Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 359 (2006) 603–608

Inorganica Chimica Acta

www.elsevier.com/locate/ica

The new helical zigzag chain $\{[Ag(Pepy)(NO_3)]\}_\infty$ and mononuclear $[HPepy(FeCl_4)]$ with 3D network based on hydrogen bonds as well as π–π interactions

Xue-Fang Shi [a,b], Zhi-Yong Xing [a], Li Wu [a], Wen-Qin Zhang [a,*]

[a] *Department of Chemistry, Tianjin University, Tianjin 300072, PR China*
[b] *Department of Chemistry, Tianjin Normal University, Tianjin 300074, PR China*

Received 9 July 2005; received in revised form 8 September 2005; accepted 8 September 2005
Available online 13 October 2005

Abstract

The title complexes, $\{[Ag(Pepy)(NO_3)]\}_\infty$ (**1**) and $[HPepy(FeCl_4)]$ (**2**) (Pepy = *trans*-2-(2-phenylethyleneyl)pyridine), had been synthesized and characterized structurally by single-crystal X-ray diffraction analysis, FTIR as well as thermal analysis. The geometrical structure of complex **1** is a one-dimensional helical zigzag chain. Each Ag^I center is five-coordinated by two NO_3^- anions and one Pepy ligand while the NO_3^- anion is an uncommon tetra-dentate coordinating to two Ag^I by O atoms, respectively. The NO_3^- anions connecting with Ag^I as bridge blocks resulted in the formation of crystalline of helical polymeric chain. In the mononuclear complex **2**, the Fe^{III} center is four-coordinated by four Cl^- as $[FeCl_4]^-$ anion, which connected with hydrogen atoms from the protonated N atom and the C atoms from $HPepy^+$ to form multivalent hydrogen bonded network through N–H···Cl and C–H···Cl interactions. The two frameworks can be both considered as a 3D structure driven by diverse hydrogen bonds as well as π–π stacking interactions.

Keywords: X-ray crystal structures; Helical zigzag chain; Silver coordination polymer; Iron complex; Pyridine derivative

1. Introduction

The supramolecular chemistry has generated considerable interesting due to the attractive applications [1–8] of various supramolecular structures [9–11] through self-assembly of organic compounds with metal ions. The induction of naturally occurring helical motifs is now of great significance since the motif has been found to be a fundamental structure of proteins [12–14] as well as their potential application in asymmetric catalysis, non-linear optical materials and biomimetic chemistry [15–19]. The designing and controlling of molecular arrangements to form helical coordination polymers is normally relying on the nature of metal ion and the backbone of organic ligands. Ag^I is a favorable and fashionable connecting node for the construction of coordination polymers owing to its coordination diversity and flexibility. The polydentate ligands containing pyridine moiety are popular choices in this field as a result of the strong interactions happened between the N atom of pyridine ring and transition metal ions [20]. However, recently we synthesized one Ag^I helical coordination polymer using monodentate ligand of *trans*-2-(2-phenylethyleneyl)pyridine (Pepy) together with nitrate anion bridge block instead of polydentate ligands. Pepy is one of the pyridine derivatives and heterocyclic styryl photochemistry materials that our group has worked on [21–24]. To our best knowledge, there are few reports on heterocyclic styryl derivatives crystallography and their coordination with transition metals. As a continuation of our work, we have extended our work to use heterocyclic styryl compounds as a new kind of ligands. Herein we report the synthesis and structural characterization of a helical zigzag chain $\{[Ag(Pepy)(NO_3)]\}_\infty$ (**1**), and a

---

[*] Corresponding author. Tel.: +86 22 27407999; fax: +86 22 27403475.
E-mail address: wqzhang_tju@126.com (W.-Q. Zhang).

0020-1693/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.09.002

mononuclear complex [HPepy($FeCl_4$)] (**2**), as well as the FTIR and thermal analysis of them.

