

含潜在异构手性双臂配体的螺旋组装和手性聚集

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摘要: 采用具有潜在异构手性的双臂配体, 双吡啶二甲基联苯-2,2'-二酰肼, 合成了 4 个双核螺旋配合物。配体与 CdI_2 和 $\text{Cu}(\text{NO}_3)_2$ 反应得到双核单螺旋化合物 **1** 和 **2**, 在化合物 **2** 中, 由于 $\text{C-H}\cdots\pi$ 和 $\pi\cdots\pi$ 的协同相互作用沿 ab 面形成单一手性的二维平面。双核双螺旋化合物 **3**(Ni(II))和 **4**(Co(II))中的金属中心表现相同的绝对构型, 说明含异构手性的配体能够把金属中心的手性从一个中心传递到另一个中心。

关键词: 晶体结构; 配合物; 螺旋组装; 手性聚集

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Helical Assembly and Chiral Aggregations Based on Atropisomeric Molecular Clips

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Abstract: Molecule clip, bis (pyridin-2-ylmethylene)biphenyl-2,2'-dicarbohydrazide, with potential atropisomeric chirality was used as helicand for construction of dinuclear helicates. Reaction of the ligand with CdI_2 or $\text{Cu}(\text{NO}_3)_2$ afforded dinuclear monohelical complexes **1** and **2** equipped with the aromatic rings, and the complex interacted each other through cooperative $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ interactions to form homochiral 2D layer along ab plane. The formation of dinuclear double helicates Ni(II) and Co(II) complexes **3** and **4** were with the metal centers exhibiting the same absolute configurations. Thus the atropisomeric chiral bridging mode is main factor for the ligand to translate chirality of metal centers from one center to another. CCDC: 615179, H_2L ; 615180, **1**; 615181, **2**; 615182, **3**; 615183, **4**.

Key words: crystal structures; complex; helical assembly; chiral aggregations

0 Introduction

Helicate was introduced by Lehn in 1987 to define the metal helixes that contain one or more ligand strands and two or more metal centers^[1]. The intrinsic character of a helix, that metal centers in a helicate have the same absolute configurations, requests that the helicand (the ligand of a helicate) should be able to translate the chirality from one metal center to another and provides a new strategy

for construction of chiral supermolecular species by introducing helicates as “building blocks”^[2-14].

We have been interested in preparation of helicates by locking the ligand in a twisted chiral bridging conformation, and investigated on the intra- and inter- helicate chirality transformation through weak uncovalent interactions^[15]. Very recently, spontaneous resolution of double helicates was achieved by incorporating achiral ligands exhibiting twisted conformation^[15-23]. It is believed that potential atropisomeric

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chirality of the ligand plays an important role in controlling the chiral assemblies. As a continuance of our research work, we reported a new strategy to construct helicate by incorporating atropisomeric molecular clips as helicand to exhibit the potential mechanism of chirality translation.

1 Experimental

1.1 Materials and methods

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 on a Perkin-Elmer 240C analytical instrument. ^1H NMR spectra on DRX500 Bruker spectrometer at 298 K with TMS as an internal reference. Electrospray mass spectra were recorded on a LCQ system (Finnigan MAT, USA) using methanol as the mobile phase.

Caution!

Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amount of material should be handled with great caution.

1.2 Synthesis of H_2L

Biphenic dihydrazide was prepared according to the procedure reported in the literature^[24]. A solution of biphenic dihydrazide (1.35 g, 5 mmol) in methanol (30 mL) was added to a methanol solution (20 mL) containing pyridine-2-carboxaldehyde (1.3 g, 11.5 mmol). After 5 drops of HOAc was added, the mixture was heated at 70 °C under magnetic stirring for 2 h. A dark-yellow precipitate formed through evaporation under vacuum, which was collected by filtration, washed with ether, and dried over P_2O_5 in vacuum. The solid (yield: 80%) is air stable, soluble in DMSO, and insoluble in water. Anal. calc. (%) for $(\text{H}_2\text{L})\cdot 3\text{H}_2\text{O}$, $\text{C}_{26}\text{H}_{26}\text{N}_6\text{O}_5$: C, 62.14; H, 5.22; N, 16.72. Found (%): C, 61.67; H, 5.02; N, 16.61. ^1H NMR ($\text{DMSO}-d_6$) δ_{H} 12.23(1H, s, NH), 8.48(1H, d, $J=5$ Hz, H_1), 8.09(1H, s, H_6), 7.82(2H, d, $J=5$ Hz, $\text{H}_{4,12}$), 7.65(1H, d, $J=10$ Hz H_9), 7.56(1H, t, $J=7.5$ Hz, H_3), 7.52(1H, t, $J=7.5$ Hz, H_{11}), 7.36(1H, t, $J=5$ Hz, H_{11}), 7.28(1H, t, $J=5$ Hz, H_{10}). ESI-MS: $m/z=449[\text{L}-\text{H}]^+$. IR (solid KBr pellet): 3 405 (m), 3 193(m), 3 053(m), 1 700(s), 1 653(s), 1 560(s), 1 469

(m), 1 437(w), 1 353(w), 1 290(s), 1 244(w), 1 153(s), 1 114(w), 1 068(w), 1 002(w), 944(w), 924(w), 849(w), 768 (m), 707(w), 626(w).

