

镍螺旋化合物及其杂银配位聚合物的设计合成与结构

吴大雨 黄 薇 李 庚 谢黎霞 段春迎* 孙巧珍 孟庆金

(南京大学化学化工学院, 配位化学研究所, 配位化学国家重点实验室, 南京 210093)

摘要: 采用两个易扭转异构的双三齿有机配体, 双吡啶二甲基-6,6'-二酰肼-2,2'-连吡啶(H_2L^1)和双吡啶二乙基-6,6'-二酰肼-2,2'-连吡啶(H_2L^2), 和金属镍离子组装得到 2 个金属螺旋体(helicate), $Ni_2(HL^1)_2(PF_6)(BF_4)(CH_3OH)(H_2O)_2$ (**1**) 和 $Ni_2(HL^2)(H_2L^2)(ClO_4)_3(C_2H_5OH)(CH_3OH)(H_2O)_3$ (**2**), 并测定了它们的晶体结构。同时由配体 H_2L^3 出发, 通过逐级组装的方法, 得到一个镍-银杂金属的配位聚合物 $Ni_2Ag_2(HL^3)_2(ClO_4)_2(CH_3CN)_3$ (**3**)。单晶结构表明, 配位聚合物 **3** 中配体 H_2L^3 首先与镍离子组装成分子盒化合物(molecular box), 该结构单元进一步通过 Ag 离子与分子盒外围 N 原子配位, 使分子盒互相串连成一维配位聚合物 **3**, 分子盒聚集体沿 *c* 方向伸展成一维链结构, 链与链之间相互平行, 进一步堆积成二维孔道结构。

关键词: 螺旋; 分子盒; 多孔结构; 逐级组装; 配位聚合物

中图分类号: O614.81⁺3; O614.122

文献标识码: A

文章编号: 1001-4861(2007)07-1129-08

Nickel Helicates and Hybrid Silver Coordination Polymer: Design, Synthesis and Structure Characterization

WU Da-Yu HUANG Wei LI Geng XIE Li-Xia DUAN Chun-Ying* SUN Qiao-Zhen MENG Qing-Jin

(School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

Abstract: Two molecular clips with flexible bis-tridentate coordination sites, di(2-pyridylcarbaldehyde)-6,6'-dicarboxylic acid hydrazone-2,2'-bipyridine (H_2L^1) and di(2-acetylpyridyl)-6,6'-dicarboxylic acid hydrazone-2,2'-bipyridine (H_2L^2) have been prepared. Dinuclear double-stranded helicate $Ni_2(HL^1)_2(PF_6)(BF_4)(CH_3OH)(H_2O)_2$ (**1**) and $Ni_2(HL^2)(H_2L^2)(ClO_4)_3(C_2H_5OH)(CH_3OH)(H_2O)_3$ (**2**) based on the ligands, H_2L^1 and H_2L^2 respectively, have been synthesized, their crystal structures were determined by X-ray diffraction method. Meanwhile, the assembly between the modulated ligand, di(2-pyrazinecarbaldehyde)-6,6'-dicarboxylic acid hydrazone-2,2'-bipyridine (H_2L^3) and mixed metal salts of nickel and silver yields a 1D coordination polymer $Ni_2Ag_2(HL^3)_2(ClO_4)_2(CH_3CN)_3$ (**3**). The crystal structure revealed that, in the compound **3**, molecular box as metallocupramolecular secondary building units, can be interconnected via the external Ag-N coordination to construct metallocupramolecular aggregate. Another intriguing structure feature of the compound **3** in the solid state is that it forms two-dimensional porous frameworks through the stacking of the 1D aggregated molecular box, in which counter anions and guest solvent molecules are resided. CCDC: 640381, **1**, 640382, **2**, 640383, **3**.

Key words: helicate; molecular box; pore structure; hierarchical self-assembly; coordination polymer

There is a considerable current interest in the supramolecular synthetic approach and its application

to the quest for the controlling of molecular architecture. Metallocupramolecular chemistry is one of the

收稿日期: 2007-03-16。收修改稿日期: 2007-05-10。

国家自然科学基金资助项目(No.20131020)。

*通讯联系人。E-mail: duancy@nju.edu.cn

第一作者: 吴大雨, 男, 28 岁, 博士研究生; 研究方向: 功能配位化学。

actively pursued research areas in supramolecular chemistry, which uses the interaction between organic ligands and metal ions to construct multicomponent and/or multinuclear coordination entities^[1]. The application of metal-ligand interaction has proved to be particularly fruitful and a rich variety of metallasupramolecular architectures have been obtained in the last few years, including molecular boxes^[2], helicates^[3], rotaxanes^[4], catenanes^[5] and cages^[6]. The assembly of helical or molecular box complexes have elegantly illustrated how the specific formation of architecturally complex assemblies are directed by the interplay between relatively simple parameters such as the stereoelectronic preference of the metal ions, the nature of bonding sites of the multi-dentate ligands and so on^[7].

