PAPER www.rsc.org/njc | New Journal of Chemistry

Self-assembly of two-dimensional coordination polymers from AgX (X = BF_4^-, ClO_4^-, NO_3^- and PF_6^-) and 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine†

Maw-Cherng Suen,*[a] Chun-Wei Yeh,[b] Yuh-Wen Ho[a] and Ju-Chun Wang[c]

Received (in Gainesville, FL, USA) 12th February 2009, Accepted 1st May 2009
First published as an Advance Article on the web 31st July 2009
DOI: 10.1039/b902977j

Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J
Downloaded by University of Belgrade on 02 January 2013

Novel supramolecules of Ag(I) complexes of the type [Ag(**2-ddph**)][X] (**2-ddph** = 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine; X = BF_4^-, **1**, ClO_4^-, **2**, NO_3^-, **3** and PF_6^-, **4**) have been prepared by self-assembly of AgX with 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine (**2-ddph**) in MeOH–H_2O. The elemental analyses and IR have been recorded and all the complexes have been structurally characterized by X-ray crystallography confirming that complexes **1–4** are two-dimensional coordination polymers. The anions BF_4^- and PF_6^- in complexes **1** and **4** are not coordinated to the Ag(I) atoms while the ClO_4^- and NO_3^- anions in **2** and **3** are coordinated to the metal centers through a monodentate oxygen atom. Complexes **1–3** show 2-D brick-wall structures, while complex **4** shows square grids.

Introduction

The self-assembly of supramolecular structures using metal coordination has become the focus of intense interest over the past decade.[1] This is 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 atomic structure, which is a function of both the ligand and the metal. There has been a resurgent interest on extended organic or organometallic crystals based on hydrogen bonds and metal coordination bonds.[4–6] It is, therefore, important to try to understand, and control, the interplay between the coordination characteristics of the ligands and the metals, and the ultimate shape of the self-assembled suprastructure.

Much study has centered upon the use of supramolecular contacts between suitable molecules to generate multidimensional arrays or networks. The design of supramolecular assemblies *via* ligand design, the coordination characteristics of the metal ion, and the length of the spacer, has resulted in a variety of structural motifs.[7] Many topologically promising architectures have been constructed for Ag(I) with bidentate building blocks containing nitrogen donors. The various types of polymeric structure include 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 intra-molecular forces that determine the patterns of molecular structure and crystal packing in the solid state. So far, various ligands, such as bipyridine-type and biphenyl cyanide-type ligands, have been used for supramolecular building blocks.[9–11]

Various ligands have been used for supramolecular building blocks, but exploitation of the tridentate ligand 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine has until recently been undeveloped. The ligand possess two functionalities with pyridyl and the cyano groups. The affinity of Ag^+ for N-donor ligands, especially pyridine and the cyano group, is well known. In this paper, we report four novel supramolecular Ag(I) complexes of the types $\{[Ag(\mathbf{2\text{-}ddph})][BF_4]\}_\infty$, $[Ag(\mathbf{2\text{-}ddph})(ClO_4)]_\infty$, $[Ag(\mathbf{2\text{-}ddph})(NO_3)]_\infty$ and $\{[Ag(\mathbf{2\text{-}ddph})][PF_6]\}_\infty$.

Results and discussion

Syntheses

The ligand **2-ddph** was prepared by the reaction of 6-methyl-2-pydidinecarbaldehyde and 3-aminocrotonitrile in refluxing ethanol, in accordance with the literature procedure.[12] Complexes of the type $\{[Ag(\mathbf{2\text{-}ddph})][BF_4]\}_\infty$, **1**, $[Ag(\mathbf{2\text{-}ddph})(ClO_4)]_\infty$, **2**, $[Ag(\mathbf{2\text{-}ddph})(NO_3)]_\infty$, **3** and $\{[Ag(\mathbf{2\text{-}ddph})][PF_6]\}_\infty$, **4**, were prepared by reactions of AgX (X = BF_4^-, **1**, ClO_4^-, **2**, NO_3^-, **3** and PF_6^-, **4**) with **2-ddph** in MeOH–H_2O in the dark. All these complexes are structurally characterized by X-ray crystallography. Complexes **1–4** are all light-sensitive and insoluble in most organic solvents; crystals suitable for X-ray diffraction studies were obtained by layering a methanolic solution of **2-ddph** onto a solution of AgX (X = BF_4^-, ClO_4^-, NO_3^- and PF_6^-) in H_2O.

Structure of 2-ddph

The structure of 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine is determined by ^1H NMR, IR, elemental

---

[a] *Department of Material and Fiber, Nanya Institute of Technology, Jhongli, Taiwan, R.O.C.*
[b] *Department of Chemistry, Chung-Yuan Christian University, Jhongli, Taiwan, R.O.C.*
[c] *Department of Chemistry, Soochow University, Taipei, Taiwan, R.O.C.*

† CCDC reference numbers for the ligand **2-ddph** and the complexes **1–4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 612145, 612148, 612147, 612146, 612149. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b902977j

Downloaded by University of Belgrade on 02 January 2013
Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J

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

N(1)–C(3)	1.146(5)	N(2)–C(4)	1.151(5)
N(11)–C(16)	1.365(5)	N(11)–C(12)	1.381(5)
N(25)–C(24)	1.333(4)	N(25)–C(26)	1.359(5)
N(3)–C(7)	1.139(5)	N(4)–C(8)	1.144(5)
N(31)–C(36)	1.361(5)	N(31)–C(32)	1.385(5)
N(45)–C(44)	1.339(5)	N(45)–C(46)	1.349(5)
C(16)–N(11)–C(12)	122.2(4)	C(24)–N(25)–C(26)	117.6(3)
N(1)–C(3)–C(13)	178.6(5)	N(2)–C(4)–C(15)	176.2(5)
N(11)–C(12)–C(1)	115.5(4)	N(25)–C(26)–C(21)	121.3(4)
C(15)–C(16)–N(11)	120.2(4)	C(36)–N(31)–C(32)	120.9(4)
N(11)–C(16)–C(2)	114.5(4)	N(3)–C(7)–C(33)	177.1(5)
N(25)–C(24)–C(23)	123.3(4)	N(25)–C(24)–C(14)	117.9(3)
C(44)–N(45)–C(46)	118.5(4)	C(33)–C(32)–N(31)	120.7(4)
N(4)–C(8)–C(35)	178.9(5)	N(31)–C(32)–C(5)	114.5(4)
C(35)–C(36)–N(31)	121.3(4)	N(45)–C(44)–C(34)	118.1(4)
N(31)–C(36)–C(6)	114.5(4)	N(45)–C(46)–C(41)	120.9(5)
N(45)–C(44)–C(43)	122.2(4)	N(45)–C(46)–C(47)	118.9(5)