1.3 Synthesis of complex $\text{Cd}_2\text{I}_4(\text{H}_2\text{L})\cdot 2\text{DMF}$ (1)

A solution of CdI_2 (37 mg, 0.1 mmol) in 10 mL of methanol was added to H_2L (45 mg, 0.1 mmol) dissolved in methanol (10 mL) with stirring at ambient temperature. The resulting colorless solution was filtered. The filtrate was evaporated to dryness, and the residue was redissolved in the minimum volume of DMF (5 mL) and placed to evaporate. The product was obtained as pale-yellow rectangular plates suitable for X-ray structural determination after one month (yield: 25%). Anal. Calcd. (%) for $\text{Cd}_2\text{I}_4(\text{H}_2\text{L})\cdot 2\text{DMF}$, $\text{C}_{32}\text{H}_{34}\text{N}_8\text{O}_4\text{Cd}_2\text{I}_4$: C, 28.96; H, 2.58; N, 8.44. Found (%): C, 29.21; H, 2.39; N, 8.49. IR (solid KBr pellet): 3 519(m), 3 140(m), 3 013(m), 1 648(s), 1 568(m), 1 520 (s), 1 470(m), 1 437(w), 1 352(m), 1 276(s), 1 254(s), 1 155 (s), 1 095(m), 1 010(w), 927(w), 779(m), 570(w), 528(w).

1.4 Synthesis of complex $\text{Cu}_2(\text{NO}_3)_2(\text{L})(\text{CH}_3\text{OH})_2$ (2)

A solution of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (24 mg, 0.1 mmol) in 10 mL methanol was slowly added to H_2L (45 mg, 0.1 mmol) dissolved in methanol (10 mL) with stirring. The solution was filtered and kept for crystallization at ambient temperature. Dark blue crystals suitable for X-ray analysis were obtained after 1 week (yield: 30%). Anal. Calcd. (%) for $\text{Cu}_2(\text{NO}_3)_2(\text{L})(\text{CH}_3\text{OH})_2$, $\text{C}_{28}\text{H}_{26}\text{Cu}_2\text{N}_8\text{O}_{10}$: C, 44.15; H, 3.44; N, 14.71. Found (%): C, 44.03; H, 3.48; N, 14.89. IR (solid KBr pellet): 3 481 (m), 1 606(w), 1 566(w), 1 461(m), 1 427(m), 1 378(s), 1 299(s), 1 213(w), 1 152(m), 1 091(w), 1 018(w), 922(w), 775(w), 752(w).

1.5 Synthesis of complex $\text{Ni}_2(\text{HL})(\text{H}_{1.5}\text{L})(\text{BF}_4)_2(\text{PF}_6)_{0.5}(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3$ (3)

A solution of $\text{Ni}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$ (34 mg, 0.1 mmol) and KPF_6 (18 mg, 0.1 mmol) in 10 mL methanol and H_2L (45 mg, 0.1 mmol) in methanol (10 mL) was treated as for **2**. The product was obtained as red-brown rectangular plates (yield: 40%). Anal. Calcd. (%) for $\text{Ni}_2(\text{HL})(\text{H}_{1.5}\text{L})(\text{BF}_4)_2(\text{PF}_6)_{0.5}(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3$, $\text{C}_{53}\text{H}_{46}\text{B}_2\text{F}_{11}\text{N}_{12}\text{Ni}_2\text{O}_8\text{P}_{0.50}$: C, 47.42; H, 3.45; N, 12.52. Found (%): C, 47.13; H, 3.88; N, 12.65. IR (solid KBr pellet): 3 418

(m), 1 624(s), 1 532(m), 1 468(m), 1 352(s), 1 305(s), 1 218(w), 1 153(s), 1 079(s), 915(w), 761(m), 520(w), 484(w).

1.6 Synthesis of complex $\text{Co}_2(\text{HL})_2(\text{ClO}_4)_2$ (**4**)

A solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37 mg, 0.1mmol) in 10 mL methanol and H_2L (45mg, 0.1mmol) in methanol (10 mL) was treated as for **2**. The product was obtained as dark red crystals (yield: 40%). Anal. Calcd. (%) for $\text{Co}_2(\text{HL})_2(\text{ClO}_4)_2$, $\text{C}_{52}\text{H}_{36}\text{Cl}_2\text{Co}_2\text{N}_{12}\text{O}_{12}$: C, 51.63; H, 3.00; N, 13.89. Found (%): C, 51.51; H, 3.41; N, 14.05. IR (solid KBr pellet): 3 418 (s), 1 612 (s), 1 565 (m), 1 531 (m), 1 470 (w), 1 352 (m), 1 307(s), 1 218(w), 1 145(s), 1 088(s), 912(w), 765(m), 695(w), 629(m), 538(w). Crystal of **4** was mounted in a glass capillary with the mother liquor to prevent the loss of the structural solvents during X-ray diffraction data collection.

