

Full Paper

Synthesis and Molecular Structures of Two [1,4-bis(3-pyridyl)-2,3-diazo-1,3-butadiene]-dichloro-Zn(II) Coordination Polymers

Gene-Hsiang Lee [†] and Hsin-Ta Wang*

Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei 106, Taiwan, ROC; [†] e-mail: ghlee@ntu.edu.tw

* Author to whom correspondence should be addressed; e-mail: htwang@ntut.edu.tw

Received: 5 June 2006; in revised form: 30 July 2006 / Accepted: 31 July 2006 / Published: 10 August 2006

Abstract: Two novel coordination polymers with 3D metal-organic frameworks (MOFs) have been synthesized by reacting 1,4-bis(3-pyridyl)-2,3-diazo-1,3-butadiene (**L**) with zinc dichloride. Both compounds have the same repeating unit consisting of a distorted tetrahedral Zn(II) center coordinated by two chlorides and two pyridyl nitrogen atoms of two bridging bimonodentate **L** ligands, however, different structural conformations have been found, one forming a helical chain and the other producing a square-wave chain. The intermolecular C–H...Cl hydrogen bonds in **1** and **2** play important roles in the formation of three-dimensional coordination polymers. Compound **1** crystallized in an orthorhombic space group Pna2₁ with a = 7.9652(3), b = 21.4716(7), c = 8.2491(3) Å, V = 1410.81(9) Å³ and Z = 4. Compound **2** crystallized in a monoclinic space group P2₁/n with a = 9.1752(3), b = 14.5976(4), c = 10.3666(3) Å, β = 98.231(2)°, V = 1374.16(7) Å³ and Z = 4.

Keywords: Coordination Polymer, Metal-organic Framework, X-ray Crystal Structure.

Introduction

The coordinative and hydrogen bond approaches have been widely used in crystal engineering in the construction of coordination compounds with one- (1D), two- (2D) or three-dimensional (3D) metal-organic frameworks (MOFs). Rigid organic ligands containing pyridine rings, such as

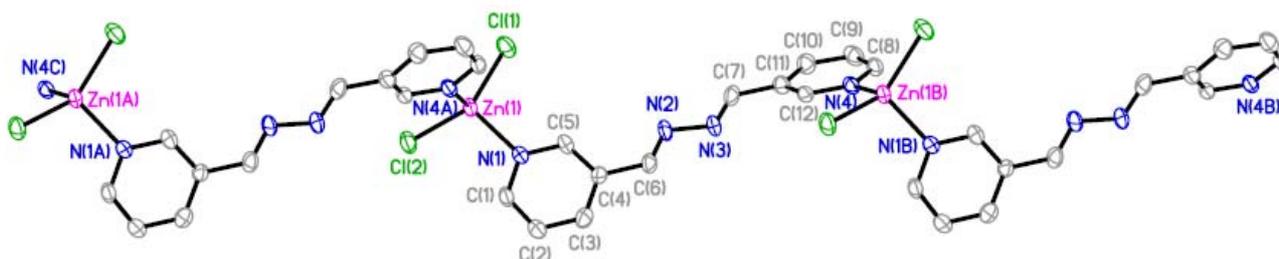
4,4'-bipyridine, 1,2-bis(4-pyridyl)ethene and 1,2-bis(4-pyridyl)ethyne, have been proven to be useful for assembling MOFs [1-5] in recent years.

The organic ligand 1,4-bis(3-pyridyl)-2,3-diazo-1,3-butadiene (**L**), containing two pyridyl groups joined by a zigzag $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ group, possesses effective sites for accommodating transition metal ions. The structure of $[\text{Co}(\text{SCN})_2(\text{L})_2 \cdot 2\text{CH}_2\text{Cl}_2]_n$ shows a 2D non-interpenetrating MOF with a distorted square pattern as the basic building unit [6]. The isomorphous structures of $[\text{Co}(\text{NO}_3)_2(\text{L})_{1.5} \cdot \text{CH}_2\text{Cl}_2]_n$ and $[\text{Cd}(\text{NO}_3)_2(\text{L})_{1.5} \cdot \text{CH}_2\text{Cl}_2]_n$ with polycyclohexane structural MOFs have also been reported [7]. In this paper, we report the synthesis of compounds **1** and **2**, both having the same chemical composition, $[\text{ZnCl}_2(\text{L})]_n$, but different MOFs.