2. Experimental

2.1. Materials and general methods

All chemical reagents are commercially available and purified by standard methods prior to use. FT-IR spectra (KBr pellets) were measured on a BIO-RAD FTS 3000 Infrared spectrometer. The melting points were measured on a Yanagimoto MP-500 apparatus (uncorrected). C, H and N elemental analysis were carried out on a Perkin–Elmer 240C elemental analyzer. Thermal stability (TG-DTA) studies were performed on a NETZSCH TG 209 thermal analyzer.

2.2. Preparations

The ligand Pepy was synthesized as follows: under an atmosphere of nitrogen, the mixture of benzaldehyde (1.60 g, 15 mmol) and 2-methylpyridine (0.93 g, 10 mmol) was added dropwise to a solution of KOH (1.15 g, 20 mmol) in DMSO (15 ml) at 60 °C for two hours. The colorless solution turned into yellow gradually. The solution was allowed to reflux for another two hours and then cooled down prior to pouring into 100 ml cold water. The precipitate was filtrated and recrystallized by using methanol/water to give white crystals (yield 76%, m.p. 363 K). FTIR (KBr, cm^{-1}): 3048 (m), 1950 (m), 1811 (w), 1750 (w), 1635 (s), 1598 (vs), 1559 (s), 1494 (s), 1472 (vs), 1448 (vs), 1320 (s), 1315 (m), 1250 (m), 1216 (m) 1156 (s), 959 (vs), 770 (vs), 729 (s), 688 (vs), 531 (s). *Anal.* Calc. for $C_{13}H_{11}N$: C, 86.14; H, 6.13; N, 7.73. Found: C, 86.33; H, 6.28; N, 7.52%.

{[AgPepy](NO_3)}$_\infty$ (1). It was prepared as follows: the mixture of Pepy (0.36 g, 2 mmol) in acetonitrile (10 ml) and $AgNO_3$ (34 mg, 0.20 mmol) in methanol (10 ml) was stirred at room temperature for 20 min and then filtered. The filtrate was allowed to evaporate the solvent slowly at ambient temperature for one week to give colourless column single crystals of **1** suitable for X-ray analysis, yield: 32%, m.p. 495–496 K. FTIR (KBr, υ, cm^{-1}): 3426 (m), 3055 (w), 2438 (w), 1752 (w), 1633 (m); 1595 (s), 1563 (m), 1494 (s), 1419 (vs), 1359 (vs), 1291 (vs), 1156 (w), 1024(w), 962 (s), 768 (s), 728 (m), 692 (s), 532 (m). *Anal.* Calc. for $C_{13}H_{11}AgN_2O_3$: C, 44.47; H, 3.16; N, 7.98. Found: C, 44.62; H, 3.28; N, 7.81%.

[HPepy($FeCl_4$)] (2). Hydrochloric acid (10%) was added to the mixture of Pepy (0.36 g, 2 mmol) in methanol (10 ml) and $FeCl_3 \cdot 6\,H_2O$ (0.34 g, 2 mmol) in ethanol (10 ml) until the pH was 3, during which the colorless solution turned yellow. The solution was stirred at room temperature for 30 min and then filtered. The filtrate was allowed to evaporate slowly at ambient temperature to give single yellow crystals of **2** suitable for X-ray analysis, yield: 39%, m.p. 425–426 K. FTIR (KBr, υ, cm^{-1}): 3263 (m), 3173 (m), 2980 (w), 2369 (w), 1610 (s), 1537 (m), 1459 (s), 1388 (m), 1299 (m), 1237 (m), 1205 (m), 1168 (m), 1075 (w), 964 (s), 767 (s), 523 (s). *Anal.* Calc. for $C_{13}H_{12}Cl_4FeN$: C, 41.10; H, 3.19; N, 3.69. Found: C, 41.31; H, 3.29; N, 3.56%.

