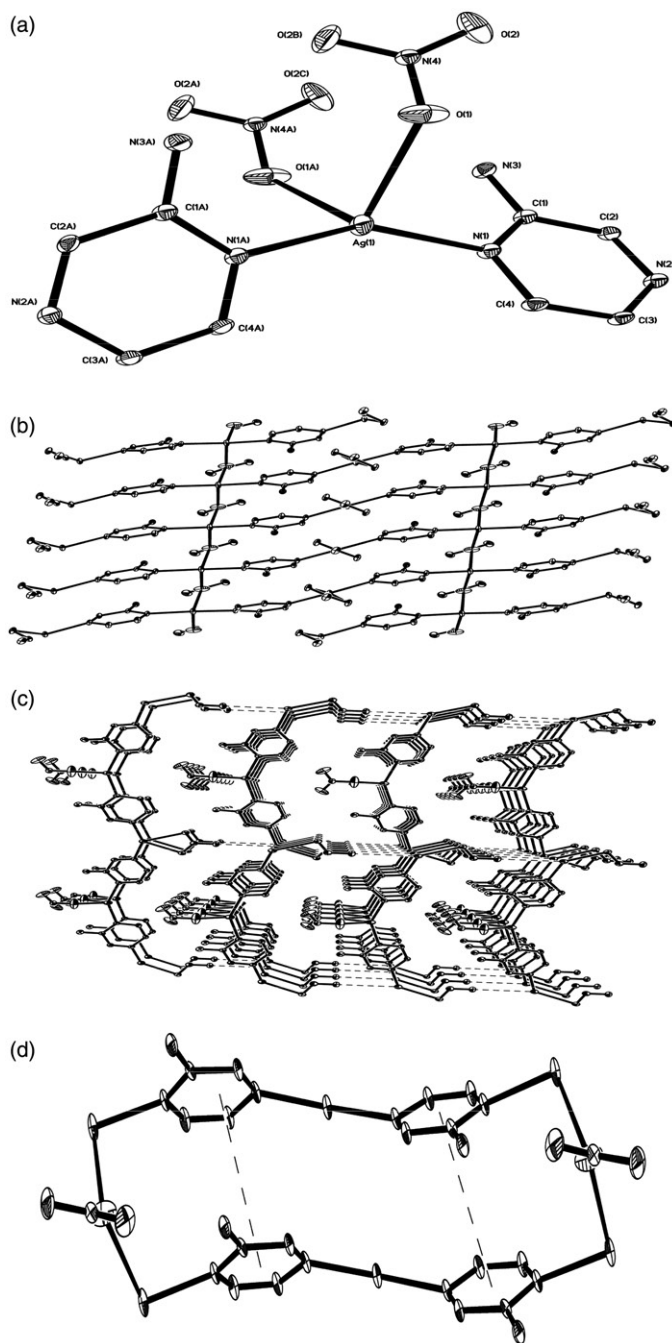


Figure 1. (a) An ORTEP showing the coordination geometry of silver for **1**. (b) The 2-D pleated rectangular grids by the APZ, Ag(I) and  $\text{NO}_3^-$ . (c) Packing diagram for **1** showing interactions between the layers. (d) The macrocylic building units for **1** showing  $\pi \cdots \pi$  interactions between layers.

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

<b>Complex 1</b>			
Ag(1)–N(1A)	2.187(8)	Ag(1)–N(1)	2.187(8)
Ag(1)–O(1B)	2.482(12)	Ag(1)–O(1)	2.482(12)
Ag(2)–N(2C)	2.227(9)	Ag(2)–N(2)	2.227(9)
Ag(2)–O(3C)	2.583(9)	Ag(2)–O(3)	2.583(8)
N(1A)–Ag(1)–N(1)	148.1(5)	N(1A)–Ag(1)–O(1B)	93.6(3)
N(1)–Ag(1)–O(1B)	108.1(3)	N(1A)–Ag(1)–O(1)	108.1(3)
N(1)–Ag(1)–O(1)	93.6(3)	O(1B)–Ag(1)–O(1)	94.1(6)
N(2C)–Ag(2)–N(2)	151.1(5)	N(2C)–Ag(2)–O(3C)	115.4(3)
N(2)–Ag(2)–O(3C)	91.4(3)	N(2C)–Ag(2)–O(3)	91.4(3)
N(2)–Ag(2)–O(3)	115.4(3)	O(3C)–Ag(2)–O(3)	49.5(3)
<b>Complex 2</b>			
Ag–N(1)	2.200(2)	Ag–N(2A)	2.216(2)
Ag–Ag(A)	3.2879(6)		
N(1)–Ag–N(2A)	166.71(9)	N(1)–Ag–Ag(B)	105.51(6)
N(2A)–Ag–Ag(B)	84.65(6)		