Results and Discussion

Compound **1** was synthesized by reacting of ZnCl_2 with **L** (molar ratio 1:1) under solvothermal conditions. Figure 1 shows the crystal structure of compound **1**. The structure reveals that compound **1** consists of a distorted tetrahedral $\text{Zn}(\text{II})$ center coordinating to two chlorides and two pyridyl nitrogen atoms from two symmetry-related **L** ligands [$\text{Zn}(1)-\text{Cl}(1) = 2.2229(11) \text{ \AA}$; $\text{Zn}(1)-\text{Cl}(2) = 2.2123(9) \text{ \AA}$; $\text{Zn}(1)-\text{N}(1) = 2.049(3) \text{ \AA}$; $\text{Zn}(1)-\text{N}(4\text{A}) = 2.057(3) \text{ \AA}$, symmetry operation code: $\text{A} = -x+3/2, y+1/2, z-1/2$]. Some selected bond lengths and angles around the Zn center are listed in Table 1. It is noteworthy that the ligand **L** is not planar, but twisted around the $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ with a dihedral angle of $46.65(13)^\circ$ between the two pyridine rings and acts as a *bis*-monodentate mode to the $\text{Zn}(\text{II})$ ion. Hence, a 1D polymeric helical chain is formed. The distance between the neighboring zinc ions is $12.1834(4) \text{ \AA}$.

Figure 1. One-dimensional polymeric helical chain of compound **1**. Atomic displacement ellipsoids were plotted at 50% probability level.