1.7 Crystal 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-monochromatic Mo $K\alpha$ radiation $\lambda = 0.071\ 073$ nm, using SMART and SAINT^[25] programs. The structures were solved by direct methods and refined on F^2 by using full-matrix least-squares methods

with SHELXTL version 5.1^[26]. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined by using the riding model. For complex **3**, one of the BF_4^- anion was refined disordered. Each F atom was disordered in three positions with the site occupancy factor (s.o.f.) were fixed at 0.55, 0.25 and 0.20, respectively. Also, the B-F separations and F-B-F angles were constrained to fit the ideal tetrahedron with the thermal parameter constrained as similar for the neighboring atoms. For complex **4**, the two perchlorate anions were refined disordered. In detail, the three oxygen atoms of one perchlorate anion were disordered in two positions with the s.o.f. were fixed at 0.5. The four oxygen atoms of another were all refined disordered. The s.o.f. was fixed at 0.5, and restraints were used to fit the ideal tetrahedron and the thermal parameters were also constrained softly. In addition, the methanol molecules in complexes **3** and **4** were refined disordered. Details of the data collection, structure solution and refinement were given in Table 1.

CCDC: 615179, H_2L ; 615180, **1**; 615181, **2**; 615182, **3**; 615183, **4**.

Table 1 Crystallographic data for H_2L and complexes **1**~**4**

	H_2L	1	2	3	4
Empirical formula	$\text{C}_{26}\text{H}_{26}\text{N}_6\text{O}_5$	$\text{C}_{32}\text{H}_{34}\text{Cd}_2\text{I}_4\text{N}_8\text{O}_4$	$\text{C}_{28}\text{H}_{26}\text{Cu}_2\text{N}_8\text{O}_{10}$	$\text{C}_{53}\text{H}_{46}\text{B}_2\text{F}_{11}\text{N}_{12}\text{Ni}_2\text{O}_8\text{P}_{0.50}$	$\text{C}_{53.5}\text{H}_{42}\text{Cl}_2\text{Co}_2\text{N}_{12}\text{O}_{13.5}$
Formula weight	502.53	1 327.07	761.65	1 342.54	1 257.75
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a / nm	0.837 0(2)	2.189 6(2)	1.729 5(2)	1.156 2(2)	1.981 9(3)
b / nm	0.868 1(2)	0.941 76(9)	0.900 11(9)	1.362 8(3)	1.588 3(3)
c / nm	1.791 9(5)	2.106 7(2)	2.034 7(2)	3.836 7(8)	1.744 3(3)
α / (°)	79.523(5)				
β / (°)	88.226(6)	103.969(2)	96.984(2)	96.696(4)	97.937(3)
γ / (°)	85.725(5)				
V / nm ³	1.276 5(6)	4.215 6(7)	3.143 9(5)	6.004(2)	5.438 3(15)
Z	2	4	4	4	4
$F(000)$	528	2 488	1 552	2 738	2 572
μ / mm ⁻¹	0.093	3.981	1.422	0.737	0.786
Number of reflections measured	6 384	10 137	7 537	29 348	26 548
Number of unique reflections	4 409	3 704	2 777	10 565	9 531
R_{int}	0.053 2	0.100 5	0.072 5	0.097 3	0.053 7

Continued Table 1

R_1	0.055 9	0.044 5	0.031 0	0.066 8	0.057 1
wR_2 (all data)	0.114 9	0.132 3	0.084 2	0.161 1	0.132 8
Goodness-of-fit	1.011	1.001	1.009	0.977	0.994

2 Results and discussion

2.1 Structure of ligand H_2L

The ligand H_2L was prepared by mixing biphenic dihydrazide with 2-pyridinecarldehyde. Crystals suitable for X-ray diffraction were obtained through slow evaporating a methanol solution in air. As shown in Fig.1, the non-planarity of the whole moiety apparently arising from steric hindrance of closely spaced benzene rings leads to the two pyridine moieties position on twisted conformation of the biphenyl fragment, and gives rise to a helix. The main source of the helical twist in the ligand is the dihedral angle of 73° about the benzene rings. Like the related benzil-based Schiff-based ligands^[15c,15d], the special helical conformation of the ligand provides an opportunity to translate chirality from one metal center to the other, forming helical species^[27]. The C-N and N-N bond distances are all intermediate within the normal single and double bonds, indicating the extensive delocalization of the whole moiety. Intramolecular hydrogen bonds of the type $N(3)-H(3A) \cdots O(2)$ with the $N \cdots O$ separation being 0.293 nm and $N-H \cdots O$ angle being 168° , respectively, are found to stabilize the helical conformation.