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

different APZ ligands and the silver from adjacent chains generate a distorted planar triangular geometry. The Ag...Ag separation of 3.288 Å is comparable to those [2.970–3.312 Å] found in other silver coordination polymers with pyridyl donors [16], indicating weak Ag...Ag interaction. Adjacent chains are bridged with Ag forming 22-membered macrocyclic building units, which interlink the 1-D metallocycles into 2-D pleated rectangular grids formed between adjacent chains. The 22-membered {Ag<sub>6</sub>N<sub>8</sub>C<sub>8</sub>} metallocycles in **2** are 3.288 × 14.053 Å<sup>2</sup>. The 2-D pleated rectangular grids are further linked by Ag...O interactions, N–H...F, N–H...O and C–H...O hydrogen bonds to form 3-D supramolecular structures (H...F = 2.474 Å, ∠N–H...F = 123.8°; H...O = 2.254 Å, ∠N–H...O = 152.4°; H...O = 2.471 Å, ∠C–H...O = 141.8°; Ag...O = 2.642, 2.726 Å), as shown in figure 2(c). The phenyls in the macrocyclic building units interact through π–π stacking [15], and the distance between the centers of the rings is 3.769 Å for **2**, as shown in figure 2(d).

The structural difference between **1** and **2** is that NO<sub>3</sub><sup>−</sup> in **1** are bonded to silver through their unidentate oxygens in the macrocyclic building unit, while the CF<sub>3</sub>COO<sup>−</sup> in **2** is not coordinated with the metal center. The 2-D pleated rectangular grids 3.633 × 13.642 Å<sup>2</sup> in **1** are shorter than the grids 3.288 × 14.053 Å<sup>2</sup> in **2**. The nitrogens of APZ bonded to the Ag(I) are not linear and the N–Ag–N angle is 151.1(5)° for **1** and 166.71(9)° for **2**. The average Ag–N distances are similar in **1** and **2** (Table 2).

#### 4. Conclusions

Coordination chemistry of AgX (X = NO<sub>3</sub><sup>−</sup> and CF<sub>3</sub>COO<sup>−</sup>) with APZ was investigated. The synthesis and structural characterization for [Ag(NO<sub>3</sub>)(APZ)]<sub>n</sub> (**1**) and {[Ag(APZ)<sub>2</sub>][CF<sub>3</sub>COO]·H<sub>2</sub>O}<sub>n</sub> (**2**) are reported. Complexes **1** and **2** show 2-D pleated rectangular grids, in which Ag(I) and APZ form 24-member and 22-member rings, respectively. The nitrates show μ<sup>2</sup>, η<sup>1</sup>-NO<sub>3</sub><sup>−</sup> and bidentate coordination in **1**. The results indicate that the coordination chemistry of APZ is versatile. The 2-D pleated rectangular grids and π...π stacking interactions in **1** and **2** are also shown. Ag...O interaction and hydrogen bonds are found to support the supramolecular structures.