analysis and single-crystal X-ray diffraction. In ^{1}H NMR spectrum of **2-ddph**, the proton resonances are observed at 9.46 and 4.43 ppm as singlets, are attributed to the dihydropyridine protons (–NH and –CH), respectively. The IR spectra of **2-ddph** shows a $-C{\equiv}N$ group absorption band at 2198 cm^{-1}. Crystals of **2-ddph** conform to the space group $P2_1/n$ with eight molecules in the unit cell. Selected bond distances and angles for **2-ddph** are given in Table 1. Two independent **2-ddph** molecules are found in the asymmetric unit of **2-ddph** as shown in Fig. 1(a). The **2-ddph** ligands are not co-planar with the dihedral angle between the pyridine and dihydropyridine rings averaging 90.4°. It can be seen in Fig. 1(b) that the **2-ddph** ligand forms hydrogen-bonded loop structures in the solid state through the self-complementary N–H···N hydrogen bonds. The H···N distances in the N–H···N interaction are 2.070(1) and 2.121(2) Å, with N–H···N angles of 170.1(2) and 174.1(2)°, respectively. The packing diagram (Fig. 1(c)) of **2-ddph** shows 2-D supramolecular layers in the solid state by intermolecular hydrogen bonding between C–H groups of the pyridine rings and the cyano nitrogen atoms in adjacent loops [C–H···N = 2.541(2) and 2.592(2) Å and ∠C–H···N = 145.5(2) and 131.5(3)°, respectively].

Structure of complexes 1–3

The crystal structures of complexes **1–3** belong to the space group $P2_1/c$. The representative asymmetric units and ORTEP diagrams showing the geometry of Ag atoms in complexes **1** and **2** are depicted in Fig. 2 while Table 2 lists the bond distances and angles around Ag for complexes **1–3**. The Ag atom which is coordinated by two cyano nitrogen atoms from two different **2-ddph** ligands [Ag–N = 2.299(2) and 2.311(3) Å] and one pyridyl nitrogen atom from another **2-ddph** [Ag–N = 2.226(2) Å] is distorted triangular planar in complex **1** [∠N(1)–Ag–N(4A) + ∠N(1)–Ag–N(3B) + ∠N(3B)–Ag–N(4A) = 355.4°]. The asymmetric unit and the coordination environment of complex **3** is similar to complex **2**, in which Ag atoms are additionally bonded to a monodentate oxygen atom of the anion groups. In complexes **2** and **3**, the Ag atoms which are coordinated by two cyano nitrogen atoms from two different **2-ddph** ligands [Ag–N = 2.293(2) to 2.495(3) Å], one pyridyl nitrogen atom of another **2-ddph** [Ag–N = 2.235(4) to 2.267(2) Å] and one monodentate oxygen atom of the anion [Ag–O(1) = 2.48(3) and 2.431(7) Å] are best described as having distorted tetrahedral configuration.

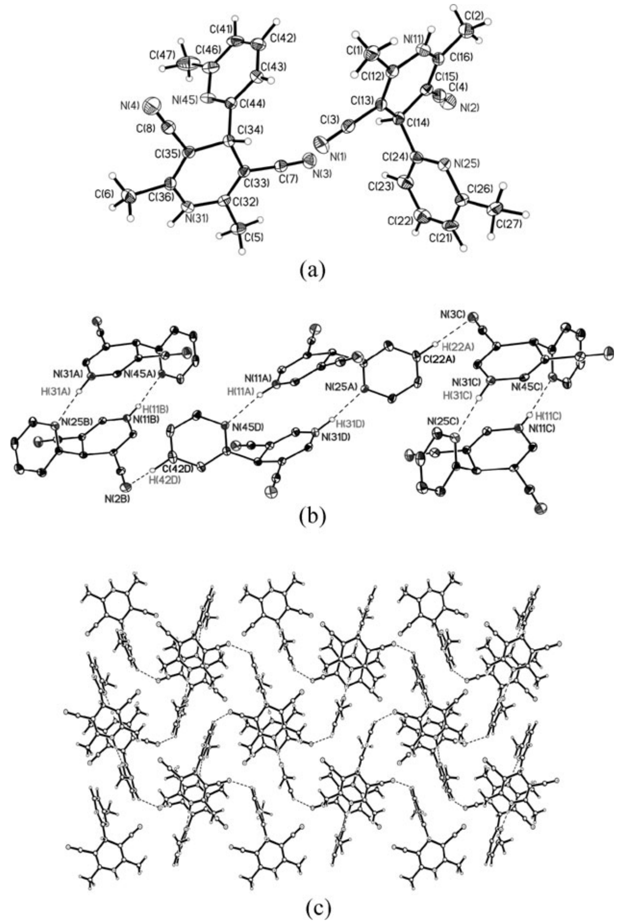

Fig. 1 (a) An ORTEP drawing of **2-ddph**. (b) The packing diagram of **2-ddph** showing self-complementary N–H···N hydrogen bonds forming the loops. The methyl groups and other hydrogen atoms are omitted for clarity. (c) The packing diagram of **2-ddph** showing the 2-D supramolecular layer.

The structural difference between complexes **1**, **2** and **3** are that the BF_4^- anions in **1** are not coordinated to the Ag(I) atoms whereas the ClO_4^- and NO_3^- anions in **2** and **3** coordinate to the metal center through a monodentate oxygen atom. It is seen from Table 2 that the Ag–N$_{\text{cyano}}$ distances are longer than the Ag–N$_{\text{pyridyl}}$ distances in complexes **1–3**, while the average Ag–N distances to the Ag atoms are all similar in these three complexes. The bonded **2-ddph** ligands are not flat in complexes **1–3** with dihedral angles between the pyridine and dihydropyridine rings of 102.7, 101.9 and 82.8°, respectively. Each Ag(I) is coordinated to three **2-ddph** ligands and each **2-ddph** bridged three Ag(I) atoms in these three complexes. The cyano groups of **2-ddph** ligands bonded to the Ag(I) atoms are not linear and the Ag–N–C angles are 142.5(2), 169.5(3)° for **1**, 170.5(4), 140.0(4)° for **2** and 132.6(2), 175.5(3)° for **3**, respectively.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2009