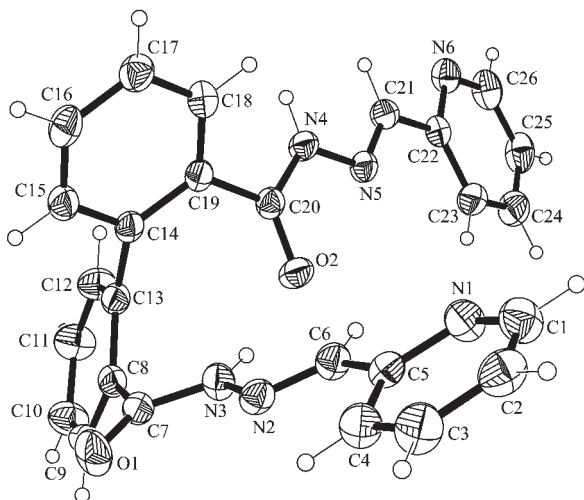
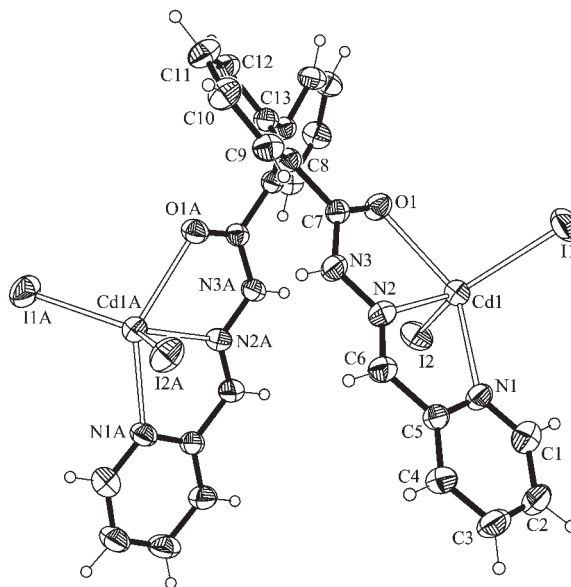


Fig.1 Molecular structure of H_2L with the atomic-numbering scheme

2.2 Structure of single helical complex **1**

Reaction of ligand H_2L with CdI_2 yielded complex **1**, which crystallized in a monoclinic crystal system. As shown in Fig.2, molecules of complex **1** also exhibit a helical confirmation with two symmetric related $Cd(II)$ coordination moieties being positioned on the opposite sides. The atropisomerically chiral bridging mode of the ligand translates the chirality of the first metal center to the second one. The twist angle between two benzene rings (*ca.* 59°) is significantly smaller than that in free ligand (73°). Each $Cd(II)$ center is bound by one tridentate N_2O of one arms and two iodide atoms to attain a distorted trigonal bipyramidal geometry with the two iodide atoms and the imine nitrogen atom comprising the equatorial plane, the oxygen atom and pyridine nitrogen atom positioned at the axial positions. The $Cd \cdots Cd$ separation is *ca.* 0.692 nm. Hydrogen bonds are also found between amide groups NH and oxygen atom of the DMF molecules with the $N(3) \cdots O(2)$ separation being 0.288 nm and $N(3)-H(3B) \cdots O(2)$ angle of



Symmetry code A: $1-x, y, 0.5-z$

Fig.2 Molecular structure with atomic-numbering scheme of complex **1**

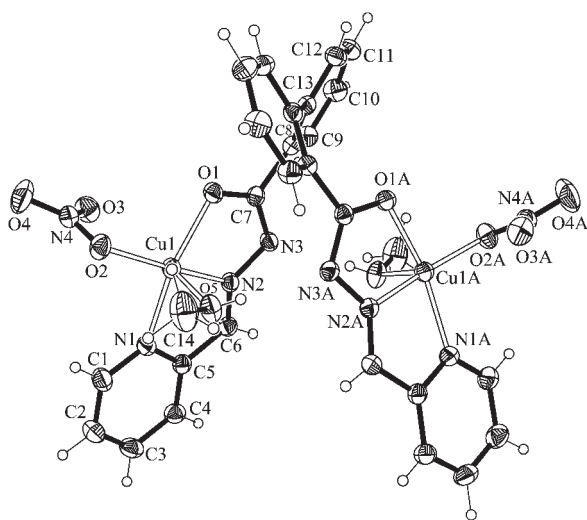
131° respectively. It seems that the presence of the solvent DMF molecules weakens the interhelicate interactions, and leads to the helicate packing in the normal $C2/c$ space group with the P- and M- helicates arrayed alternately to give the achiral crystal^[28].

2.3 Structure of single helical complex 2

Reaction of $\text{Cu}(\text{NO}_3)_2$ to replace CdI_2 with the ligand gave complex **2**. Similarly, complex **2** (Fig.3) also exhibits a dinuclear monohelical fashion with the twist angle between the two benzene rings (*ca.* 52°). Each copper (II) ion is coordinated in a tetragonal pyramide (topological parameter of 0.06)^[29] with pyridine N(1), imine nitrogen N(2) atoms, the carbonyl O(1) and nitrate oxygen O(5) atoms comprising the basal plane and the methanol oxygen atom positioned the apical position. The measured C(7)-O(1) bond distance of 0.127 2(2) nm is longer than 0.121 3(6) nm in complex **1** and 0.120 7(3) nm in free ligand, indicating that the ligands lose their amide protons and act as mononegative ligands. Intramolecular hydrogen bonds between the coordination methanol group O(5) and the deprotonated imine nitrogen N(3) are also found to stabilize the helical fashion with the O-H...N angle of 178° and O...N separation being 0.279 nm, respectively. It is believed that the two-fold hydrogen bonding induces the resulting helicate with smaller twisted angle and shorter metal-metal separation (Cu...Cu separation of 0.59 nm vs 0.69 nm of Cd...Cd separation

ion in complex **1**).