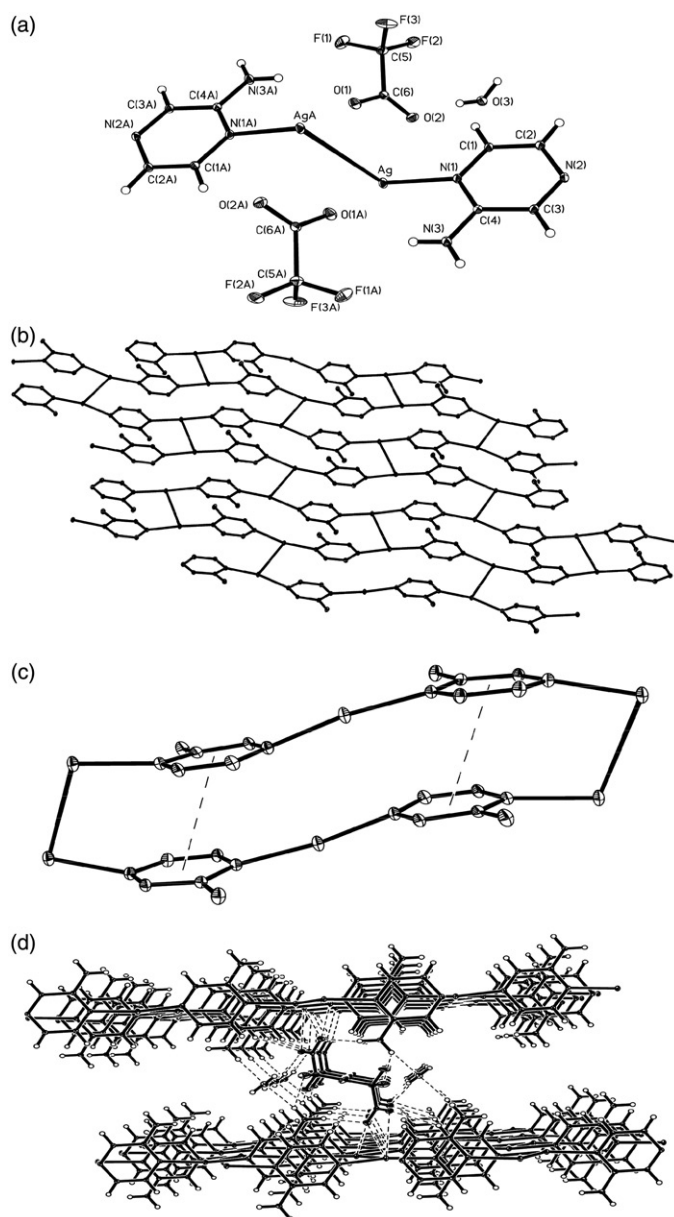


Figure 2. (a) The asymmetric unit of **2**. (b) The 2-D pleated rectangular grids by APZ ligands and Ag(I). (c) The macroscopic building units for **2** showing  $\pi \cdots \pi$  interactions between layers. (d) A diagram showing interactions among the pleated rectangular grids of **2** and CF<sub>3</sub>COO<sup>-</sup>.

### Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication numbers CCDC 746694 and 746695. These data can be obtained free

of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

We are grateful to the Nanya Institute of Technology and the National Science Council of the Republic of China for support.