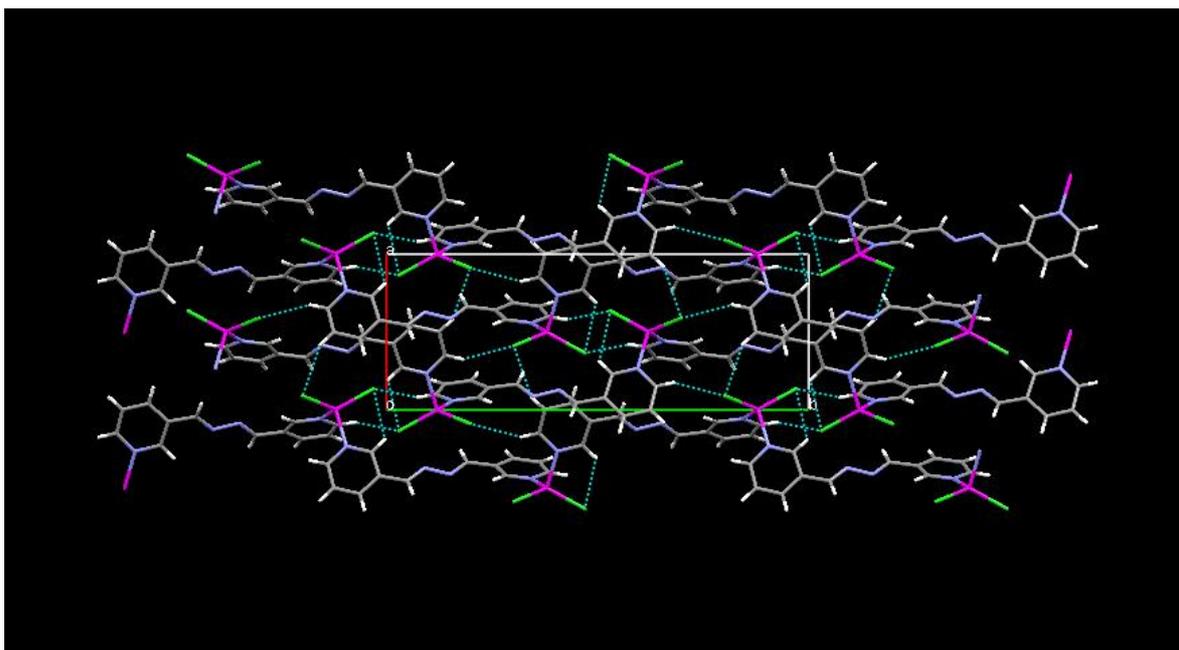


Hydrogen bonding has been widely used in constructing coordination polymers [8-10]. Intermolecular $\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonds were observed in our coordination polymers. The packing diagram viewed along the *c* axis is shown in Figure 2. Two Cl^- anions produce four intermolecular $\text{C}-\text{H} \cdots \text{Cl}$ interactions in the crystal packing [$\text{C}(8)-\text{H} \cdots \text{Cl}(1)$, $3.554(4) \text{ \AA}$; $\text{C}(9)-\text{H} \cdots \text{Cl}(1)$, $3.629(4) \text{ \AA}$; $\text{C}(1)-\text{H} \cdots \text{Cl}(2)$, $3.546(4) \text{ \AA}$ and $\text{C}(12)-\text{H} \cdots \text{Cl}(2)$, $3.445(4) \text{ \AA}$]. These $\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonds formed between adjacent 1D polymer helical chains result in a 3D network.

Table 1. Selected bond lengths and angles around the Zn(II) for compound **1**.

Bond Length [Å]		Bond Angle [°]	
Zn(1)-Cl(1)	2.2229(11)	N(1)-Zn(1)-N(4A)	99.56(13)
Zn(1)-Cl(2)	2.2123(9)	N(1)-Zn(1)-Cl(2)	110.25(10)
Zn(1)-N(1)	2.049(3)	N(4A)-Zn(1)-Cl(2)	104.18(9)
Zn(1)-N(4A)	2.057(3)	N(1)-Zn(1)-Cl(1)	107.14(9)
N(2)-C(6)	1.281(5)	N(4A)-Zn(1)-Cl(1)	107.54(9)
N(2)-N(3)	1.415(4)	Cl(2)-Zn(1)-Cl(1)	125.13(4)
N(3)-C(7)	1.272(5)	C(6)-N(2)-N(3)	109.6(3)
C(4)-C(6)	1.477(5)	C(7)-N(3)-N(2)	112.1(3)
C(7)-C(11)	1.467(5)	N(2)-C(6)-C(4)	120.0(4)
		N(3)-C(7)-C(11)	119.5(4)

Symmetry transformations used to generate equivalent atoms: A = $-x+3/2, y+1/2, z-1/2$

Figure 2. The packing diagram of compound **1**, viewed along the c axis. Dotted lines indicate hydrogen bonds.

Compound **2**, synthesized under solvothermal conditions by the reaction of ZnCl_2 with NaSCN and **L** in a 1:2:1 molar-ratio, has an unexpected but interesting structure. The molecular drawing of the 1D polymeric chain of compound **2** is shown in Figure 3. The structure reveals that the zinc ions in compound **2** also have a distorted tetrahedral geometry and bond to two chlorides and two pyridyl nitrogen atoms from two symmetry-related **L** ligands [$\text{Zn(1)-Cl(1)} = 2.2205(6)\text{Å}$; $\text{Zn(1)-Cl(2)} = 2.2336(7)\text{Å}$; $\text{Zn(1)-N(1)} = 2.047(2)\text{Å}$; $\text{Zn(1)-N(4A)} = 2.052(2)\text{Å}$, symmetry operation code: A = $-x+3/2, y+1/2, -z+1/2$]. Some selected bond lengths and angles around the Zn center are listed in Table 2. It is noteworthy that the geometry of ligand **L** is nearly planar and the dihedral angle between two pyridine rings is $2.96(16)^\circ$, which is much smaller than the $46.65(13)^\circ$ one in compound **1**. The bond angle of

N(1)-Zn(1)-N(4A) is $116.22(8)^\circ$, which is significantly larger than that of $99.56(13)^\circ$ observed in compound **1**. The structure of compound **2** reveals a 1D square-wave arrangement with the separation of neighboring zinc ions of $12.4319(6) \text{ \AA}$.

Figure 3. One-dimensional polymeric square-wave chain of compound **2**. Atomic displacement ellipsoids were drawn at 50% probability level.