Meanwhile, the rational design of novel coordination networks is of great interest, because the topology of these networks can not only present the aesthetic appeal, but also be manipulated to influence the properties and functions of the materials^[8]. One of the common strategies for the construction of coordination networks is to properly program building units made up of metal ions and organic ligands for the spontaneous self-assembly of a well-defined structural entity^[9]. Organic and/or metallic tectons can be used to generate one-dimensional coordination networks. Many 1D coordination networks constructed from smaller organic ligands have been reported^[10]. However, coordination networks constructed from metallasupramolecular secondary building units are less common^[11]. It is possible to assemble metallasupramolecules, such as helicate, molecular box, starting from ligand incorporating chelating sites. Meanwhile, it has been demonstrated recently that discrete metallo-supramolecular species of additional peripheral binding sites can further assemble into one-dimensional (1D) polymeric structures^[12]. Herein, we report a novel 1D coordination polymer starting from the assembled metallasupramolecular box via the hierarchical or multistep self-assembly strategy.

1 Experimental

1.1 Materials and instrumentation

All chemicals were of reagent grade quality

obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were carried out with a Perkin-Elmer 2400 Analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the range of 4 000~400 cm⁻¹. ¹H NMR spectra were performed on DRX500 Bruker spectrometer at 298 K with TMS as an internal reference. Electrospray mass spectrum were carried out on a LCQ system (Finnigan MAT, USA) with methanol as mobile phase.

1.2 Synthesis of the ligand H₂L¹~H₂L³

1.2.1 Di(2-pyridylcarbaldehyde)-6,6'-dicarboxylic acid hydrazone-2,2'-bipyridine (H₂L¹)

A solution of dicarboxylic acid hydrazide-2,2'-bipyridine (2 mmol, 0.54 g) in methanol (15 mL) was added to a methanol solution (10 mL) containing pyridyl-2-carbaldehyde (4 mmol, 0.43 g). After 5 drops of acetic acid was added, the yellow mixture was heated at boiling temperature under magnetic stirring for 2 h. During the reaction, a pale yellow precipitate was formed, which was collected by filtration, washed with methanol-ether, and dried in vacuo. Yield: 0.81 g, 90%. Spectroscopic data for H₂L¹: ¹H NMR (DMSO-d₆), δ 11.52 (1H, s, NH), 9.05 (1H, d, J =10.1 Hz), 8.85 (1H, d, J =5.6 Hz), 8.48 (1H, d, J =8.1 Hz), 8.24 (1H, d, J =8.5 Hz), 8.15 (1H, t, J =15.6 Hz), 8.01 (1H, t, J =13.5 Hz), 7.85 (1H, d, J =9.1 Hz), 6.52 (1H, s). IR (solid KBr pellet, cm⁻¹): 3 452.18 (m), 1 665.01 (s), 1 585.24 (m), 1 430.15 (m), 1 364.25 (m), 1 148.76 (m), 783.46 (m). ESI-MS: m/z 451.2 for [H₂L¹ + H]⁺, calc. for C₂₄H₁₉N₈O₂, 451.47.

1.2.2 Di(2-acetylpyridyl)-6,6'-dicarboxylic acid hydrazone-2,2'-bipyridine (H₂L²)

Ligand H₂L² was prepared in a manner similar to H₂L¹ except using the 2-acetylpyridine instead of pyridyl-2-carbaldehyde. Yield: 0.69 g, 72%. Spectroscopic data for H₂L²: ¹H NMR (DMSO-d₆), δ 11.31 (1H, s, NH), 9.16 (1H, d, J =8.6 Hz), 8.64 (1H, d, J =8.3 Hz), 8.52 (1H, d, J =7.1 Hz), 8.31 (1H, d, J =7.1 Hz), 8.10 (1H, t, J =11.1 Hz), 7.88 (1H, t, J =16.3 Hz), 7.56 (1H, d, J =7.1 Hz), 2.32 (3H, s, -CH₃). IR (solid KBr pellet, cm⁻¹): 3 448.58 (m), 1 663.77 (s), 1 580.94 (m), 1 433.13

(m), 1 364.08(m), 1 147.26(m), 783.46(m), 675.19(m). ESI-MS: m/z 479.3 for $[\text{H}_2\text{L}^2 + \text{H}]^+$, calc. for $\text{C}_{26}\text{H}_{23}\text{N}_8\text{O}_2$, 479.52.