## References

- [1] (a) C. Piguët, M. Borkovec, J. Hamacek, K. Zeckert. *Coord. Chem. Rev.*, **249**, 705 (2005); (b) W. Huang, H.-B. Zhu, S.-H. Gou. *Coord. Chem. Rev.*, **250**, 414 (2006); (c) P.-Z. Li, X.-M. Lu, B. Liu, S. Wang, X.-J. Wang. *Inorg. Chem.*, **46**, 5823 (2007); (d) M. Nayak, R. Koner, H. Stoeckli-Evans, S. Mohanta. *Cryst. Growth Des.*, **5**, 1907 (2005).
- [2] (a) O. Maury H. Le Bozec. *Acc. Chem. Res.*, **38**, 691 (2005); (b) G. Anandha Babu, P. Ramasamy. *J. Cryst. Growth*, **311**, 1185 (2009); (c) M. Lydia Caroline, A. Kandasamy, R. Mohan, S. Vasudevan. *J. Cryst. Growth*, **311**, 1161 (2009); (d) C. Janiak. *Dalton Trans.*, 2781 (2003); (e) D. Maspoeh, D. Ruiz-Molina, J. Veciana. *J. Mater. Chem.*, **14**, 2713 (2004); (f) S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003); (g) L. Carlucci, G. Ciani, D. Poserpio. *Coord. Chem. Rev.*, **246**, 247 (2003).
- [3] (a) M.R. Othman, S.C. Tan, S. Bhatia. *Microporous Mesoporous Mater.*, **121**, 138 (2009); (b) S. Hashimoto, K. Samata, T. Shoji, N. Taira, T. Tomita, S. Matsuo. *Microporous Mesoporous Mater.*, **117**, 220 (2009); (c) Y. Li, M. Pera-Titus, G. Xiong, W. Yang, E. Landrison, S. Miachon, J.-A. Dalmon. *J. Membrane Sci.*, **325**, 973 (2008); (d) K. Egeblad, C.H. Christensen, M. Kustova, C.H. Christensen. *Chem. Mater.*, **20**, 946 (2008); (e) D. Li, Y. Huang, K.R. Ratinac, S.P. Ringer, H. Wang. *Microporous Mesoporous Mater.*, **116**, 416 (2008); (f) L. Karwacki, E. Stavitski, M.H.F. Kox, J. Kornatowski, B.M. Weckhuysen. *Angew. Chem., Int. Ed.*, **46**, 7228 (2007); (g) M.A. Snyder, M. Tsapatsis. *Angew. Chem., Int. Ed.*, **46**, 7560 (2007).
- [4] (a) R. Koner, R.M. Nayak, G. Ferguson, J.N. Low, C. Glidewell, P. Misra, S. Mohanta. *CrystEngComm*, **7**, 129 (2005); (b) H.-L. Hu, M.-C. Suen, C.-W. Yeh J.-D. Chen. *Polyhedron*, **24**, 1497 (2005); (c) M.-C. Suen, Y.-H. Wang, Y.-F. Hsu, C.-W. Yeh, J.-D. Chen, J.-C. Wang. *Polyhedron*, **24**, 2913 (2005); (d) L. Zhao, B.H. Northrop, P.J. Stang. *J. Am. Chem. Soc.*, **130**, 11886 (2008).
- [5] (a) J. Rosenthal, J.M. Hodgkiss, E.R. Young, D.G. Nocera. *J. Am. Chem. Soc.*, **128**, 10474 (2006); (b) Y.-H. Wang, K.-L. Chu, H.-C. Chen, C.-W. Yeh, Z.-K. Chan, M.-C. Suen, J.-D. Chen, J.-C. Wang. *CrystEngComm*, **8**, 84 (2006); (c) M.-C. Suen, Y.-H. Wang, J.-C. Wang. *J. Chin. Chem. Soc.*, **51**, 43 (2004); (d) C.-W. Yeh, Y.-S. Yen, W.-B. Lin, C.-W. Su, J.-D. Chen, J.-C. Wang. *Struct. Chem.*, **16**, 141 (2005).
- [6] (a) Y.-H. Wang, M.-C. Suen, H.-T. Lee, J.-C. Wang. *Polyhedron*, **25**, 2944 (2006); (b) M.-C. Suen, T.-C. Keng, J.-C. Wang. *Polyhedron*, **21**, 2705 (2002); (c) M.-C. Suen, J.-C. Wang. *Struct. Chem.*, **17**, 315 (2006); (d) M.-C. Suen, Z.-K. Chan, J.-D. Chen, J.-C. Wang, C.-H. Hung. *Polyhedron*, **25**, 2325 (2006).
- [7] (a) Y.-F. Hsu, H.-L. Hu, C.-J. Wu, C.-W. Yeh, D.M. Proserpio, J.-D. Chen. *CrystEngComm*, **11**, 168 (2009); (b) C.-W. Yeh, J.-D. Chen, J.-C. Wang. *Polyhedron*, **27**, 3611 (2008); (c) Y.-S. Yen, C.-W. Yeh, J.-D. Chen, J.-C. Wang. *J. Cluster Sci.*, **19**, 109 (2008).
- [8] (a) I. Kalf, M. Braun, Y. Wang, U. Englert. *CrystEngComm*, **8**, 916 (2006); (b) C.M. Fitchett, P.J. Steel. *Dalton Trans.*, 4886 (2006); (c) M. Kato, T. Fujihara, D. Yano, A. Nagasawa. *CrystEngComm*, **10**, 1460 (2008).
- [9] (a) L. Cunha-Silva, R. Ahmad, M.J. Carr, A. Franken, J.D. Kennedy, M.J. Hardie. *Cryst. Growth Des.*, **7**, 658 (2007); (b) J. Wang, P. Ma, Y. Shen, J. Niu. *Cryst. Growth Des.*, **8**, 3130 (2008); (c) A. Bellusci, A. Crispini, D. Pucci, E.I. Szerb, M. Ghedini. *Cryst. Growth Des.*, **8**, 3114 (2008); (d) S. Del Piero, R. Fedele, A. Melchior, R. Portanova, M. Tolazzi, E. Zangrando. *Inorg. Chem.*, **46**, 4683 (2007).
- [10] (a) E.C. Constable, C.E. Housecroft, M. Neuburger, S. Reymann, S. Schaffner. *Aust. J. Chem.*, **61**, 847 (2008); (b) M.N. Kozlova, S. Ferlay, S.E. Solovieva, I.S. Antipin, A.I. Konovalov, N. Kyritsakas, M.W. Hosseini. *Dalton Trans.*, 5126 (2007); (c) S. Benmansour, F. Setifi, S. Triki, J.-Y. Salaun, F. Vandavelde, J. Sala-Pala, C.J. Gomez-Garcia, T. Roisnel. *Eur. J. Inorg. Chem.*, 186 (2007).