2.3. X-ray crystallographic study of complex

A single crystal of the title complex **1** with dimensions of 0.45 mm × 0.15 mm × 0.05 mm and the complex **2** with dimensions of 0.40 mm × 0.19 mm × 0.06 mm were mounted on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 293(2) K. Semi-empirical absorption corrections were applied using SABABS program. The structure was solved by direct methods (SHELXL-97) [25] and successive difference Fourier syntheses (SHELXS-97), and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically and refined with displacement parameters riding on the concerned atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The selected bond lengths and angles are presented in Tables 2 and 3.

3. Results and discussion

3.1. Crystal structures of the complexes

{[AgPepy](NO_3)}$_\infty$ (1). X-ray crystallography has established that the crystal structure of polymeric complex

Table 1
Crystal data and structure refinement summary for complex **1** and **2**

	{[AgPepy](NO_3)}$_\infty$ (**1**)	[HPepy($FeCl_4$)] (**2**)
Empirical formula	$C_{13}H_{11}AgN_2O_3$	$C_{13}H_{12}C_{14}FeN$
Formula weight	351.11	379.89
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.798(10)	6.7944(18)
b (Å)	7.324(7)	16.324(4)
c (Å)	16.919(16)	14.720(4)
β (°)	107.748(13)	92.614(4)
Volume (Å^3)	1274(2)	1630.9(7)
D_{calc} (g/cm^3)	1.830	1.547
μ (mm^{-1})	1.586	1.564
F(000)	696	764
Z	4	4
Crystal size (mm^3)	0.45 × 0.15 × 0.05	0.4 × 0.19 × 0.06
θ Range (°)	1.98–25.03	2.77–20.05
Range of h,k,l	−10/12, −8/8, −20/18	−8/8, −15/19, −17/16
Reflections collected/unique	6555/2254	8678/2875
Data/restraints/parameters	2254/0/173	2875/1/177
R[a] and wR[b]	0.0516 and 0.0996	0.0781 and 0.1566
Goodness-of-fit on F^2	1.032	1.082
Maximum residual peak and hole (e · Å^{-3})	0.363 and −0.569	0.706 and −0.394

[a] $R=\sum(||F_o| - |F_c||)/\sum|F_o|$.

[b] $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Ag1–N1	2.196(3)
Ag1–O3	2.438(3)
Ag1–O1	2.599(4)
Ag1–O2	2.635(4)
O1–N2	1.232(4)
O2–N2	1.231(4)
O3–N2	1.263(4)
N1–Ag1–O2A	98.12(10)
N1–Ag1–O3	142.02(10)
N1–Ag1–O1	127.43(12)
O3–Ag1–O1	50.42(9)
N1–Ag1–O3A	120.66(10)
O1–Ag1–O2A	134.37(7)
O3–Ag1–O2A	97.72(11)
O3A–Ag1–O2A	48.31(11)
O3–Ag1–O3A	95.37(7)
O1–Ag1–O3A	97.12(11)
N2–O1–Ag1	91.7(2)
N2–O3–Ag1	98.6(2)
N2–O3–Ag1B	97.0(2)
Ag1–O3–Ag1B	164.27(11)

Symmetry codes: A: $-x+2,\ y+1/2,\ -z+1/2$, B: $-x+2,\ y-1/2,\ -z+1/2$.

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

Fe1–Cl1	2.1577(17)
Fe1–Cl4	2.1648(19)
Fe1–Cl2	2.1774(17)
Fe1–Cl3	2.2026(18)
N1–C5	1.340(6)
N1–C1	1.341(6)
Cl1–Fe1–Cl4	109.34(8)
Cl1–Fe1–Cl2	109.75(8)
Cl4–Fe1–Cl2	108.81(9)
Cl1–Fe1–Cl3	108.41(8)
Cl4–Fe1–Cl3	111.46(9)
Cl2–Fe1–Cl3	109.06(7)