Usually, the aromatic groups equipped on chiral species have the potential for production directional $\pi \cdots \pi$ stacking and C-H... π interactions which are cooperative each other, and if such kind of interactions is strong enough, chiral supramolecular species could be created. As shown in Fig.4, the clips-like molecules in complex **2** interact one-by-one to form one dimensional chain with the pyridine rings in one side and the benzene rings in another side through cooperative C-H... π interactions. The C-H... π interaction is found between the C(12) and the symmetric related (Symm. code: $-x, 1+y, 1/2-z$) coordinated pyridine-imine plane with the M (midpoint of the interacted plane(C(1) to N(1))) and C(12)-H...M angle being 0.287 nm and 144°, respectively. Since the Cu(II) centers in the whole chain exhibit the same absolute configuration, the one-dimensional species is chiral. Meanwhile, there are interchain weak C-H...O hydrogen bonds between the coordinated nitrate anion and the CH=N group which connect the homochiral chains into a homochiral two-dimensional sheet with the metal centers in the sheet bearing the same absolute configuration. The O(3)...C(6B) separation and O(3)...H-C(6B) angle are 0.316 nm and 129°, respectively (symm. code B: $1/2-x, 1/2+y, 1/2-z$). However, due to the lack of strong enough inter-sheet interaction, the chiral layers glide each other along the *c*-direction with opposite chiral sheets stacked alternately and thus quench the chirality as a whole^[30].



Symmetry code A: $-x, y, 0.5-z$

Fig.3 Molecular structure of the helical complex **2**

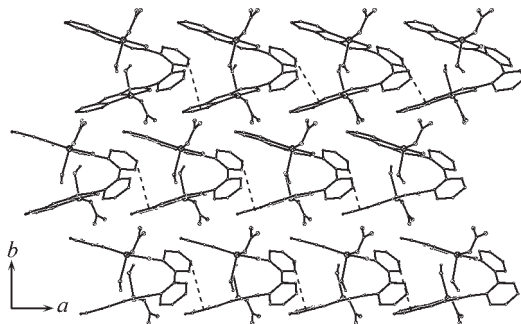


Fig.4 View of the homochiral two-dimensional layers along *ab* plane in complex **2** showing intermolecular interactions in the crystal packing

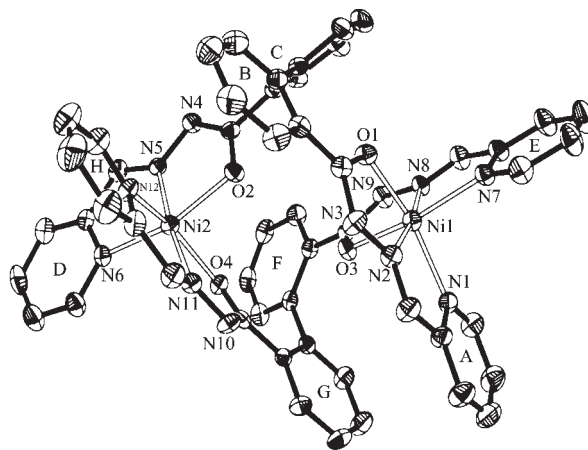
The aim of crystal engineering is to recognize and design synthons which are robust enough to be

exchanged from one structure to another, which should be general and predictable. Both complexes **1** and **2** are crystallized in monoclinic space group $C2/c$ with the C_2 symmetry of the ligand remained in the dinuclear complexes which induces dinuclear species exhibiting two same configured metal centers. Clearly, the formation of stereogenic metal centers in **1** and **2** is fully controlled by the configuration of bridging ligand. That is to say, one polydentate ligand H_2L , as an atropisomeric molecular clips, completes the task of formation helicates through the twist of the ligand itself. Consequently, the atropisomeric molecular clips can be used as a synthon for helicate formation. And the structural predicability based on such kind of molecular chips have been led to the anticipation of several dinuclear double helicates and other helical architectures.

2.4 Structure of double helical complexes **3** and **4**

To support the above hypothesis, $Ni(BF_4)_2$ and $Co(ClO_4)_2$ were used to substitute the copper salt for the formation of helicates **3** and **4**. As shown in Fig.5, molecules of **3** and **4** are dinuclear double helicates with the two metal centers in one molecule exhibited the same configuration and the chirality of the ligands are also replicated. These two chelating units coordinate to a nickel(II) ion in a mer configuration with pairs of carbonyl O atoms and pyridyl N atoms bearing a cis relationship, whereas the imine N atoms are trans to each other as found in related metal complexes. The measured C-O bond distances of *ca.* 0.124 nm in an average are between the formal single and double bonds, which indicates that the ligands might partly loss their imine proton and act as mononegative ligands. An interesting feature of the dication is that four arms of the two ligands span both the nickel ions. One arm of a ligand passes above the $Ni \cdots Ni$ axis and the other of the same ligand goes beneath, with the cation appearing more like a box than a double helix. There are also intramolecular $\pi \cdots \pi$ stacking interactions between the pyridine rings A, H and the benzene rings B, G, respectively. Although these stacking interactions are weak, compared to the coordination bonds, it could be

suggested that these kinds of interactions should be important in the molecular assembly and molecular packing^[31].