- [11] (a) Y.-F. Hsu, J.-D. Chen. *Eur. J. Inorg. Chem.*, 1488 (2004); (b) H.-L. Hu, C.-W. Yeh, J.-D. Chen. *Eur. J. Inorg. Chem.*, 4696 (2004), and references therein; (c) F. Luo, J. Zheng, S.R. Batten. *Chem. Commun.*, 3744 (2007).
- [12] *XSCANS, Release, 2.1*, Siemens Energy & Automation, Inc., Madison, WI, USA (1995).
- [13] *SHELXTL 5.10*, Bruker Analytical X-ray Instruments Inc., Karlsruhe, Germany (1997).
- [14] (a) C.-W. Yeh, T.-R. Chen, J.-D. Chen, J.-C. Wang. *Cryst. Growth Des.*, **9**, 2595 (2009); (b) H.-P. Wu, C. Janiak, G. Rheinwald, H. Lang. *J. Chem. Soc., Dalton Trans.*, 183 (1999); (c) J.L. Sagué, M. Meuwly, K.M. Fromm. *CrystEngComm*, **10**, 1542 (2008); (d) A.Y. Robin, J.L. Sagué, K.M. Fromm. *CrystEngComm*, **8**, 403 (2006); (e) T.V. Slenters, J.L. Sagué, P.S. Brunetto, S. Zuber, A. Fleury, L. Mirolo, A.Y. Robin, M. Meuwly, O. Gordon, R. Landmann, A.U. Daniels, K.M. Fromm. *Materials*, **3**, 3407 (2010).
- [15] (a) L. Carlucci, G. Ciani, D.W.V. Gudenberg, D.M. Proserpio. *Inorg. Chem.*, **36**, 3812 (1997); (b) C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000); (c) A.N. Khlobystov, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schroder. *Coord. Chem. Rev.*, **222**, 155 (2001); (d) A.J. Black, G. Baum, N.R. Champness, S.S.M. Chung, P.A. Cooke, D. Fenske, A.N. Khlobystov, D.A. Lemenovskii, W.S. Li, M. Schroder. *J. Chem. Soc., Dalton Trans.*, 4285 (2000); (e) T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi. *Inorg. Chem.*, **36**, 576 (1997).
- [16] (a) B.-L. Fei, W.-Y. Sun, T. Okamura, W.-X. Tang, N. Ueyama. *New J. Chem.*, **25**, 210 (2001); (b) M.-L. Tong, Y.-M. Wu, J. Ru, X.-M. Chen, H.-C. Chang, S. Kitagawa. *Inorg. Chem.*, **41**, 4846 (2002); (c) M.-L. Tong, X.-M. Chen, B.-H. Ye. *Inorg. Chem.*, **37**, 5278 (1998); (d) R.P. Feazell, C.E. Carson, K.K. Klausmeyer. *Inorg. Chem.*, **45**, 2627 (2006); (e) L. Carlucci, G. Ciani, D.W.v. Gudenberg, D.M. Proserpio. *Inorg. Chem.*, **36**, 3812 (1997).