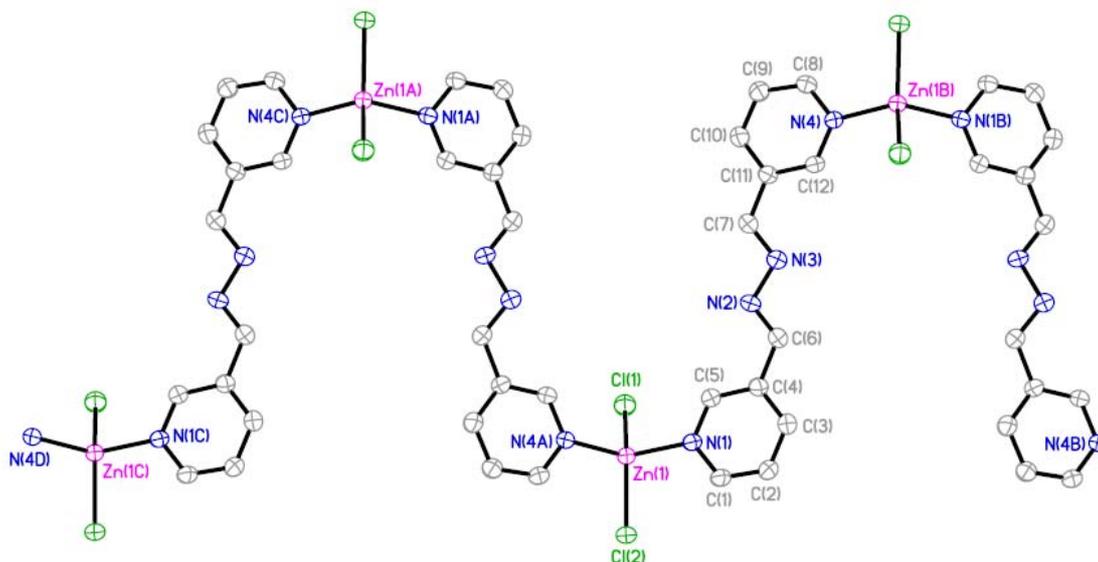


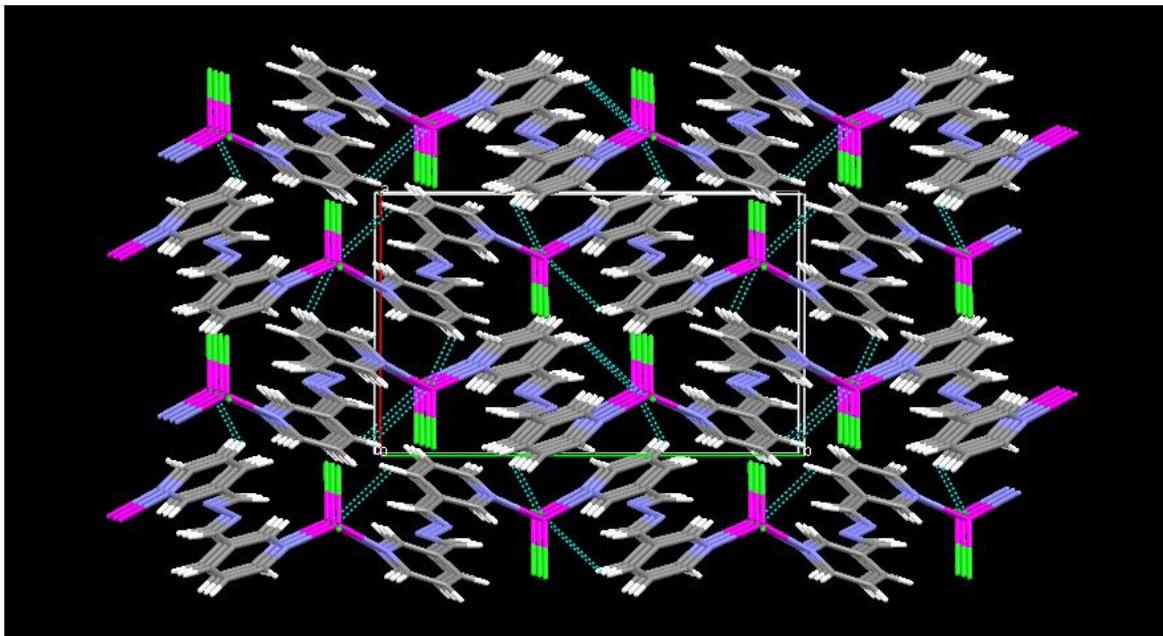
Table 2. Selected bond lengths and angles around the Zn(II) for compound **2**.