Hydrogen atoms and anions are omitted for clarity

Fig.5 Molecular structure of the double helical complex **3**

Complex **3** crystallized in a centro-symmetry space group $P2_1/c$, molecules connect each other to form one dimensional homochiral chains through cooperative $C-H \cdots \pi$ and synergic $\pi \cdots \pi$ interactions (Fig.6). The pyridine ring A interacts with the pyridine rings H and D in the neighbour helicate (symm. code: $x, 1+y, z$) through $\pi \cdots \pi$ stacking interactions and $C-H \cdots \pi$ interactions, respectively, to connect the helicates together in a homochiral chain. The $\pi \cdots \pi$ stacking interaction is characterized by the dihedral angle of 17.5° between stacked pairs (A and H) with the shortest interplane atom \cdots atom separation being 0.335 nm, and the $C-H \cdots \pi$ interaction is defined by $H \cdots M$ (midpoint of the interacted plane D) separation and $C(2)-H(2A) \cdots M$ angle being 0.259 nm and 171.4° , respectively. At the same time, the chains with one chirality interacted (symm. code $1-x, -y, -z$)

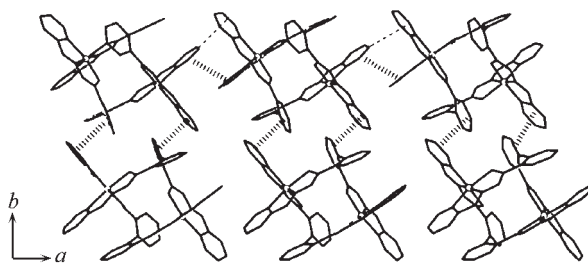


Fig.6 View of the packing structure of complex **3** through $C-H \cdots \pi$ and $\pi \cdots \pi$ synergic interactions

Table 2 Selective bond length (nm) and angles ($^{\circ}$)

Ligand H ₂ L					
O(1)-C(7)	0.120 7(3)	O(2)-C(20)	0.122 1(3)	N(3)-C(7)	0.135 9(3)
N(4)-C(20)	0.135 0(3)	N(2)-N(3)	0.136 2(3)	N(4)-N(5)	0.137 1(3)
N(5)-C(21)	0.127 1(3)	N(2)-C(6)	0.126 9(3)		
Complex 1					
Cd(1)-N(2)	0.232 9(4)	Cd(1)-N(1)	0.243 6(4)	Cd(1)-O(1)	0.246 1(3)
Cd(1)-I(1)	0.268 3(1)	Cd(1)-I(2)	0.269 3(1)	O(1)-C(7)	0.121 3(6)
N(2)-C(6)	0.126 9(6)	N(2)-N(3)	0.135 2(6)	N(3)-C(7)	0.136 6(6)
N(2)-Cd(1)-N(1)	67.8(2)	N(1)-Cd(1)-O(1)	133.9(1)	N(2)-Cd(1)-O(1)	66.1(1)
N(1)-Cd(1)-I(1)	102.6(1)	N(2)-Cd(1)-I(1)	121.8(1)	N(2)-Cd(1)-I(2)	111.0(1)
O(1)-Cd(1)-I(1)	100.0(1)	O(1)-Cd(1)-I(2)	97.8(1)	N(1)-Cd(1)-I(2)	99.8(1)
I(1)-Cd(1)-I(2)	127.0(1)				
Complex 2					
Cu(1)-N(2)	0.192 4(2)	Cu(1)-O(2)	0.195 6(2)	Cu(1)-O(1)	0.199 4(2)
Cu(1)-N(1)	0.203 6(2)	Cu(1)-O(5)	0.2247(2)	O(1)-C(7)	0.127 2(2)
N(2)-C(6)	0.127 1(3)	N(2)-N(3)	0.137 2(2)	N(3)-C(7)	0.133 2(3)
N(2)-Cu(1)-O(2)	168.8(1)	N(2)-Cu(1)-O(1)	79.0(1)	N(2)-Cu(1)-N(1)	80.2(1)
O(2)-Cu(1)-O(1)	100.3(1)	O(1)-Cu(1)-N(1)	158.0(1)	O(2)-Cu(1)-N(1)	98.8(1)
O(2)-Cu(1)-O(5)	90.2(1)	N(2)-Cu(1)-O(5)	100.9(1)		
Complex 3					
Ni(1)-N(8)	0.198 5(4)	Ni(1)-N(2)	0.198 9(4)	Ni(1)-O(1)	0.206 4(4)
Ni(1)-O(3)	0.207 5(3)	Ni(1)-N(7)	0.208 2(5)	Ni(1)-N(1)	0.209 5(5)
Ni(2)-N(5)	0.195 8(4)	Ni(2)-O(2)	0.202 5(3)	Ni(2)-N(3)	0.207 6(4)
Ni(2)-N(11)	0.197 4(4)	Ni(2)-O(2)	0.202 5(3)	Ni(2)-N(12)	0.207 6(4)
Ni(2)-N(6)	0.207 7(4)	Ni(2)-O(4)	0.215 0(3)	O(1)-C(7)	0.123 8(6)
O(2)-C(20)	0.126 4(6)	O(3)-C(33)	0.123 1(6)	O(4)-C(46)	0.124 4(6)
N(8)-Ni(1)-N(2)	172.2(2)	N(8)-Ni(1)-O(1)	98.3(2)	N(2)-Ni(1)-O(1)	76.6(2)
N(5)-Ni(2)-N(11)	173.2(2)	N(5)-Ni(2)-O(2)	77.9(2)	N(11)-Ni(2)-O(2)	95.3(2)
Complex 4					
Co(1)-N(2)	0.183 8(2)	Co(1)-N(8)	0.185 2(2)	Co(1)-O(3)	0.187 5(2)
Co(1)-O(1)	0.187 9(2)	Co(1)-N(7)	0.191 7(2)	Co(1)-N(1)	0.192 5(3)
Co(2)-N(11)	0.185 0(2)	Co(2)-N(5)	0.185 5(2)	Co(2)-O(2)	0.187 2(2)
Co(2)-O(4)	0.187 9(2)	Co(2)-N(12)	0.192 1(2)	Co(2)-N(6)	0.192 2(2)
N(2)-Co(1)-N(8)	174.3(1)	N(2)-Co(1)-O(3)	93.8(1)	N(8)-Co(1)-O(3)	82.2(1)
N(2)-Co(1)-O(1)	82.2(1)	N(11)-Co(2)-N(5)	172.2(1)	N(11)-Co(2)-O(2)	92.1(1)
N(5)-Co(2)-O(2)	81.7(1)	N(11)-Co(2)-O(4)	81.8(1)		