1.2.3 Di(2-pyrazinecarbaldehyde)-6,6'-dicarboxylic acid hydrazone-2,2'-bipyridine (H_2L^3)

Ligand H_2L^3 was prepared in a manner similar to H_2L^1 except using the 2-pyrazinecarbaldehyde instead of 2-pyridylcarbaldehyde. Yield: 0.63 g, 65.2%. Spectroscopic data for H_2L^3 : ^1H NMR ($\text{DMSO}-d_6$), δ 11.24 (1H, s, NH), 9.75 (1H, d, $J=11.2$ Hz), 9.74 (1H, d, $J=5.6$ Hz), 8.52 (1H, d, $J=7.5$ Hz), 8.36 (1H, d, $J=9.2$ Hz), 8.12 (1H, t, $J=11.2$ Hz), 7.68 (1H, d, $J=8.2$ Hz), 5.38 (1H, s). IR (solid KBr pellet, cm^{-1}): 3 458.28 (m), 1 660.58(s), 1 588.94 (m), 1 432.75 (m), 1 365.96 (m), 1 146.56(m), 785.32(m). ESI-MS: m/z 481.3 for $[\text{H}_2\text{L}^3 + \text{H}]^+$, calc. for $\text{C}_{24}\text{H}_{21}\text{N}_{10}\text{O}_2$, 481.50.

1.3 Synthesis of the complex 1~3

1.3.1 Preparation of compound $\text{Ni}_2(\text{HL}^1)_2(\text{PF}_6)(\text{BF}_4)(\text{CH}_3\text{OH})(\text{H}_2\text{O})_2$ (**1**)

$\text{Ni}(\text{PF}_6)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 0.037 g) dissolved in 15 mL methanol was added dropwise to a suspension of H_2L^1 (0.1 mmol, 0.045 g) in 10 mL methanol. The solution was stirred at boiling temperature for 20 min to get a clear solution, into which the excessive NaBF_4 (0.5 mmol, 0.055 g) was added and allowed to stand at room temperature. After several days, green block crystals suitable for X-ray diffraction were obtained (0.043 g, 67.4%). Anal calc. (%) for $\text{Ni}_2(\text{C}_{24}\text{H}_{17}\text{N}_8\text{O}_2)_2(\text{PF}_6)(\text{BF}_4)(\text{CH}_3\text{OH})(\text{H}_2\text{O})_2$: H 3.22, C 44.74, N 17.05. Found (%): H 3.54, C 45.19, N 17.11. ESI-MS: m/z 1013.65 (calc. for $[\text{Ni}_2(\text{L}^1)(\text{HL}^1)]^+$, 1 013.16) and 507.85 (calc. for $[\text{Ni}_2(\text{HL}^1)_2]^{2+}$, 508.14). IR (solid KBr pellet, cm^{-1}): 3 442.79 (m), 1 616.67(s), 1 579.98(s), 1 537.53(s), 1 309.10(s), 1 156.29(s), 1 083.80(s), 915.20(w), 779.74(s), 747.99(s), 483.34(w).

1.3.2 Preparation of compound $\text{Ni}_2(\text{HL}^2)(\text{H}_2\text{L}^2)(\text{ClO}_4)_3(\text{C}_2\text{H}_5\text{OH})(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3$ (**2**)

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 0.037 g) dissolved in 15 mL methanol was added to a suspension of H_2L^2 (0.1 mmol, 0.048 g) in 10 mL methanol. The solution was stirred at boiling temperature for 20 min to obtain a clear solution and allowed to stand at room temperature.

After several days, pale-red block crystals suitable for X-ray diffraction were obtained (0.046g, 62.5%). Anal calc.(%) for $\text{Ni}_2(\text{C}_{26}\text{H}_{21}\text{N}_8\text{O}_2)(\text{C}_{26}\text{H}_{22}\text{N}_8\text{O}_2)(\text{ClO}_4)_3(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_4$: H 3.79 C 43.58 N 15.71. Found (%): H 3.85, C 43.19, N 16.05. ESI-MS: m/z 1 171.31 (calc. for $[\text{Ni}_2(\text{HL}^1)_2(\text{ClO}_4)]^+$, 1 171.17). IR (solid KBr pellet, cm^{-1}): 3 422.9 (m), 2 443.01 (m), 1 647.59 (m), 1 571.26(m), 1 507.91 (m), 1 151.70 (s), 1 120.96 (s), 1 090.71 (s), 758.22(w), 627.83(w).

1.3.3 Preparation of compound $\text{Ni}_2\text{Ag}_2(\text{HL}^3)_2(\text{ClO}_4)_2(\text{CH}_3\text{CN})_3$ (**3**)

To the combined methanol solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 0.037 g) and ligand H_2L^3 (0.1 mmol, 0.048 g), AgNO_3 (0.1 mmol, 0.017 g) dissolved in 10 mL CH_3CN solution was added dropwise. After refluxing for 30 min, the resulting solution was filtered and allowed to stand in dark. After several days, yellow block crystals suitable for X-ray diffraction were obtained (0.043g, 67.4%). Anal calc. (%) for $\text{Ni}_2\text{Ag}_2(\text{C}_{24}\text{H}_{19}\text{N}_{10}\text{O}_2)_2(\text{ClO}_4)_2(\text{CH}_3\text{CN})_3$: H 2.94, C 40.27, N 20.02. Found(%): H 3.05, C 41.19, N 19.81. IR (solid KBr pellet, cm^{-1}): 3 405.67 (m), 1 647.18 (m), 1 561.06 (m), 1 348.50(m), 1 303.50(m), 1 157.01(s), 1 083.82(s), 831.6(w), 783.59 (m), 751.37(m).