Bond Length [\AA]		Bond Angle [$^\circ$]	
Zn(1)-Cl(1)	2.2205(6)	N(1)-Zn(1)-N(4A)	116.22(8)
Zn(1)-Cl(2)	2.2336(7)	N(1)-Zn(1)-Cl(2)	104.83(6)
Zn(1)-N(1)	2.047(2)	N(4A)-Zn(1)-Cl(2)	107.56(6)
Zn(1)-N(4A)	2.052(2)	N(1)-Zn(1)-Cl(1)	103.00(6)
N(2)-C(6)	1.262(3)	N(4A)-Zn(1)-Cl(1)	105.31(6)
N(2)-N(3)	1.415(3)	Cl(2)-Zn(1)-Cl(1)	120.49(3)
N(3)-C(7)	1.274(3)	C(6)-N(2)-N(3)	111.7(2)
C(4)-C(6)	1.473(3)	C(7)-N(3)-N(2)	111.5(2)
C(7)-C(11)	1.466(3)	N(2)-C(6)-C(4)	121.3(2)
		N(3)-C(7)-C(11)	120.7(2)

Symmetry transformations used to generate equivalent atoms: A = $-x+3/2, y+1/2, -z+1/2$.

The packing diagram viewed along the *c* axis is shown in Figure 4. Similar to compound **1**, compound **2** also shows intermolecular C–H \cdots Cl hydrogen bonds [C(3)–H \cdots Cl(2), $3.509(4) \text{ \AA}$ and C(9)–H \cdots Cl(2), $3.507(3) \text{ \AA}$] to form a 3D network. The pyridyl rings in the adjacent polymeric chains are nearly parallel. They have the shortest distances of 3.85 \AA and 4.22 \AA respectively. The result indicates the presence of weak π - π stacking. In contrast, compound **1** does not show π - π interactions in the crystal packing, because the two pyridyl rings attached to the $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ are twisted.

Figure 4. The packing diagram of compound **2**, viewed along the *c* axis. Dotted lines indicate hydrogen bonds.



Conclusions

We have successfully synthesized two novel coordination polymers. Although the compounds have the same chemical composition, $[\text{ZnCl}_2(\text{L})]_n$, they show different structural conformations with one forming a helical chain and the other a square-wave chain, determined by X-ray crystallography. The intermolecular C–H \cdots Cl hydrogen bonds in **1** and **2** play important roles in the formation of 3D coordination polymers.

Acknowledgements

The authors would like to thank the National Science Council, Republic of China, for support under grant NSC 932622E027027CC3.

Experimental

General

Solvents and metal salts for syntheses (analytical grade) were used without further purification. The ligand **L** was prepared according to the literature [7]. IR spectra were recorded using KBr discs on a Nicolet FT-IR CGB- 2400 FT-IR spectrophotometer. Elemental analysis (EA) were performed on a Heraeus CHN-Rapid elemental analyzer.

Synthesis of compound 1

A mixture of ZnCl₂ (27.2 mg, 0.2 mmol) and **L** (42.0 mg, 0.2 mmol) in ethanol (5 mL) was placed in a 23 mL Teflon-lined stainless steel autoclave container and heated at 150 °C for 48 h. Afterwards the mixture was cooled to room temperature at a rate of 5°C/h. The resulting colorless crystals were collected in 50% yield. IR (ν_{\max} , cm⁻¹): 1632.9 (s), 1605.0 (s), 1467.1 (m), 1432.9 (s), 1311.4 (m), 1215.4 (w), 1192.3 (m), 1126.7 (w), 1103.1 (w), 1057.3 (m), 1031.7 (w), 966.6 (w), 935.1 (w), 882.8 (w), 815.3 (w), 697.1 (m), 653.7 (m); Elemental analysis: Calcd.: C, 41.59; H, 2.91; N, 16.17. Found: C, 41.82; H, 2.88; N, 16.52.