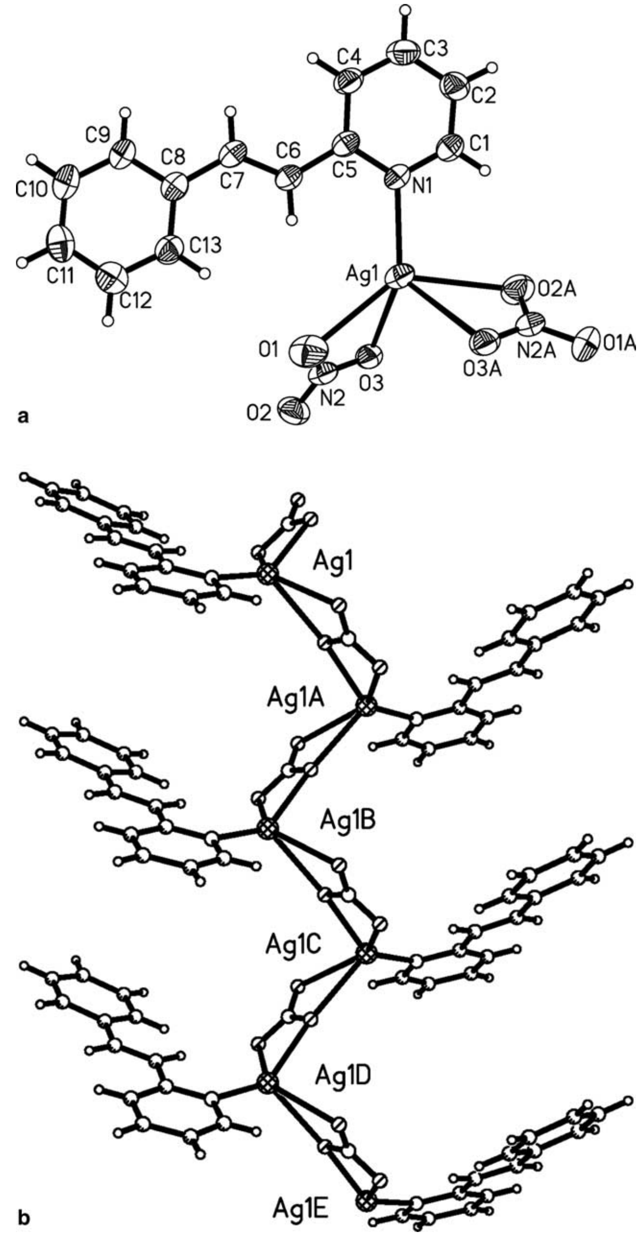

Fig. 1. (a) Coordination environment of the metal Ag^I in complex **1**. (b) Showing the helical zigzag chain along *a* axis.

1 consists of a one-dimensional helical chain, which displays a zigzag coordination geometry comprised N atoms from Pepy ligands and O atoms from nitrate bridge ligands. The drawing and atomic labeling of the fragment of complex **1** are shown in Fig. 1(a).

In one crystallographic unit there is one Pepy ligand and two NO_3^- anions, while the NO_3^- anion is an uncommon μ_4-bridge ligand (μ_4- O1, O2, O3, O3) coordinating to two Ag^I by O atoms, respectively. Each Ag^I center is five-coordinated in a heavily distorted square pyramid geometry formed by one Ag–N bond with N atom from Pepy ligand and four Ag–O bonds with O atoms from two different nitrate anions. The Ag^I is situated 1.257(3) Å above the center of the distorted square consisting of O1, O3, O2A and O3A atoms, and the N1 atom of ligand at the apex of the distorted square pyramid coordinates with the Ag^I center with Ag–N bond distance of 2.196(3) Å and the distances of Ag–O bonds vary from 2.438(3) to 2.635(4) Å. All the Ag-donor bond distances and angles are within the expected range [6,10,11,26]. The angles around Ag^I range from 48.32(11)° to 134.33(7)° in which the angle of O3A–Ag1–O2A bonds is the smallest due to the nitrate adopting a tetra-dentate coordination mode.