Downloaded by University of Belgrade on 02 January 2013
Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J

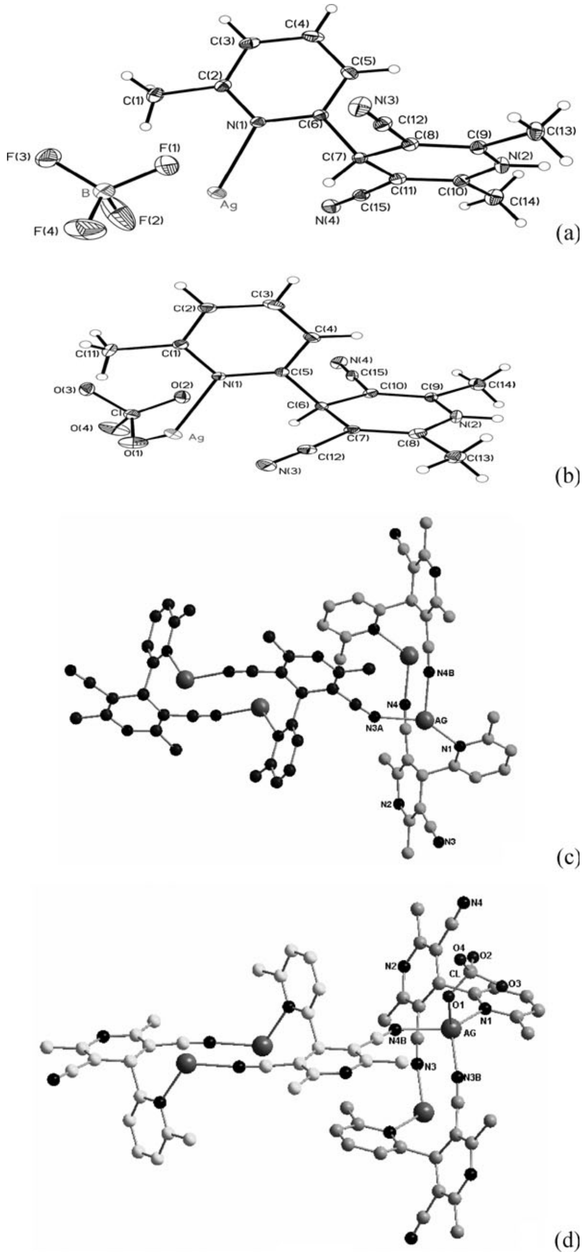

Fig. 2 (a) An ORTEP drawing of the asymmetric unit for **1**. (b) An ORTEP drawing of the asymmetric unit for **2**. (c) A view of the local coordination of Ag in **1**. (d) A view of the local coordination of Ag in **2**.

Noticeably, the **2-ddph** ligand bridges Ag(I) through the pyridyl nitrogen atoms and the nitrogen atoms of the cyano groups, generating a head-to-tail aggregated $\{Ag(\textbf{2-ddph})\}_2$ 14-membered ring, Fig. 3(a). The $\{Ag(\textbf{2-ddph})\}_2$ rings are further extended into a 2-D wave-like layer by sharing Ag(I) joints and **2-ddph** edges, Fig. 3(b) for **1**. The 2-D brick-wall structures of complexes **1–3** contain 30-membered rings (Fig. 3(c)), in which four Ag(I) atoms are at the apexes of the rectangle and the length and width of the rectangle are defined by the distances from cyano to cyano groups and cyano to pyridyl groups. It can been seen from Table 3 that the sizes of the rectangles and the Ag···Ag distances in the $\{Ag(\textbf{2-ddph})\}_2$ rings for complexes **1–3** are similar, although slight differences have been found for complex **3**.

Table 2 Selected bond distances (Å) and angles (°) for complexes **1–4**

Complex **1**			
Ag–N(1)	2.226(2)	Ag–N(4A)[a]	2.299(2)
Ag–N(3B)	2.311(3)		
N(1)–Ag–N(4A)	124.46(8)	N(1)–Ag–N(3B)	140.25(9)
N(4A)–Ag–N(3B)	90.60(9)		
Complex **2**			
Ag–N(1)	2.235(4)	Ag–N(3A)	2.299(5)
Ag–N(4B)	2.354(4)	Ag–O(1)	2.48(3)
N(1)–Ag–N(3A)	124.87(14)	N(1)–Ag–N(4B)	137.28(16)
N(3A)–Ag–N(4B)	91.64(16)	N(1)–Ag–O(1)	113.1(7)
N(3A)–Ag–O(1)	85.5(8)	N(4B) –Ag–O(1)	88.7(8)
Complex **3**			
Ag–N(1)	2.267(2)	Ag–N(4A)	2.293(2)
Ag–N(3B)	2.495(3)	Ag–O(1)	2.431(7)
N(1)–Ag–N(4A)	120.41(8)	N(1)–Ag–N(3B)	126.84(8)
N(4A)–Ag–N(3B)	89.83(9)	N(1)–Ag–O(1)	122.35(19)
N(4A)–Ag–O(1)	106.4(2)	O(1)–Ag–N(3B)	81.50(18)
Complex **4**			
Ag–N(1)	2.236(3)	Ag–N(4A)	2.185(3)
Ag–N(3B)	2.304(3)		
N(1)–Ag–N(4A)	138.24(10)	N(1)–Ag–N(3B)	108.86(11)
N(4A)–Ag–N(3B)	112.62(11)		

[a] Symmetry transformations used to generate equivalent atoms: (A): $-x + 3, -y + 1, -z$; (B): $-x + 3, y - 1/2, -z + 1/2$ for **1**; (A): $-x + 2, -y + 2, -z$; (B): $-x + 2, y + 1/2, -z + 1/2$ for **2**; (A): $-x + 1, -y, -z$; (B): $-x + 1, y - 1/2, -z + 1/2$ for **3**; (A): $x - 1, y, z$; (B): $x, -y + 1/2, z-1/2$ for **4**.