1.4 Structure determination

Suitable crystals were selected for single-crystal X-ray diffraction structural analysis and the data were collected on a Siemens SMART-CCD diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\ 073$ nm), using the SMART and SAINT programs^[13]. 45 frames of data were collected at 298K with an oscillation range of $1^\circ/\text{frame}$ and an exposure time of 10 s/frame. Indexing and unit cell refinement were based on all observed reflections from those 45 frames. The structures were solved by direct method and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1^[14]. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined by using the riding model. Crystallographic data and parameters for data collection and refinement of the compounds are summarized in Table 1.

CCDC: 640381, **1**; 640382, **2**; 640383, **3**.

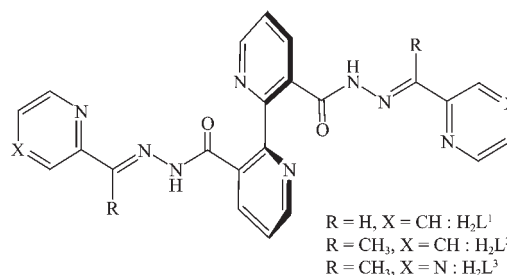
Table 1 Crystallographic data and refinement parameters for compounds 1~3

	1	2	3
Empirical formula	C ₄₉ H ₃₆ BF ₁₀ N ₁₆ Ni ₂ O ₇ P	C ₅₅ H ₃₀ Cl ₃ N ₁₆ Ni ₂ O ₂₁	C ₅₄ H ₄₂ Ag ₂ Cl ₂ N ₂₃ Ni ₂ O ₁₂
Formula weight	1 310.14	1 494.88	1 609.17
Crystal system	$P\bar{1}$	$C2/c$	$P\bar{1}$
Space group	Triclinic	Monoclinic	Triclinic
<i>a</i> / nm	1.220 4(19)	2.557 7(3)	1.162 1(3)
<i>b</i> / nm	1.320 7(2)	1.298 73(17)	1.228 3(3)
<i>c</i> / nm	2.001 7(3)	4.059 7(6)	1.246 0(3)
α / (°)	72.392(4)		69.081(4)
β / (°)	86.493(4)	92.277(3)	83.069(4)
γ / (°)	76.211(4)		75.290(4)
<i>V</i> / nm ³	2.986 2(8)	13.475(3)	1.606(7)
<i>Z</i>	2	8	1
μ / mm ⁻¹	0.75	0.762	1.339
Number of reflections measured	12 913	32 889	8111
Number of unique reflections (<i>uR</i> , <i>R</i> _{int})	9 431 (0.155 2, 0.078 2)	11 808 (0.142 6, 0.070 7)	5 579 (0.199 6, 0.074 2)
Goodness of fit (<i>S</i>)	1.022	1.127	1.044

2 Results and discussion

Following our design, the analogous ligands H₂L¹~H₂L³ (Scheme 1) are prepared in a four-step synthesis route.^[15] In the design of the ligands, the N₂O tridentate coordination sites were employed for chelating the metal ions and often, such the coordination mode was easily deprotonized on the imino group during the coordination. The ease of availability of these ligands has allowed us to systematically investigate the effects of modifications to the ligand backbone by which the precise topography of the arrays should be controlled. These ligands are constrained by their connectivity of bipyridine block acting as a bis-tridentate ligand, thus preventing from the formation of a mononuclear complex. The bis-tridentate coordination sites in the ligands looks like a pocket and the free rotation of the pocket makes two tridentate sites toward either the same direction or the opposite to correspondingly yield the molecular box and helicate. Meanwhile, the rigid nature of the bis-tridentate ligands makes them suitable for the synthesis of cyclic structure, and it can potentially be used to construct a dinuclear metallacycle when combined with a suitable metal center. Furthermore, the aggregation of metallacycles into 1D polymer can be supported by additional

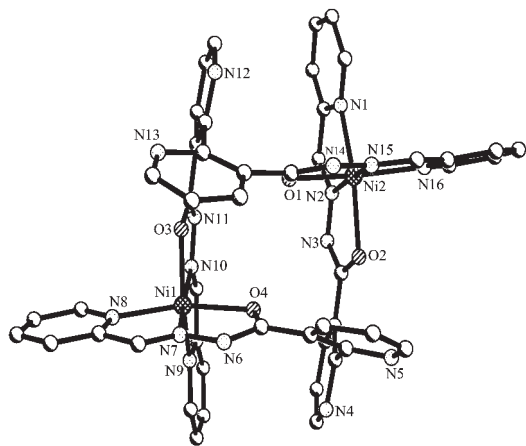
coordination sites.