Along with *b* axis each Ag^I cation connects two NO_3^- anion ligands in two different directions. The adjacent Ag^I centers are linked together by O3 atoms that act as μ_2-coordinated bridges. The adjacent Pepy ligands adopt W-style configurations along with *c*-axis. The two pyridine groups are inclined to the Ag^I center with a dihedral angle of 49.4° while the Pepy, NO_3^- and Ag^I center three motifs constructed a zigzag helix in the *b* axis (Fig. 1(b)). It is noteworthy that the period of the helices and the translation vector in the columns is 7.324(1) Å, while the distances of neighboring adjacent Ag^I centers are separated by

4.990(1) Å. Both of the distances are far longer than the sum of van der Waals radii of two free silver atoms (3.44 Å) [1] indicating the absence of ligand-supported Ag···Ag interactions.

Between the two neighboring helical chains, O3 atoms exist interactions with H4 of pyridine ring to form C–H···O hydrogen bonds (O···C = 3.329 Å, H···O = 2.561 Å, C–H···O = 140.2°). These hydrogen bonds further extend the 1 D helical chains spreading on *bc* plane and forming quasi 2D structure as illustrated in Fig. 2.

In addition, the Pepy ligands of two adjacent helical chain staggered antiparallel with centroid–centroid separation of pyridine rings to phenyl ring by 3.590(2) Å perpendicular and 1.245(2) Å offset distances indicating the presence of face-to-face π–π stacking interactions which further packs the crystal as 3D structure viewing down the *b* axis in Fig. 3.

*[HPepy(FeCl$_4$)] (**2**)*. In the mononuclear complex, there is one tetrachloroiron(III) anion and one Pepy ligand in which the N atom is protonated with H1A. The Cl3 atom of the [FeCl$_4$]$^-$ anion interacts with H1A and H1 through N1–H1A···Cl3 and C1–H1···Cl3 while the Cl4 atom interacts with H13 from phenyl ring to form C13–H13···Cl4 hydrogen bonds as illustrated in Fig. 4.

In addition, there also exist other kinds of hydrogen bonding interactions between adjacent mononuclear complexes. The Cl1 atom links with H1AA, H2A, H11C and H12C which come from the phenyl ring or pyridyl ring of another two mononuclear complexes and Cl2 links H2B and H3B which come from the pyridyl ring of a fourth mononuclear complex through C–H···Cl hydrogen bonds to form 2D network (see Fig. 5 and Table 4).

The Pepy ligand is quasi-plane with the dihedral angle between the pyridinyl ring and the phenyl ring being 3.4°. In the unit-cell packing of **1**, viewing along the *a* axis, we can see that there are π–π stacking interactions between pyridinyl and phenyl ring of the ligand. The centroids of the phenyl and pyridine rings is separated by 3.347(2) Å

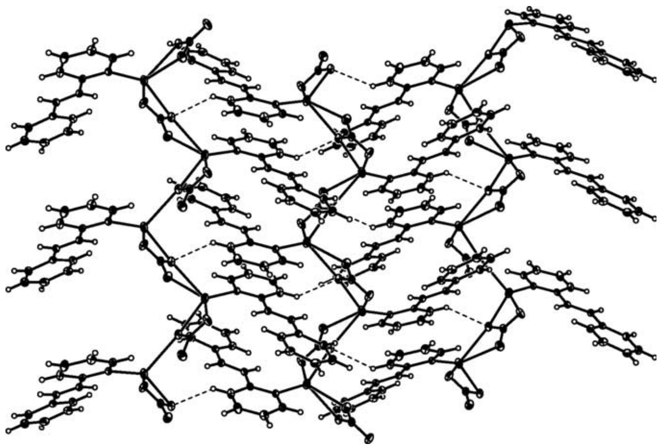

Fig. 2. The 2D structure of complex **1** formed by C–H···O hydrogen bonds between adjacent helical zigzag chains.