In complexes **1–3**, the 2-D networks are further linked by the anions and through Ag···X interactions (X = O or F), N–H···X and C–H···X (X = O, F, N) hydrogen bonds to form 3-D supramolecular structures [Ag···F = 2.581(2)–3.227(3) Å, C–H···F = 2.545(2) Å, ∠C–H···F = 164.0(2)°, N–H···F = 1.988(2)–2.135(1) Å, ∠N–H···F = 142.7(1)–162.8(2)° for **1**; C–H···O = 2.007(1)–2.239(2) Å, ∠C–H···O = 141.0(1)–159.4(3)° for **2**; Ag···O = 2.692(3) Å, C–H···O = 2.455(2)–2.546(3) Å, O–H···N = 2.864(2) Å, O–H···O = 2.594(2)–2.907(3) Å for **3**]. Fig. 4 shows a representative packing diagram for **2**.

Structure of complex 4

A single-crystal X-ray structural analysis of crystals of **4**, obtained by layering a methanolic solution of **2-ddph** on top of an aqueous solution of $AgPF_6$, revealed the formation of a complex of $\{[Ag(\textbf{2-ddph})][PF_6]\}_n$. The structure of complex **4** was solved in the space group $P2_1/n$. Selected bond distances and angles are listed in Table 2. The asymmetric unit of **4**, Fig. 5(a), contains one Ag atom, one PF_6^- anion and one **2-ddph** group. The bonded **2-ddph** ligands are not flat with the dihedral angle between the pyridine and dihydropyridine rings being 87.3°. Along the *c* axis, adjacent Ag(I) atoms are linked to each other through the cyano nitrogen atoms of the tridentate **2-ddph** ligands to form an infinite zigzag chain (Fig. 5(b)). The Ag···Ag distance in the molecular chain separated by the bridging **2-ddph** is 6.805 Å. Fig. 5(c) shows the coordination geometry about the Ag metal center.

Downloaded by University of Belgrade on 02 January 2013
Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J

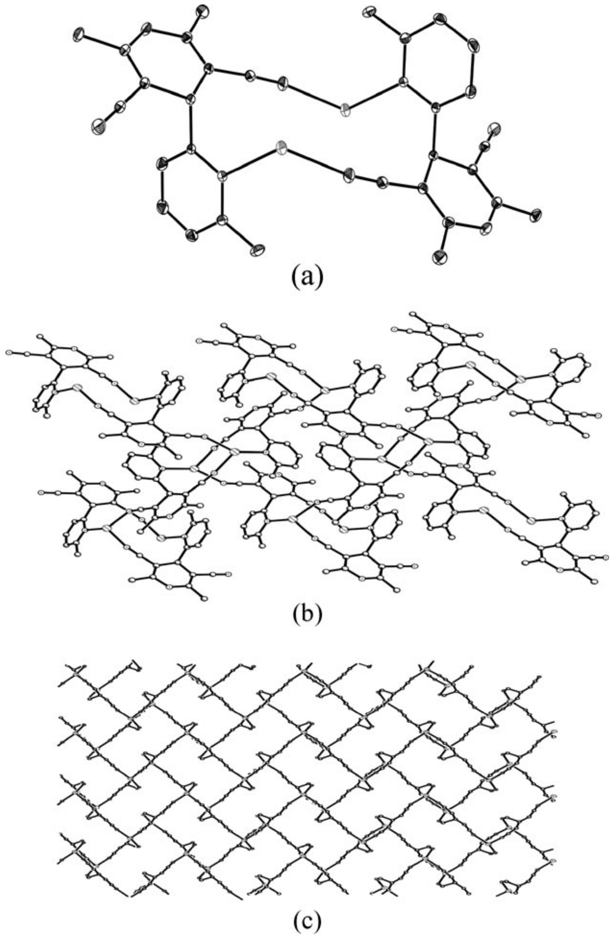

Fig. 3 (a) ORTEP drawing showing the coordination geometry of the silver metal center and the Ag_2(**2-ddph**)$_2$ building blocks in **1–3**. (b) The packing diagram shows the Ag_2(**2-ddph**)$_2$ building blocks bound together by Ag–N bonds into a two-dimensional framework in complexes **1–3**. (c) The rectangular 2-D network formed by the tridentate **2-ddph** ligands and Ag(I) atoms. Only the Ag atoms, cyano groups and parts of pyridyl groups of **2-ddph** are shown for clarity.

Table 3 The Ag···Ag distances (Å) in the {Ag(**2-ddph**)}$_2$ rings and the sizes (Å) of the rectangles for complexes **1–3**

Complex	Ag···Ag	Length	Width
1	3.902	11.135	7.810
2	3.959	11.214	7.886
3	4.511	11.467	7.888

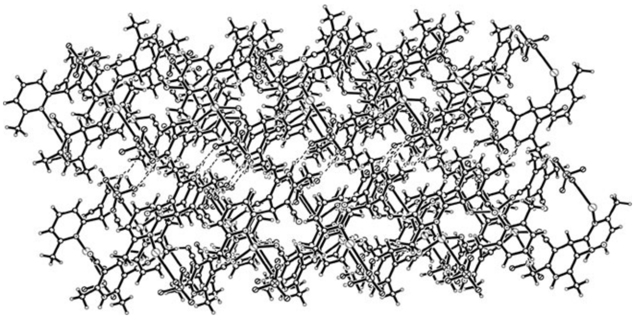

Fig. 4 Packing diagram for **2** showing the interactions between the layers.

The Ag atom, which is coordinated by two cyano nitrogen atoms from two different **2-ddph** ligands [Ag–N = 2.185(3) and 2.304(3) Å] and one pyridyl nitrogen atom from another **2-ddph** [Ag–N = 2.236(3) Å], formed a distorted triangular planar in complex **4** [∠N(1)–Ag–N(4A) + ∠N(1)–Ag–N(3B) + ∠N(3B)–Ag–N(4A) = 359.7°]. The silver metal center adopts a slightly distorted triangular planar coordination geometry. Each Ag(I) coordinated to three **2-ddph** ligands and each **2-ddph** bridged three Ag(I) atoms in complex **4**. The cyano groups of **2-ddph** bonded to the Ag(I) atoms are bent and the Ag–N–C angles are 158.9(3) and 160.5(3)°, respectively. The cyano groups in complex **4** bonded to Ag(I) atoms with linear C–C–N angles of 177.8(4) and 174.5(4)°, respectively. When looking down the *b* axis, 2-D grids were formed by zigzag chains (Fig. 5(c)), while 21-membered grids are formed by three Ag(I) atoms and two **2-ddph** ligands. A schematic drawing of the 2-D frameworks of complex **4** is shown in Fig. 5(d), where the Ag atoms are linked through the bent **2-ddph** ligands. The complex shows rectangular Ag···Ag distances of 6.655 × 6.805 $Å^2$. In complex **4**, the 2-D networks are further linked by the anions and through N–H···F [N–H···F = 2.151(2)–2.546(1) Å, ∠N–H···F = 146.1(3)–164.5(2)°] and C–H···F [C–H···F = 2.316(1)–2.466(2) Å, ∠C–H···F = 138.6(2)–139.0(1)°] hydrogen bonds to form 3-D supramolecular structures. Fig. 5(e) shows a representative packing diagram for **4**.