the chains with opposite handedness through $\pi \cdots \pi$ stacking interactions to form two-dimensional racemic sheets with the dihedral angle about 19.8° and the shortest interplanar atom \cdots atom distance separation of 0.332 nm, respectively.

As for complex **4**, which crystallized in space group $C2/c$, there are no obvious intermolecular $\pi \cdots \pi$ interactions involving the aromatic rings. The crystal packing is simply controlled by the weak electrostatic interactions with the anions.

In summary, a series of helical structural complexes containing biphenyl ligand H_2L (bis(pyridin-2-ylmethylene) biphenyl-2,2'-dicarbohydrazide) were readily assembled from the known fashion that the ligands wrap around and coordinate to transition-metal ions^[30,31]. Coordinated to the metal centers in a bridge mode, the atropisomer chirality of the ligand is fixed, and the chirality of the metal centers could be translate from one metal center to another. Such synthons are stable enough in different metal centers with different coordination environment. Hydrogen-bonding, $C-H \cdots \pi$ and / or $\pi \cdots \pi$ interactions are observed in the complexes, which facilitate efficient in crystal structures and packing.

References:

- [1] Lehn J M, Rigault A, Siegel J, et al. *Proc. Natl. Acad. Sci., U.S.A.*, **1987**,2565~2568
- [2] Albrecht M, Dehn S, Fröhlich R. *Angew. Chem. Int. Ed. Engl.*, **2006**,45:2792~2794
- [3] Baylies C J, Riis-Johannessen T, Harding L P, et al. *Angew. Chem. Int. Ed. Engl.*, **2005**,44:6909~6912
- [4] Xu J, Parac T N, Raymond K N. *Angew. Chem., Int. Ed. Engl.*, **1999**,38:2878~2882
- [5] Albrecht M, Kotila S. *Angew. Chem., Int. Ed. Engl.*, **1995**,34:2134~2137
- [6] Kersting B, Meyer M, Powers R E, et al. *J. Am. Chem. Soc.*, **1996**,118:7221~7222
- [7] Hutin M, Frantz R, Nitschke J R. *Chem. Eur. J.*, **2006**,12:4077~4082
- [8] Telfer S G, Kuroda R, Lefebvre J, et al. *Inorg. Chem.*, **2006**,45:4592~4601
- [9] Serr B R, Andersen K A, Elliott C M, et al. *Inorg. Chem.*, **1988**,27:4499~4504
- [10](a) Amabilino D B, Stoddart J F. *Chem. Rev.*, **1995**,95:2725~2828
(b) Yashima E, Maeda K, Okamoto Y. *Nature*, **1999**,399:449~451
- [11](a) Lehn J M. *Supramolecular Chemistry*, Weinheim: VCH Press, **1995**.
(b) Piguet C, Bernardinelli G, Hopfgartner G. *Chem. Rev.*, **1997**,97:2005~2062
(c) Albrecht M. *Chem. Rev.*, **2001**,101:3457~3498
(d) Bunzli J C G, Piguet C. *Chem. Rev.*, **2002**,102:1897~1928
(e) Lawrence D S, Jiang T, Levett M. *Chem. Rev.*, **1995**,95:2229~2260
- [12](a) Cantuel M, Bernardinelli G, Muller G, et al. *Inorg. Chem.*, **2004**,43:1840~1849 and references therein
(b) Nanda K K, Mohanta S, Flörke U, et al. *J. Chem. Soc., Dalton Trans.*, **1995**:3831~3836
- [13] Nakano T, Okamoto Y. *Chem. Rev.*, **2001**,101:4013~4038