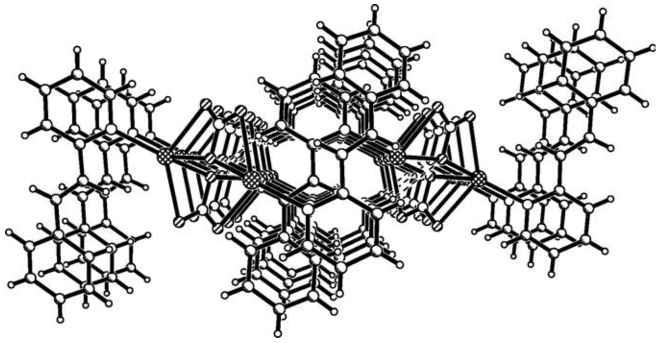

Fig. 3. Showing the Pepy ligands of two adjacent helical chain staggered and the π–π stacking interactions down *b* axis.

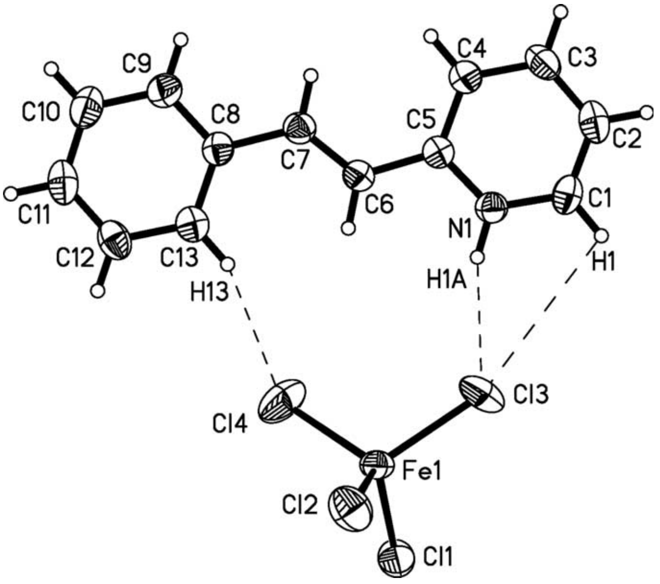

Fig. 4. ORTEP drawing of complex **2** showing the atomic numbering scheme with 30% displacement ellipsoids probability.

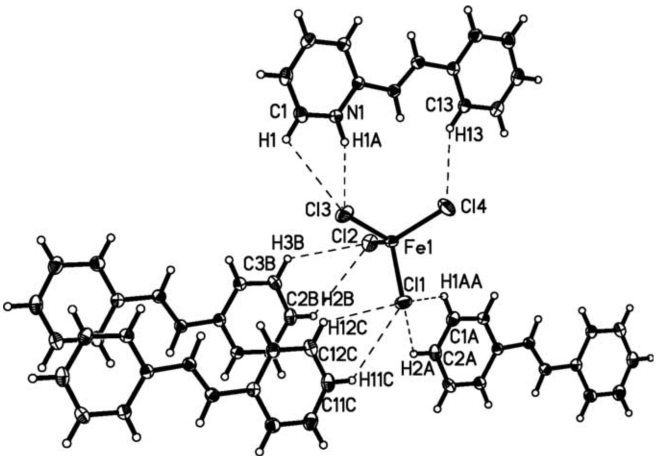

Fig. 5. Showing hydrogen bonds between [FeCl$_4$]$^-$ anion and aromatic rings from different complexes. These interactions organized complex **2** as 2D network.