Scheme 1 Chemical structures of ligand H₂L¹~H₂L³

2.1 Crystal structure of 1~2

Reaction between nickel salts and H₂L¹ or H₂L² in boiling methanol gave compounds **1** and **2**, respectively. As shown in Fig.1, these compounds were best described as double-stranded helicates with two metallic centers that occupies at the helical axis being separated about 0.601(4) and 0.628(6) nm, for **1** and **2**, respectively. The compound **1** crystallizes in the triclinic system and the whole molecule of double helicate is found in the asymmetric unit. The ligand H₂L¹ could fancily wrap around the two metal ions with the two metal centers displayed the same absolute configuration. Each metal center occupies a six-coordinated pseudooctahedral environment surrounded by N₂O pocket-like coordination sites provided by ligand anion HL⁻. The bis-tridentate ligand H₂L¹ exhibits a

trans configuration and acts as bridging ligand through 2,2'-bipyridyl block. All the bond distances in the two arms are intermediate between the corresponding single bond and double bond, indicating extensive delocalization over the entire molecular skeleton. The coordination to the metal ions also forces the twisting within the ligand H_2L^1 , the two arms are almost perpendicular with each other with the torsion angle of disubstituted bipyridyl groups is *ca.* 88° . The crystal packing of compound **1** is less compact since the observed structure adopt a pseudotetragonal arrangement of each layer. Furthermore, these layers lead to pseudohexagonal AB close-packed arrangements, and counter anions and free solvent molecules are resided in the cavities formed by the structure packing along the crystallographic *b* axis (Fig.2). From the viewpoint of chiral aggregation, the helicates with the same handedness arrange them together in a column along crystallographic *b* axis, which are interconnected via $\pi \cdots \pi$ stacking between coordinated pyridyl rings with the shortest interatomic distance of 0.332 4 nm for C48 \cdots C22A (symm code A: $+x, -1+y, +z$). Due to the fact that compound **1** is crystallized in centric space group $P\bar{1}$, it



Selected bond distances (nm) for compound **1**:

Ni1-N7 0.195 7(5), Ni1-N10 0.198 0(5), Ni1-N8 0.206 8(5),
Ni1-N9 0.208 2(5), Ni1-O3 0.208 9(4), Ni1-O4 0.210 5(4),
Ni2-N15 0.196 5(5), Ni2-N2 0.198 4(5), Ni2-O1 0.203 8(4),
Ni2-N16 0.206 8(5), Ni2-N1 0.207 7(5), Ni2-O2 0.213 0(4),
O1-C42 0.125 9(7), O2-C7 0.122 6(6), O3-C31 0.121 4(7),
O4-C18 0.123 2(7), N2-C6 0.129 0(7), N2-N3 0.135 8(6),
N3-C7 0.136 9(7), N4-C12 0.135 1(8), N6-C18 0.134 6(8),
N6-N7 0.137 3(6), N7-C19 0.128 2(8)

Fig.1 Crystal structure of $Ni_2(HL^1)_2(PF_6)(BF_4)(CH_3OH)(H_2O)_2$ (**1**) with 30% probability ellipsoids

is speculated that the 1D column-like chiral aggregates exit as a racemic mixture.

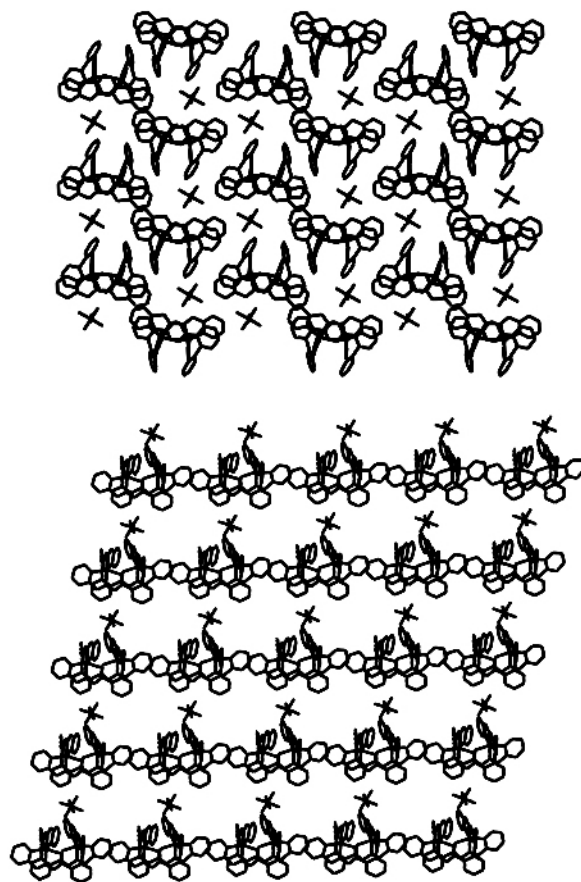
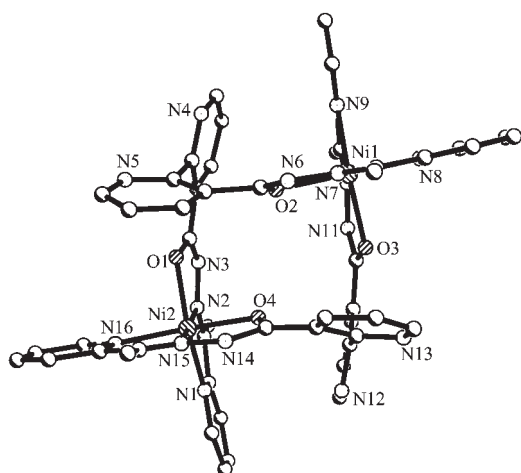