- [14](a) Cui Y, Joong S, Lin W. *J. Am. Chem. Soc.*, **2003**,125:6014~6015
(b) Fu Y T, Lynch V M, Lagow R J. *J. Chem. Soc., Chem. Commun.*, **2004**:1068~1069
(c) Yamaguchi T, Yamazaki F, Ito T. *J. Am. Chem. Soc.*, **2001**,123:743~744
(d) Vishweshwar P, Thaimattan R, Jaskolski M, et al. *J. Chem. Soc., Chem. Commun.*, **2002**:1830~1831
(e) Mukherjee A, Saha M K, Nethaji M, et al. *J. Chem. Soc., Chem. Commun.*, **2004**:716~717
(f) Song Y, Yu J, Li Y, et al. *Angew. Chem. Int. Ed.*, **2004**,43:2399~2402 and references therein
(g) Fraser C S A, Eisler D J, Jennings M C, et al. *J. Chem. Soc., Chem. Commun.*, **2002**:1224~1225
- [15](a) Fang C J, Duan C Y, Guo D, et al. *Chem. Commun.*, **2001**:2540~2541
(b) Fang C J, Duan C Y, He C, et al. *Chem. Commun.*, **2000**:1187~1188
(c) Bai Y, Duan C Y, Cai P, et al. *Dalton Trans.*, **2005**:2678~2680
(d) Sun Q Z, Bai Y, He G J, et al. *Chem. Commun.*, **2006**:2777~2778
- [16] Bermejo M R, González-Noya A M, Pedrido R M, et al. *Angew. Chem. Int. Ed.*, **2005**,44:4182~4187
- [17] Lewiński J, Zachara J, Justyniak I, et al. *Coord. Chem. Rev.*, **2005**,249:1185~1199
- [18] Piguet C, Borkovec M, Hamacek J, et al. *Coord. Chem. Rev.*, **2005**,249:705~726
- [19] Knof U, Von Zelewsky A. *Angew. Chem. Int. Ed. Engl.*, **1999**,38:302~322
- [20] Hamacek J, Blanc S, Elhabiri M, et al. *J. Am. Chem. Soc.*, **2003**,125:1541~1550
- [21] Habermehl N C, Angus P M, Kilah N L, et al. *Inorg. Chem.*, **2006**,45:1445~1462
- [22] Williams A. *Chem. Eur. J.*, **1997**,3:15~19
- [23] Provent C, Williams A F. in *Transition Metals in Supramolecular Chemistry* (Ed.: J. P. Sauvage). New York: Wiley, **1999**. 135
- [24](a) Kalb L, Grob O. *Ber.*, **1926**,69:736~739
(b) Labriola R. *J. Org. Chem.*, **1940**,5:329~333
- [25] SMART and SAINT, Area Detector Control and Integration Software; Siemens Analytical X-ray Systems, Inc.: Madison,

- WI, **1996**.
- [26]Sheldrick G M. *SHELXTL V5.1, Software Reference Manual*, Bruker, AXS, Inc.: Madison, WI, **1997**.
- [27](a)Gieck C, Derstroff V, Block T, et al. *Chem. Eur. J.*, **2004**, **10**:382~392
- (b)Erxleben A. *Inorg. Chem.*, **2001**,**40**:2928~2931
- (c)Childs L J, Pascu M, Clarke A J, et al. *Chem. Eur. J.*, **2004**, **10**:4291~4300
- [28]Custelcean R, Gorbunova M G. *Cryst. Eng. Comm.*, **2005**,**7**: 297~301
- [29]Addison A W, Rao T N, Reedijk J, et al. *J. Chem. Soc., Dalton Trans.*, **1984**:1349~1356
- [30]Brock C P, Schweizer W B, Dunitz J D. *J. Am. Chem. Soc.*, **1991**,113:9811~9820
- [31](a)Mo H, Fang C J, Duan C Y, et al. *J. Chem. Soc., Dalton Trans.*, **2003**:1229~1234
- (b)Mo H, Guo D, Duan C Y, et al. *J. Chem. Soc., Dalton Trans.*, **2002**:3422~3424
- (c)Guo D, He C, Duan C Y, et al. *New J. Chem.*, **2002**,**26**: 796~802
- (d)Guo D, Pang K L, Duan C Y, et al. *Inorg. Chem.*, **2002**,**41**: 5978~5985