Table 4
Hydrogen bonds lengths (Å) and angles (°) for complex **2**

D–H···A	D–H	H···A	D···A	D–H···A
C1A–H1AA···Cl1	0.930	3.250	3.760	116.6
C2A–H2A···Cl1	0.930	3.065	3.665	123.8
C11C–H11C···C11	0.930	3.115	3.753	127.4
C12C–H12C···C11	0.930	3.059	3.724	129.9
C2B–H2B···C12	0.930	3.205	3.820	125.4
C3B–H3B···C12	0.930	3.116	3.778	129.7
N1–H1A···C13	0.900	2.396	3.261	161.4
C1–H1···C13	0.930	2.505	3.268	103.2
C13–H13···Cl4	0.930	2.779	3.614	149.9

Symmetry codes: A: x, $1/2 - y$, $-1/2 + z$, B: $1 - x$, $1/2 + y$, $3/2 - z$, C: x, $1/2 - y$, $1/2 + z$.

perpendicular and 1.780(2) Å offset distances. These hydrogen bond and π–π stacking interactions connect the molecular ions into a 3D structure along *a* axis as illustrated in Fig. 6.

In summary, a new Ag^{I} complex helical zigzag chain complex **1** and a Fe^{III} complex **2** was prepared and structurally characterized. The Ag^{I} complex helical polymer had adequately exhibited that the N atoms of pyridine rings and O atoms of nitrates have excellent coordination ability. To our best knowledge, this Ag^{I} complex helical chains polymer is rare for it contained inorganic nitrate bridge blocks and organic backbone ligand with only one N atom comprised. The multiple hydrogen bonding interactions is even more important in crystal **2** for its not only linking the HPepy^{+} cation and $[FeCl_4]^-$ anion together as a mononuclear structure but also arranging into 3D structure. Meanwhile complexes **1** and **2** both exist the aromatic rings face-to-face π–π stacking interactions. This work demonstrates that the extended structural motifs can be constructed to build construct helical architecture through tailored backbone of the organic ligands as well as employing inorganic nitrate as synergic ligands.

3.2. FTIR spectrum and thermal analysis

The FTIR spectrum of **1** is remarkably characteristic of a group of strong broad peaks at 1419–1291 cm^{-1}, which are associated with the presence of coordinated nitrate anions. Absorption peaks at 1633–1494 cm^{-1} can be attributed to the stretching vibration of C=N and C=C bonds of Pepy. The FTIR spectrum of **2** is remarkably characteristic of a group of absorption peaks at 1611–1459 cm^{-1} can be attributed to the stretching vibration of C=N and C=C bonds of Pepy.

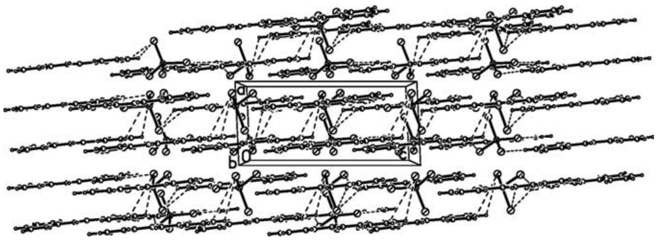

Fig. 6. Packing diagram of **2** viewed layers along the *b* axis.

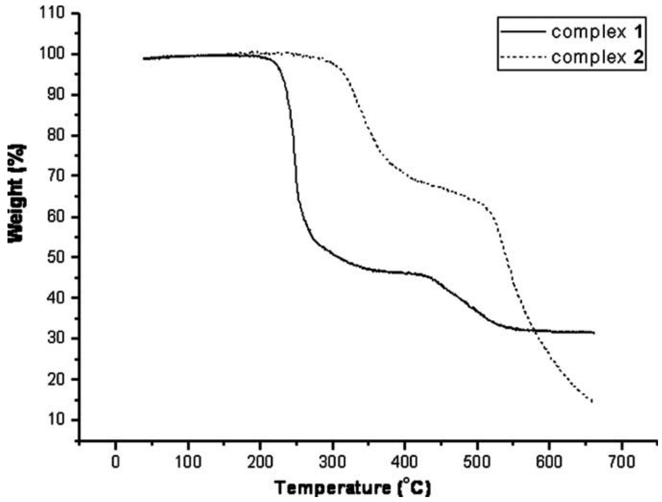

Fig. 7. TG-DTA of complex **1** and **2**.