Fig.2 Crystal packing of compound **1** along crystallographic *b* axis (up) and *c* axis (down), respectively

The crystal structure of compound **2** is shown in Fig.3. The compound **2** crystallized in a monoclinic system with space group $C2/c$. The presence of three ClO_4^- anion per helicate indicates that the helicate **2** has trivalent oxidation state, the ligands lost only one of all the protons as a whole. Each Ni center adopt pseudo-octahedral configuration and is coordinated by two sets of N_2O unit. The dihedral angles between the disubstituted 2,2'-bipyridyl block is 85.7° . As shown in the compound **1**, the coordination pockets rotate in opposite position to assemble as a helicate and the metallic center has the homochirality. Based on the fact that the compound **2** crystallized in the achiral space group $C2/c$, the discrete helicate, which is inherently chiral, aggregate as a racemate of *P* for right-handed and *M* for left-handed with an equivalent makeup.



Selected bond distances (nm) for compound **2**:

Ni1-N7 0.196 3(5), Ni1-N10 0.199 7(5), Ni1-O2 0.204 2(4),
Ni1-N9 0.206 1(5), Ni1-N8 0.208 2(5), Ni1-O3 0.210 8(4),
Ni2-N2 0.195 1(6), Ni2-N15 0.197 9(5), Ni2-O1 0.203 6(4),
Ni2-N1 0.206 5(6), Ni2-N16 0.207 2(6), Ni2-O4 0.210 4(4)

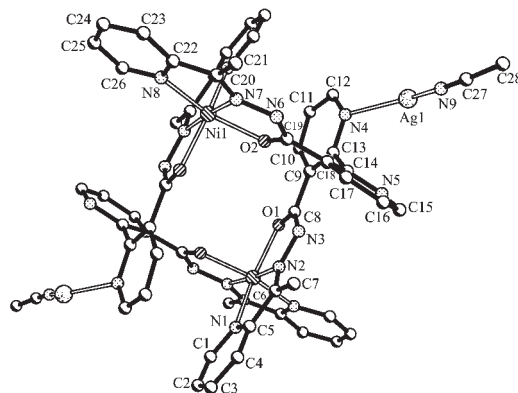
Fig.3 Crystal structure of $\text{Ni}_2(\text{HL}^2)(\text{H}_2\text{L}^2)(\text{ClO}_4)_3(\text{C}_2\text{H}_5\text{OH})(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3$ (**2**) with 30% probability ellipsoids

Clearly, the formation of stereogenic metal centers in compound **1** and **2** is fully controlled by the twisting nature of the bridging ligand. Hence, it seems that the designed ligand H_2L is suitable to assemble some metal helicate, in which the chirality of one metal center can be transferred to another one. And the structure predicability based on such the molecular clips have led to the anticipation of several dinuclear double helicates.

2.2 Crystal structure of **3**

Compound **3** is obtained by refluxing the combined $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ solution containing 1 equiv of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 1 equiv of ligand H_2L^3 and 1 equiv of AgNO_3 for 2 h in the dark. The structure of compound **3** can be described as a one-dimensional infinite polymer. A dimeric $[\text{M}_2\text{L}_2]$ cage structure is formed with the ligand bridging between the two metal centers, whose coordination environments are almost identical to that of compound **2**. The twisting mode between two tridentate pockets surprisingly results in a molecular box with the desired aryl-lined cavity. As depicted in Fig.4, the dinuclear metallamacrocyclic, $[\text{Ni}_2(\text{HL}^3)_2]$ retains the box tectonic feature different from that observed as the helical structure in the compound **2**. The intramolecular $\pi \cdots \pi$ stacking interaction was also found within the

individual box with the shortest atom \cdots atom separation of 0.358 5 nm and dihedral angle of 12.68° . It is observed that two bipyridyl N atoms on a ligand backbone can be coordinated to the different silver ions, as a consequence, the individual molecular box is interconnected by double-silver bridges to form a 1D infinite array of cages. As shown in Fig.5, the bridging Ag ion is coordinated by two N atoms from the different boxes, and the coordination are completed by a CH_3CN molecule and a disordered anion ClO_4^- . The shortest and adjacent Ag-Ag distances are 0.389 4 nm, while the separation between the Ag centers across the metallacycles are 1.246 0 nm. As shown in Fig.6, the molecular box stacks on top of each other along the crystallographical c -axis to result in the arrays of metallacycles. Furthermore, the 1D polymeric chains lie parallel each other to align themselves along the (001) direction, among which the free solvent molecules and perchlorate anions are resided(Fig.6).