Synthesis of compound 2

A mixture of ZnCl₂ (27.2 mg, 0.2 mmol), NaSCN (42.4mg, 0.4 mmol) and **L** (42.0 mg, 0.2 mmol) in ethanol (5 mL) was placed in a 23 ml Teflon-lined stainless steel autoclave container and heated at 150 °C for 48 h. Afterwards the mixture was cooled to room temperature at a rate of 5°C/h. The light brown crystals were collected in 55% yield. IR (ν_{\max} , cm⁻¹): 1632.0 (s), 1605.0 (s), 1473.8 (s), 1430.9 (s), 1309.9 (m), 1215.4 (m), 1187.9 (m), 1126.2 (m), 1101.6 (m), 1057.3 (s), 1030.8 (m), 971.0 (m), 948.8 (m), 883.7 (s), 814.3 (s), 699.1 (vs), 652.8 (s); Elemental analysis: Calcd.: C, 41.59; H, 2.91; N, 16.17. Found: C, 41.93; H, 2.90; N, 16.49.

X-ray techniques

Suitable single crystals were mounted on a glass fiber. The data collection was carried out on a NONIUS Kappa CCD diffractometer with Mo-K α ($\lambda = 0.71073$ Å) radiation with the crystal cooled to 150K in a stream of N₂ from Oxford Cryostream-700 cooler. A preliminary orientation matrix and the unit cell parameters were determined from the 15 frames, each frame corresponding to a 1° ω scan in 20 sec. Data were measured (program COLLECT [11]) by using an ω scan of 0.5° per frame for 20 sec. until a complete data had been collected. Program DENZO-SMN [12] was used for cell refinement and data reduction. The SORTAV [13] program was used to apply absorption correction. The structure was solved by direct method with the SHELXS97 [14] and refined on F² with SHELXL97 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to the ideal geometry applying an appropriate riding model. The molecular graphic were plotted using SHELXTL [16] and MERCURY [17]. Crystallographic data are listed in Table 3. CCDC-605741 and 605742 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html. [or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic and experimental data for compounds **1** and **2**.

Compound	1	2
Formula	C ₁₂ H ₁₀ N ₄ C ₁₂ Zn	C ₁₂ H ₁₀ N ₄ C ₁₂ Zn
Formula weight	346.51	346.51
Crystal system	Orthorhombic	monoclinic
Space group	Pna2 ₁	P2 ₁ /n
Formula per unit cell, Z	4	4
Unit-cell dimensions	a = 7.9652(3) Å b = 21.4716(7) Å c = 8.2491(3) Å α = β = γ = 90°	a = 9.1752(3) Å b = 14.5976(4) Å c = 10.3666(3) Å α = γ = 90°, β = 98.231(2)°
Unit-cell volume, V (Å ³)	1410.81(9)	1374.16(7)
D _{calcd.} (g/cm ³)	1.631	1.675
Absorption coefficient, μ(mm ⁻¹)	2.109	2.165
F(000)	696	696
Crystal size (mm)	0.50 x 0.08 x 0.05	0.25 x 0.15 x 0.03
θ ranges (°) for data collection	1.90 ~ 27.50	2.43 ~ 27.50
Index ranges	-10 ≤ h ≤ 10 -27 ≤ k ≤ 23 -10 ≤ l ≤ 10	-11 ≤ h ≤ 11 -17 ≤ k ≤ 18 -13 ≤ l ≤ 13
Reflections collected	9123	9083
Independent reflections	3184 (R _{int} = 0.0641)	3145 (R _{int} = 0.0453)
Completeness to θ=27.50 (%)	100.0	99.7
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.900 and 0.418	0.939 and 0.700
Refinement method	Full-matrix L. S. on F ²	Full-matrix L. S. on F ²
Data / restraints / parameters	3184 / 1 / 172	3145 / 0 / 173
Goodness-of-fit on F ²	1.007	1.013
Final R indices [I > 2σ(I)]	R1 = 0.0398, wR2 = 0.0695	R1 = 0.0326, wR2 = 0.0598
R indices (all data)	R1 = 0.0718, wR2 = 0.0765	R1 = 0.0694, wR2 = 0.0672
Largest diff. peak and hole (e/ Å ³)	0.320 and -0.394	0.347 and -0.363

References

1. Janiak, C. Engineering coordination polymers towards applications. *Dalton Trans.* **2003**, 2781-2804.
2. Barnett, S. A.; Champness, N. R. Structural diversity of building-blocks in coordination Framework synthesis—combining M(NO₃)₂ junctions and bipyridyl ligands. *Coord. Chem. Rev.* **2003**, *246*, 145-168.