The thermal analysis showed that complex **1** was stable up to 220.5 °C. The first weight loss was observed in the temperature of 220.5–325.0 °C to liberate Pepy (theoretical, 51.62%; experimental, 51.86%) with an endothermic peak at 246.6 °C. The second weight loss was gave off from 407.0 to 556.5 °C due to the decomposition of the silver nitrate to Ag_2O and NO_2 (theoretical, 13.10%; experimental, 13.16%). And the thermal analysis of complex **2** showed that it is stable up to 272.0 °C. The first weight loss was observed in the temperature of 272.0–403.7°C to liberate HCl and Cl_2 (theoretical, 28.26%; experimental, 30.23%) with an endothermic peak at 336.6 °C. The second weight loss was gave off from 498.0 to 636.0 °C due to the decomposition of the Pepy ligands (theoretical, 47.71%; experimental, 48.62%) (see Fig. 7).

Appendix A. Supplementary data

The supplementary crystallographic data for the structures analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 275174 and 276322. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.09.002.

References

[1] D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375.
[2] O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (1998) 474.
[3] D.R. Smith, Coord. Chem. Rev. 172 (1998) 558.
[4] X.H. Bu, W. Chen, S.L. Lu, R.H. Zhang, D.Z. Liao, W.M. Bu, M. Shionoya, F. Brisse, J. Ribas, Angew. Chem. Int. Ed. 40 (2001) 3201.

[5] S.R. Batten, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 1460.
[6] A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schröder, Coord. Chem. Rev. 183 (1999) 117.
[7] M.J. Zaworotko, Angew. Chem. Int. Ed. 37 (1998) 1211.
[8] N.J. Melcer, G.D. Enright, J.A. Ripmeester, G.K.H. Shimizu, Inorg. Chem. 40 (2001) 4641.
[9] U.S. Schubert, C. Eschbaumer, Angew. Chem., Int. Ed. Engl. 41 (2002) 2892.
[10] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem. Int. Ed. 38 (1999) 2638.
[11] C. Kaes, M.W. Hosseini, C.E.F. Rickard, B.W. Skelton, A.H. White, Angew. Chem. Int. Ed. 37 (1998) 920.
[12] L.A. Guccia, J.-M. Lehn, J.C. Homo, M. Shumutz, Angew. Chem. Int. Ed. 39 (2000) 233.
[13] R.B. Prince, L. Brunsveld, E.W. Meijer, J.S. Moore, Angew. Chem. Int. Ed. 39 (2000) 228.
[14] A.E. Rowan, R.J.M. Nolte, Angew. Chem. Int. Ed. 37 (1998) 63.
[15] A. Aumüller, P. Erk, G. Klebe, S. Hünig, J.U.v. Schütz, H.-P. Werner, Angew. Chem. Int. Ed. 25 (1986) 740.
[16] K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama, M. Oda, Inorg. Chem. 39 (2000) 3301.
[17] E.J. Corey, C.L. Cymin, M.C. Noe, Tetrahedron Lett. 35 (1994) 69.
[18] K. Maruoka, N. Murase, H. Yamamoto, J. Org. Chem. 58 (1993) 2938.
[19] C. Chen, K.S. Suslick, Coord. Chem. Rev. 128 (1993) 293.
[20] M.K. Kalra, H. Zhang, D.Y. Son, Inorg. Chem. Commun. 7 (2004) 1019.
[21] X.F. Shi, H.M. Liu, W.Q. Zhang, Acta Crystallogr., Sect. E 60 (2004) o1255.
[22] W.Q. Zhang, S.L. Jiang, Y.M. Zhou, Chin. J. Appl. Chem. 14 (1997) 37.
[23] W.Q. Zhang, S.L. Li, Z.M. Zhang, Chem. J. Chin. Univ. 21 (2000) 556.
[24] W.Q. Zhang, G.Q. Wang, Y. Zheng, Acta Phys. Chim. Sin. 12 (2002) 517.
[25] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Determination, University of Göttingen, Germany, 1997.
[26] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, Science 283 (1999) 1148.