Selected bond length (nm) and angles ($^\circ$):

Ni1-N4ⁱⁱ 0.197 9(6), Ni1-N8 0.199 0(6), Ni1-O2 0.204 0(7),
Ni1-O1ⁱⁱ 0.207 4(7), Ni1-N9 0.208 9(7), Ni1-N1ⁱⁱ 0.212 2(7),
N3-N4 0.1372(7), C8-O1 0.127 7(9), C19-O2 0.126 0(9),
N6-N7 0.137 2(9)
N2ⁱⁱ-Ni1-N7 176.1(2), N2ⁱⁱ-Ni1-O2 99.28(18),
N7-Ni1-O2 77.73(18), N2ⁱⁱ-Ni1-O1ⁱⁱ 77.50(19),
N7-Ni1-O1ⁱⁱ 100.04(19), O2-Ni1-O1ⁱⁱ 92.76(19),
N2ⁱⁱ-Ni1-N8 105.12(20), N7-Ni1-N8 77.89(20),
O2-Ni1-N8 155.61(20), O1ⁱⁱ-Ni1-N8 92.44(20),
N2ⁱⁱ-Ni1-N1ⁱⁱ 77.58(22), N7-Ni1-N1ⁱⁱ 104.73(22),
O2-Ni1-N1ⁱⁱ 8.96(20), O1ⁱⁱ-Ni1-N1ⁱⁱ 154.96(19),
N8-Ni1-N1ⁱⁱ 96.24(21)

Symmetry code: ⁱ $-x, 1-y, -z$; ⁱⁱ $-x, 1-y, -1-z$

Fig.4 Crystal structure of compound **3** emphasizing the coordination of Ag^+ to pyridyl N atoms with 30% probability ellipsoids

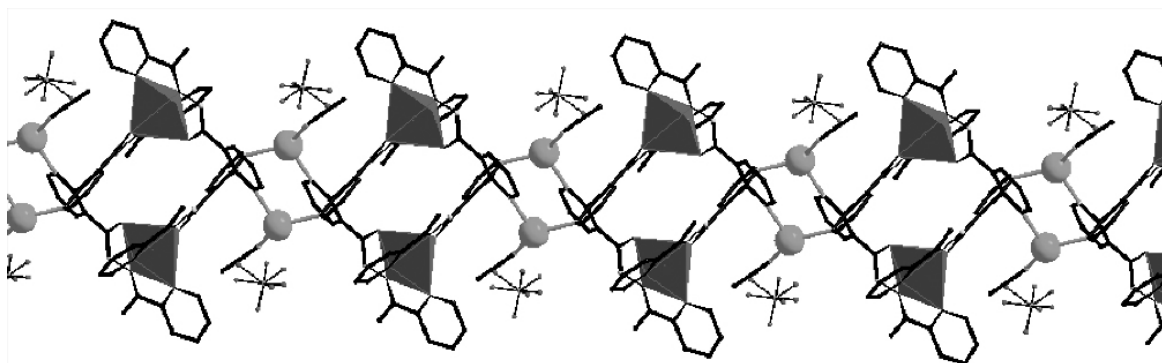


Fig.5 Polymeric structure of **3** showing the polyhedra representation of interconnected molecular box with H atoms omitted for clarity