The small anions BF_4^-, ClO_4^- and NO_3^- in complexes **1–3** link 2-D cationic layers through Ag···X (X = F or O) interactions and/or C–H···X and N–H···X hydrogen bonds, while the large PF_6^- anions in **4** interact through C–H···F and N–H···F hydrogen bonds among 2-D nets. The size of the counterion may affect the structures of the Ag(I) complexes containing **2-ddph** ligands. All the Ag(I) ions in complexes **1–4** bridge through tridentate **2-ddph** ligands forming 2-D frameworks, with complexes **1–3** forming 2-D brick-wall structures and complex **4** forming 2-D grids. Fig. 6(a) shows one type of the tridentate **2-ddph** ligands upon coordination to Ag(I) ions being converted into linear ligands forming 2-D brick-wall structures in complexes **1–3**, while another type of ligand converted into bent ligands form 2-D grids in complex **4** as shown in Fig. 6(b).

Conclusions

In this study, the coordination chemistry of AgX (X = BF_4^-, ClO_4^-, NO_3^-, PF_6^-) with 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine was investigated. The synthesis and structures of four novel complexes [Ag(**2-ddph**)][X] have been successfully accomplished. Unique 2-D brick-wall structures were seen in complexes **1–3** and complex **4** shows square grids, in which the Ag(I) atoms and **2-ddph** ligands form 30- and 21-membered rings, respectively. The results indicate that the coordination chemistry of the **2-ddph** ligand is versatile. It is also shown that the 2-D networks adopted by complexes **1–3** were hardly altered by changing their counter ions.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2009

Downloaded by University of Belgrade on 02 January 2013
Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J

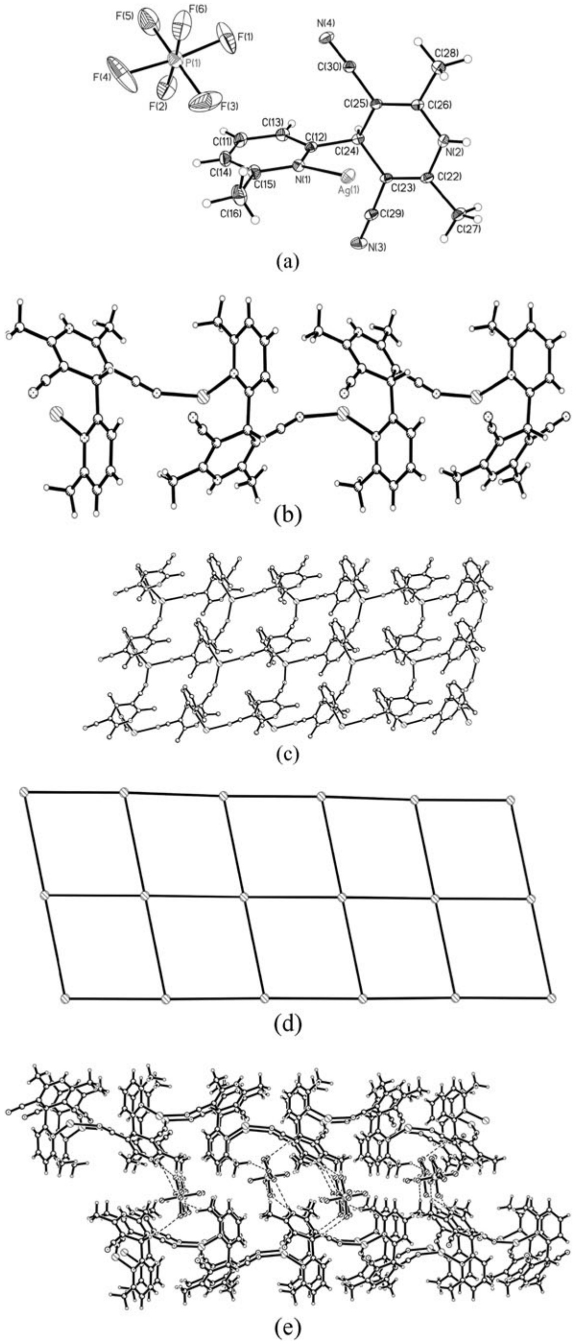

Fig. 5 (a) An ORTEP drawing of the asymmetric unit for **4**. (b) A zigzag chain formed by the bidentate **2-ddph** groups and Ag centers running along the *c* axis. (c) The polymeric structure of **4**. (d) Schematic drawing for complex **4**. (e) A diagram showing the interactions among the square cationic grids of **4** and PF_6^- anions.

Experimental

General procedures

All manipulations were carried out under air. The visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. IR spectra were obtained from a Jasco FT/IR-460 plus spectrometer. Elemental analyses were obtained from a PE 2400 series II CHNS/O analyzer.

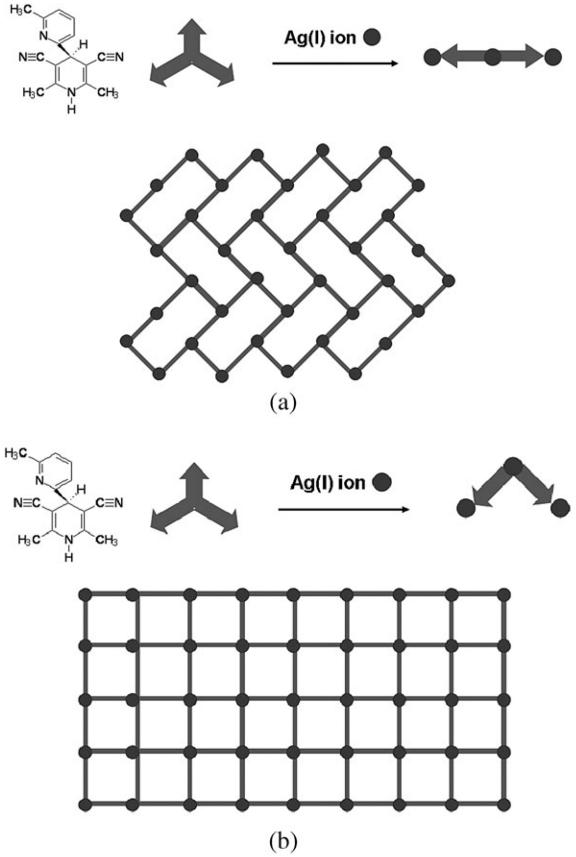

Fig. 6 (a), (b) Tridentate **2-ddph** ligands coordinate to Ag(I) ions forming two types of 2-D frameworks.