3. Hagrman, P. J.; Hagrman, D.; Zubieta, J. Organic-Inorganic Hybrid Materials: From "Simple" Coordination Polymers to Organodiamine-Templated Molybdenum Oxides. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2638-2684.
4. Prior, T. J.; Bradshaw D.; Teat, S. J.; Rosseinsky, M. J. Designed layer assembly: a three-dimensional framework with 74% extra-framework volume by connection of infinite two-dimensional sheets. *Chem. Commun.*, **2003**, 500-501.
5. Tseng, B. C.; Chen, B. S.; Lee, S. Y.; Liu, W. H; Lee, G. H.; Peng, S. M. Anion-directed assembly of supramolecular zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide. *New J. Chem.* **2005**, *29*, 1254-1257.
6. Dong, Y. B.; Smith, M. D.; zur Loye, H. C. New Inorganic–Organic Coordination Polymers Generated from Rigid or Flexible Bidentate Ligands and $\text{Co}(\text{NCS})_2 \cdot x\text{H}_2\text{O}$. *J. Solid State Chem.* **2000**, *155*, 143-153.
7. Dong, Y. B.; Smith, M. D.; Layland, R. C.; zur Loye, H. C. A Novel Noninterpenetrating Polycyclohexane Network: A New Inorganic/Organic Coordination Polymer Structural Motif Generated by Self-Assembly of "T-Shaped" Moieties. *Chem. Mater.* **2000**, *12*, 1156-1161.
8. Yaghi, O. M.; Li, Hailian, Groy, T. L. Construction of Porous Solids from Hydrogen-Bonded Metal Complexes of 1,3,5-Benzenetricarboxylic Acid. *J. Am. Chem. Soc.* **1996**, *118*, 9096-9101.
9. Blake, A. J.; Hill, S. J.; Hubberstey, P.; Li, W. S., Rectangular grid two-dimensional sheets of copper(II) bridged by both co-ordinated and hydrogen bonded 4,4'-bipyridine (4,4'-bipy) in $[\text{Cu}(\mu\text{-}4,4'\text{-bipy})(\text{H}_2\text{O})_2(\text{FBF}_3)_2] \cdot 4,4'\text{-bipy}$. *J. Chem. Soc., Dalton Trans.* **1997**, 913-914.
10. Yang, C. H.; Chuo, C. M.; Lee, G. H.; Wang, C. C. Self-assembly of two mixed-ligands metal-organic coordination polymers, $[\text{M}^{\text{II}}_2(\text{DPA})_2(\text{C}_4\text{O}_4)(\text{C}_2\text{O}_4)]$ (M = Cu, Zn). *Inorg. Chem. Comm.* **2003**, *6*, 135-140.
11. COLLECT, *Nonius 2000*; Nonius BV: Delft, The Netherlands, **2000**.
12. Otwinowski, Z.; Minor, W. *Method. Enzymol.* **1997**, *276*, 307-326.
13. Blessing, R. H. An empirical correction for absorption anisotropy. *Acta Cryst., Sect. A.* **1995**, *51*, 33-38.
14. Sheldrick, G. M. Phase annealing in *SHELX-90*: direct methods for larger structures. *Acta Cryst.* **1990**, *A46*, 467-473.
15. Sheldrick, G. M. *SHELXL97*, Program for the refinement of crystal structure; University of Göttingen: Göttingen, Germany, **1997**.
16. SHELXTL V6.1; Bruker AXS, Inc: Madison, Wisconsin, USA, **2000**.
17. Bruno, I. J.; Cole, J. C. ; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. New software for searching the Cambridge Structural Database and visualizing crystal structures, *Acta Cryst.* **2002**, *B58*, 389-397.

Sample Availability: Samples of the title compounds may be obtained from the authors.