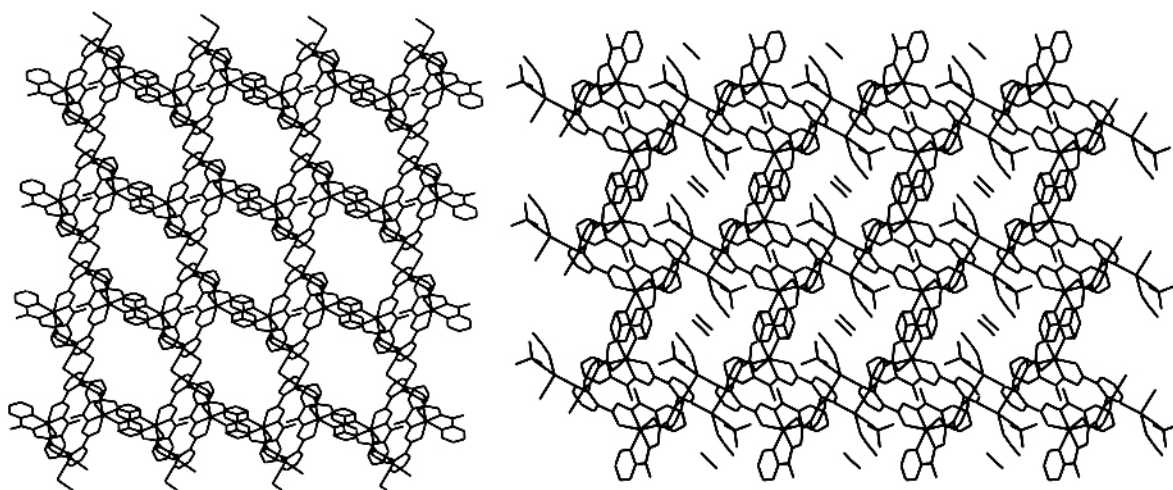


Fig.6 View of crystal packing along the *b* direction of **3** showing the porous structure, in which the anions and solvent molecules are resided

In summary, we have synthesized a series of metallocupramolecular compounds including helicate (**1**~**2**) and the 1D coordination polymer (**3**) starting from the bridging bis-tridentate ligands. Due to the flexible nature of ligand, the assembly process may produce either helicate or molecular box. This compound **3** exhibits a new 1D extended structure consisting of dinuclear metallocupramolecular cages. The structural motif and the packing of $[\text{Ni}(\text{HL}^1)](\text{AgCH}_3\text{CN}) \cdot 0.5\text{CH}_3\text{CN}$ appear to exhibit the 2D porous structure. Further studies will include investigation into the homochirality crystal materials^[16] starting from the well-programmed metal helicate and this work is in progress.

References:

- [1] (a)Lehn J M. *Supramolecular Chemistry-Concepts and Perspectives*. Weinheim: VCH, **1995**.
- [2] (a)Hannon M H, Painting C L, Errington W. *Chem. Comm.*, **1997**:307~309
(b)Blake A J, Champness N R, Khlobystov A N, et al. *Angew. Chem. Int. Ed.*, **2000**,**39**:2317~2320
- [3] Hannon M J, Painting C L, Alcock N W. *Chem. Comm.*, **1999**:2023~2025
- [4] (a)Hoffart D J, Loeb S J. *Angew. Chem. Int. Ed.*, **2005**,**44**:901~904
(b)Fuller A M, Leigh D A, Lusby P J, et al. *Angew. Chem. Int. Ed.*, **2004**,**43**:3914~3918
- [5] (a)Mobian P, Kern J M, Sauvage J P. *J. Am. Chem. Soc.*, **2003**, **125**:2016~2017
(b)Balzani V, Credi A, Langford S J, et al. *J. Am. Chem. Soc.*, **2000**,**122**:3542~3543
- [6] Ibukuro F, Kusakawa T, Fujita M. *J. Am. Chem. Soc.*, **1998**, **120**:8561~8562
- [7] Knof U, Zelewsky A V. *Angew. Chem. Int. Ed.*, **1999**,**38**:302~322
- (b)Philp D, Stoddart J F. *Angew. Chem. Ed. Engl.*, **1996**,**35**: 1155~1196

- [8] (a) Gier T E, Bu X H, Feng P Y, et al. *Nature*, **1998**, **395**:154~155
(b) Hollingsworth M D. *Science*, **2002**, **295**:2410~2412
- [9] (a) Lu J Y, Babb A M. *Inorg. Chem.*, **2001**, **40**:3261~3262
(b) Reger D L, Semeniuc R F, Smith M D. *Inorg. Chem.*, **2001**, **40**:6545~6546
(c) Lu J Y, Macias J, Lu J, et al. *Cryst. Growth & Des.*, **2002**, **2**:485~487
- [10] (a) Du M, Bu X H, Huang Z, et al. *Inorg. Chem.*, **2003**, **42**:552~559
(b) Burdakov A B, Gladkikh E A, Nefedova E V, et al. *Cryst. Growth & Des.*, **2004**, **4**:595~598
(c) Wu C D, Zhang L, Lin W B. *Inorg. Chem.*, **2006**, **45**:7278~7285
- [11] Cui Y, Ngo H L, Lin W B. *Inorg. Chem.*, **2002**, **41**:1033~1035
- [12] Alexander B, Annegret K H, Jack M H, et al. *Eur. J. Inorg. Chem.*, **2000**, **5**:823~826
- [13] *SMART and SAINT, Area Detector Control and Integration Software*, Siemens Analytical X-Ray Systems, Inc: Madison, WI, **1996**.
- [14] Sheldrick G M. *SHELXTL V5.1*, Software Reference Manual, Bruker AXS, Inc: Madison, WI, **1997**.
- [15] Wu D Y, Xie L X, Duan C Y, et al. *Dalton Trans.*, **2006**:3528~3533
- [16] (a) Sun Q Z, Bai Y, Duan C Y, et al. *Chem. Commun.*, **2006**:2777~2779
(b) Fang C J, Duan C Y, Guo D, et al. *Chem. Commun.*, **2001**:2540~2541