Materials

The reagents AgX (X = BF_4^-, ClO_4^-, NO_3^- and PF_6^-) were purchased from Aldrich Chemical Co. The ligand 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine was prepared according to a known procedure.[12]

Syntheses

The complexes were synthesized by reaction of AgX (X = BF_4^-, ClO_4^-, NO_3^- and PF_6^-) with 2,6-dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine in MeOH–H_2O in the dark.

1. 2,6-Dimethyl-3,5-dicyano-4-(6-methyl-2-pyridyl)-1,4-dihydropyridine (**2-ddph**) (0.025 g, 0.10 mmol) in 5 ml MeOH was layered onto a solution of $AgBF_4$ (0.019 g, 0.10 mmol) in 5 ml H_2O. The resulting solution was slowly diffused for several weeks and kept in the dark to give colorless crystals. Yield: 0.014 g (32%). Anal. Calc. for $C_{15}H_{14}AgBF_4N_4$: C, 40.49; H, 3.17; N, 12.59. Found: C, 40.23; H, 3.13; N, 12.60%. IR (KBr disk, cm^{-1}): 3338(br), 3284(m), 3122(m), 3078(m), 2841(m), 2209(m), 1660(m), 1600(m), 1571(m), 1507(m), 1435(m), 1390(m), 1325(m), 1282(m), 1170(m), 1099(m), 1015(s), 994(m), 829(m), 782(m), 684(m), 519(m).

2. Complex **2** was prepared as for **1**. Yield 0.012 g (28%). Anal. Calc. for $C_{15}H_{14}AgClN_4O_4$: C, 39.37; H, 3.08; N, 12.24. Found: C, 39.32; H, 3.03; N, 12.25%. IR (KBr disk): 3317(m),

Downloaded by University of Belgrade on 02 January 2013
Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J

Table 4 Crystal data for **2-ddph** and complexes **1–4**

Compound	**2-ddph**	**1**	**2**	**3**	**4**
Formula	$C_{15}H_{14}N_4$	$C_{15}H_{14}AgBF_4N_4$	$C_{15}H_{14}AgClN_4O_4$	$C_{15}H_{14}AgN_5O_3$	$C_{15}H_{14}AgF_6N_4P$
M	250.30	444.98	457.62	420.18	503.14
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	11.3722(19)	10.6811(8)	10.682(3)	10.598(3)	6.6550(8)
b/Å	15.558(4)	11.9175(9)	11.957(4)	11.630(3)	20.7600(18)
c/Å	15.257(3)	13.2109(10)	13.386(4)	13.640(3)	13.537(2)
β/°	94.475(10)	102.1170(10)	102.245(7)	103.949(4)	102.726(12)
V/Å^3	2691.2(10)	1644.2(2)	1668.5(7)	1631.6(7)	1824.2(4)
Z	8	4	4	4	4
D_c/g cm^{-3}	1.236	1.798	1.822	1.711	1.832
F(000)	1056	880	912	840	992
μ(Mo-Kα)/mm^{-1}	0.077	1.273	1.397	1.259	1.258
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Range (2θ) for data collection/°	4.32–50.00	3.90–52.08	3.90–52.12	3.96–52.12	5.00–49.98
GOF^c	1.008	1.017	1.087	1.121	1.047
Final R indices [$I > 2\sigma(I)$]^{ab}	$R1 = 0.0656$, $wR2 = 0.0927$	$R1 = 0.0315$, $wR2 = 0.0942$	$R1 = 0.0433$, $wR2 = 0.0773$	$R1 = 0.0336$, $wR2 = 0.1044$	$R1 = 0.0305$, $wR2 = 0.0648$
R indices (all data)	$R1 = 0.1739$, $wR2 = 0.1103$	$R1 = 0.0391$, $wR2 = 0.1021$	$R1 = 0.0889$, $wR2 = 0.0884$	$R1 = 0.0390$, $wR2 = 0.1100$	$R1 = 0.0340$, $wR2 = 0.0666$
Largest diff. peak, hole/e Å^{-3}	0.167, −0.154	0.513, −0.775	0.472, −0.730	0.486, −0.879	0.524, −0.709

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$; $a = 0.0000$, $b = 0.6484$, **2-ddph**; $a = 0.0750$, $b = 0.0000$, **1**; $a = 0.0250$, $b = 0.0000$, **2**; $a = 0.0000$, $b = 0.6468$, **3**; $a = 0.0000$, $b = 3.9307$, **4**. ^{c} Quality-of-fit $= [\sum w(|F_o^2| - |F_c^2|)^2/N_{\text{observed}} - N_{\text{parameters}}]]^{1/2}$.

3241(m), 3185(m), 3076(m), 2993(m), 2942(m), 2840(m), 2203(m), 1659(m), 1599(m), 1571(m), 1506(m), 1435(m), 1380(m), 1323(m), 1281(m), 1132(s), 1089(m), 925(m), 838(m), 623(m), 521(m).

3. Complex **3** was prepared as for **1**. Yield: 0.013 g (31%). Anal. Calc. for $C_{14}H_{12}AgN_5O_5$: C, 35.50; H, 2.55; N, 14.79. Found: C, 35.65; H, 2.49; N, 14.76%. IR (KBr disk): 3281(br), 3195(m), 3094(m), 2999(m), 2950(m), 2847(m), 2199(m), 1655(m), 1659(m), 1600(m), 1514(m), 1379(m), 1281(m), 1165(m), 1103(m), 1034(m), 909(m), 824(m), 777(m), 657(m), 605(m), 532(m).

4. Complex **4** was prepared as for **1**. Yield: 0.018 g (35%). Anal. Calc. for $C_{17}H_{14}AgF_6N_4P$: C, 38.73; H, 2.67; N, 10.63. Found: C, 38.81; H, 2.65; N, 10.58%. IR (KBr disk): 3367(br), 3237(m), 3184(m), 3096(m), 2933(m), 2831(m), 2200(m), 1434(m), 1395(m), 1267(m), 970(m), 844(m), 558(m).

X-Ray crystallography

The diffraction data for **1** was collected on a Bruker P4 diffractometer, which was equipped with graphite-monochromated Mo-Kα (λ(Mo-Kα) = 0.71073 Å) radiation. Data reduction was carried by standard methods with use of well-established computational procedures.[13] Basic information pertaining to crystal parameters and structure refinement is summarized in Table 4. The structure factors were obtained after Lorentz and polarization corrections. The positions of the heavy atoms, including the silver atoms, were located by the direct method. The anions of **1** and **4** are disordered with fluorine atoms located equally over two positions. The anions in **2** and **3** are also disordered with the oxygen atoms in two positions with 0.4 : 0.6 occupancy. For the ligand **2-ddph** and complex **4**, all the hydrogen atoms, except the methyl hydrogen atom, H27A, H27B and H27C in **2-ddph** and H16A, H16B, H16C, H27A, H27B, H27C, H28A, H28B and H28C in **4**, were located in the difference electron density map and refined isotropically. The hydrogen atoms of **1–3** and H27A, H27B and H27C in **2-ddph** and H16A, H16B, H16C, H27A, H27B, H27C, H28A, H28B and H28C in **4** were placed in geometrically calculated position using the HADD program and refined using a riding model. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements.[14] The final residuals of the final refinement were $R_1 = 0.0656$, $wR_2 = 0.0927$. The crystallographic procedures for **2-ddph**, **2**, **3** and **4** were similar to those for **1**. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 4.

Acknowledgements

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

References

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*b*) *Transition Metals in Supramolecular Chemistry*, ed. L. Fabbrizza and A. Poggi, Kluwer Academic, Dordrecht, 1994; (*c*) *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, Pergamon Press, Oxford, 1995; (*d*) K. Biradha and M. Fujita, *Adv. Supramol. Chem.*, 2000, **6**, 1; (*e*) C. Piguet, M. Borkovec, J. Hamacek and K. Zeckert, *Coord. Chem. Rev.*, 2005, **249**, 705; (*f*) W. Huang, H.-B. Zhu and S.-H. Gou, *Coord. Chem. Rev.*, 2006, **250**, 414; (*g*) P.-Z. Li, X.-M. Lu, B. Liu, S. Wang and X.-J. Wang, *Inorg. Chem.*, 2007, **46**, 5823; (*h*) M. Nayak, R. Koner, H. Stoeckli-Evans and S. Mohanta, *Cryst. Growth Des.*, 2005, **5**, 1907.

2 (*a*) O. Maury and H. Le Bozec, *Acc. Chem. Res.*, 2005, **38**, 691; (*b*) G. Anandha Babu and P. Ramasamy, *J. Cryst. Growth*, 2009, **311**, 1185; (*c*) M. Lydia Caroline, A. Kandasamy, R. Mohan and

Published on 31 July 2009 on http://pubs.rsc.org | doi:10.1039/B902977J
Downloaded by University of Belgrade on 02 January 2013

S. Vasudevan, *J. Cryst. Growth*, 2009, **311**, 1161; (*d*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*e*) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (*f*) D. Maspoch, D. Ruiz-Molina and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2713; (*g*) S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 2003, **246**, 103; (*h*) L. Carlucci, G. Ciani and D. Poserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.

3 (*a*) M. R. Othman, S. C. Tan and S. Bhatia, *Microporous Mesoporous Mater.*, 2009, **121**, 138; (*b*) S. Hashimoto, K. Samata, T. Shoji, N. Taira, T. Tomita and S. Matsuo, *Microporous Mesoporous Mater.*, 2009, **117**, 220; (*c*) Y. Li, M. Pera-Titus, G. Xiong, W. Yang, E. Landrivon, S. Miachon and J.-A. Dalmon, *J. Membrane Sci.*, 2008, **325**, 973; (*d*) K. Egeblad, C. H. Christensen, M. Kustova and C. H. Christensen, *Chem. Mater.*, 2008, **20**, 946; (*e*) D. Li, Y. Huang, K. R. Ratinac, S. P. Ringer and H. Wang, *Microporous Mesoporous Mater.*, 2008, **116**, 416; (*f*) L. Karwacki, E. Stavitski, M. H. F. Kox, J. Kornatowski and B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2007, **46**, 7228; (*g*) M. A. Snyder and M. Tsapatsis, *Angew. Chem., Int. Ed.*, 2007, **46**, 7560.

4 (*a*) R. Koner, M. Nayak, G. Ferguson, J. N. Low, C. Glidewell, P. Misra and S. Mohanta, *CrystEngComm*, 2005, 129; (*b*) H.-L. Hu, M.-C. Suen, C.-W. Yeh and J.-D. Chen, *Polyhedron*, 2005, **24**, 1497; (*c*) M.-C. Suen, Y.-H. Wang, Y.-F. Hsu, C.-W. Yeh, J.-D. Chen and J.-C. Wang, *Polyhedron*, 2005, **24**, 2913; (*d*) L. Zhao, B. H. Northrop and P. J. Stang, *J. Am. Chem. Soc.*, 2008, **130**, 11886; (*e*) M.-C. Suen and J.-C. Wang, *J. Chin. Chem. Soc.*, 2008, **55**, 782.

5 (*a*) J. Rosenthal, J. M. Hodgkiss, E. R. Young and D. G. Nocera, *J. Am. Chem. Soc.*, 2006, **128**, 10474; (*b*) M.-C. Suen and J.-C. Wang, *J. Coord. Chem.*, 2007, **60**, 2197; (*c*) Y.-H. Wang, K.-L. Chu, H.-C. Chen, C.-W. Yeh, Z.-K. Chan, M.-C. Suen, J.-D. Chen and J.-C. Wang, *CrystEngComm*, 2006, 84; (*d*) M.-C. Suen, Y.-H. Wang and J.-C. Wang, *J. Chin. Chem. Soc.*, 2004, **51**, 43; (*e*) C.-W. Yeh, Y.-S. Yen, W.-B. Lin, C.-W. Su, J.-D. Chen and J.-C. Wang, *Struct. Chem.*, 2005, **16**, 141.

6 (*a*) M.-C. Suen and J.-C. Wang, *J. Coord. Chem.*, 2007, **60**, 257; (*b*) Y.-H. Wang, M.-C. Suen, H.-T. Lee and J.-C. Wang, *Polyhedron*, 2006, **25**, 2944; (*c*) M.-C. Suen and J.-C. Wang, *Struct. Chem.*, 2006, **17**, 315; (*d*) M.-C. Suen, Z.-K. Chan, J.-D. Chen, J.-C. Wang and C.-H. Hung, *Polyhedron*, 2006, **25**, 2325; (*e*) M.-C. Suen, H.-A. Tsai and J.-C. Wang, *J. Chin. Chem. Soc.*, 2006, **53**, 305.

7 (*a*) Y.-F. Hsu, H.-L. Hu, C.-J. Wu, C.-W. Yeh, D. M. Proserpio and J.-D. Chen, *CrystEngComm*, 2009, **11**, 168; (*b*) C.-W. Yeh, J.-D. Chen and J.-C. Wang, *Polyhedron*, 2008, **27**, 3611; (*c*) Y.-Y. Wu, C.-W. Yeh, Z.-K. Chan, C.-H. Lin, C.-H. Yang, J.-D. Chen and J.-C. Wang, *J. Mol. Struct.*, 2008, **890**, 48; (*d*) C. Chen, Z.-K. Chan, C.-W. Yeh and J.-D. Chen, *Struct. Chem.*, 2008, **19**, 87; (*e*) Y.-S. Yen, C.-W. Yeh, J.-D. Chen and J.-C. Wang, *J. Cluster Sci.*, 2008, **19**, 109.

8 (*a*) M. B. Duriska, S. R. Batten and D. J. Price, *Aust. J. Chem.*, 2006, **59**, 26; (*b*) H.-A. Tsai, M.-S. Hu, M.-Y. Teng, M.-C. Suen and J.-C. Wang, *Polyhedron*, 2008, **27**, 2035; (*c*) Y.-H. Wang, H.-T. Lee and M.-C. Suen, *Polyhedron*, 2008, **27**, 1177; (*d*) I. Kalf, M. Braun, Y. Wang and U. Englert, *CrystEngComm*, 2006, 916; (*e*) C. M. Fitchett and P. J. Steel, *Dalton Trans.*, 2006, 4886; (*f*) M. Kato, T. Fujihara, D. Yano and A. Nagasawa, *CrystEngComm*, 2008, 1460; (*g*) P. Chandrasekaran, J. T. Mague and M. S. Balakrishna, *Dalton Trans.*, 2007, 2957; (*h*) M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173.

9 (*a*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638, and references therein; (*b*) L. Cunha-Silva, R. Ahmad, M. J. Carr, A. Franken, J. D. Kennedy and M. J. Hardie, *Cryst. Growth Des.*, 2007, **7**, 658; (*c*) J. Wang, P. Ma, Y. Shen and J. Niu, *Cryst. Growth Des.*, 2008, **8**, 3130; (*d*) A. Bellusci, A. Crispini, D. Pucci, E. I. Szerb and M. Ghedini, *Cryst. Growth Des.*, 2008, **8**, 3114; (*e*) S. Del Piero, R. Fedele, A. Melchior, R. Portanova, M. Tolazzi and E. Zangrando, *Inorg. Chem.*, 2007, **46**, 4683; (*f*) M. C. Aragoni, M. Arca, M. Crespo, F. A. Devillanova, M. B. Hursthouse, S. L. Huth, F. Isaia, V. Lippolis and G. Verani, *CrystEngComm*, 2007, 873.

10 (*a*) S. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1998, and references therein; (*b*) E. C. Constable, C. E. Housecroft, M. Neuburger, S. Reymann and S. Schaffner, *Aust. J. Chem.*, 2008, **61**, 847; (*c*) J.-E. Lee, J. Y. Lee, J. Seo, S. Y. Lee, H. J. Kim, S. Park, K.-M. Park, L. F. Lindoy and S. S. Lee, *Polyhedron*, 2008, **27**, 3004; (*d*) M. N. Kozlova, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2007, 5126; (*e*) B. J. O'Keefe and P. J. Steel, *CrystEngComm*, 2007, 222; (*f*) S. Benmansour, F. Setifi, S. Triki, J.-Y. Salaun, F. Vandevelde, J. Sala-Pala, C. J. Gomez-Garcia and T. Roisnel, *Eur. J. Inorg. Chem.*, 2007, 186; (*g*) Y. Guari, J. Larionova, M. Corti, A. Lascialfari, M. Marinone, G. Poletti, K. Molvinger and C. Guérin, *Dalton Trans.*, 2008, 3658.

11 (*a*) Y.-F. Hsu and J.-D. Chen, *Eur. J. Inorg. Chem.*, 2004, 1488; (*b*) H.-L. Hu, C.-W. Yeh and J.-D. Chen, *Eur. J. Inorg. Chem.*, 2004, 4696, and references therein; (*c*) M.-C. Suen, H.-A. Tsai and J.-C. Wang, *J. Chin. Chem. Soc.*, 2005, **52**, 1085; (*d*) L.-M. Chiang, C.-W. Yeh, Z.-K. Chan, K.-M. Wang, Y.-C. Chou, J.-D. Chen, J.-C. Wang and J. Y. Lai, *Cryst. Growth Des.*, 2008, **8**, 470; (*e*) H.-C. Chen, H.-L. Hu, Z.-K. Chan, C.-W. Yeh, H.-W. Jia, C.-P. Wu, J.-D. Chen and J.-C. Wang, *Cryst. Growth Des.*, 2007, **7**, 698; (*f*) C.-Y. Lin, Z.-K. Chan, C.-W. Yeh, C.-J. Wu, J.-D. Chen and J.-C. Wang, *CrystEngComm*, 2006, **8**, 841; (*g*) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (*h*) F. Luo, J. Zheng and S. R. Batten, *Chem. Commun.*, 2007, 3744.

12 (*a*) L. Dagnino, M. C. Li-Kwong-Ken, M. W. Wolowyk, H. Wynn, C. R. Triggle and E. E. Knaus, *J. Med. Chem.*, 1986, **29**, 2524; (*b*) L. Dagnino, M. C. Li-Kwong-Ken, H. Wynn, M. W. Wolowyk, C. R. Triggle and E. E. Knaus, *J. Med. Chem.*, 1987, **30**, 640.

13 *XSCANS, Release, 2.1*, Siemens Energy & Automation, Inc, Madison, WI, USA, 1995.

14 *SHELXTL 5.10*, Bruker Analytical X-ray Instruments Inc., Karlsruhe, Germany, 1997.