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Article

Design and Crystal Structures of Triple Helicates with Crystallographic Idealized D_3 Symmetry: The Role of Side Chain Effect on Crystal Packing

Guo Dong, Pang Ke-liang, Duan Chun-ying,* He Cheng, and Meng Qing-jin*

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China

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Novel crystallographic D_3-symmetric binuclear triple molecular helices $[Co_2L^1_3][BF_4]_4$ (**1**), $[Zn_2L^1_3][BF_4]_4$ (**2**), $[Mn_2L^1_3][BF_4]_4$ (**3**), $[Co_2L^2_3][BF_4]_4$ (**4**), $[Zn_2L^2_3][BF_4]_4$ (**5**), and $[Mn_2L^2_3][BF_4]_4$ (**6**) have been achieved to establish the side chain effect on molecular packing, where L^1 is $[(C_5H_4N)C(CH_3){=}N{-}(C_6H_4){-}]_2CH_2$ and L^2 is $[(C_5H_4N)C(CH_3){=}N{-}(C_6H_4){-}]_2O$, respectively. Crystal structure analyses show that each helix crystallizes in a hexagonal crystal system with space group $P\bar{3}c1$ and the general axis of the helix occupies the crystallographic 3-fold axial position with the other three crystallographic 2-fold symmetries perpendicular to it. Each metal center is bound to three pyridylimine units to attain C_3 pseudooctahedral coordination geometry with respective equivalent metal–N (CH=N) and metal–N (pyridyl) bonds. It is speculated that the existence of the methyl group might minimize the potential intermolecular interactions, which would be the essential factor controlling the helices formed in idealized crystallographic D_3 symmetry. Moreover, crystallographic idealized C_3-symmetric helicates $[Co_2L^3_3][BF_4]_4$ (**7**), $[Zn_2L^3_3][BF_4]_4$ (**8**), $[Ni_2L^3_3][BF_4]_4$ (**9**), and $[Cu_2L^3_3][BF_4]_4$ (**10**) were also structurally characterized for comparison, where L^3 is $[(C_5H_4N)C(CH_3){=}N{-}]_2$. All the results indicate that the existence of the methyl group in the side chain of aromatic ligands could effectively reduce the potential π–π intermolecular interactions and the side chain effect of the methyl group in crystal packing is robust enough to be exchanged from one network structure to another, which ensures the generality and predictability of the crystallographic idealized symmetry formation to a certain extent.

Introduction

Crystal engineering—the planning and construction of crystalline supramolecular architectures from modular building blocks—permits the rational design of functional molecular materials that exhibit technologically useful behavior[1] such as conductivity and superconductivity, ferromagnetism, and nonlinear optical properties. To date, many supramolecular synthons (defined as structural units which can be formed or assembled by known or conceivable synthetic operations involving intermolecular interaction)[2] were designed and recognized to organize molecules into one-, two-, or three-dimensional networks,[3] and found robust enough to be exchanged from one network structure to another, which ensures generality and predictability.[4−7] In the practice of crystal engineering the major challenge is that a crystal structure is a compromise between interactions of varying strengths, directionalities, and distance-dependent properties.[8] One promising way to increase the predictability is to exploit the interfering effects of one interaction type on another to

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* Author to whom all correspondence should be addressed. E-mail: duancy@nju.edu.cn. Phone: +86-25-3597006. Fax: +86-25-3314502.

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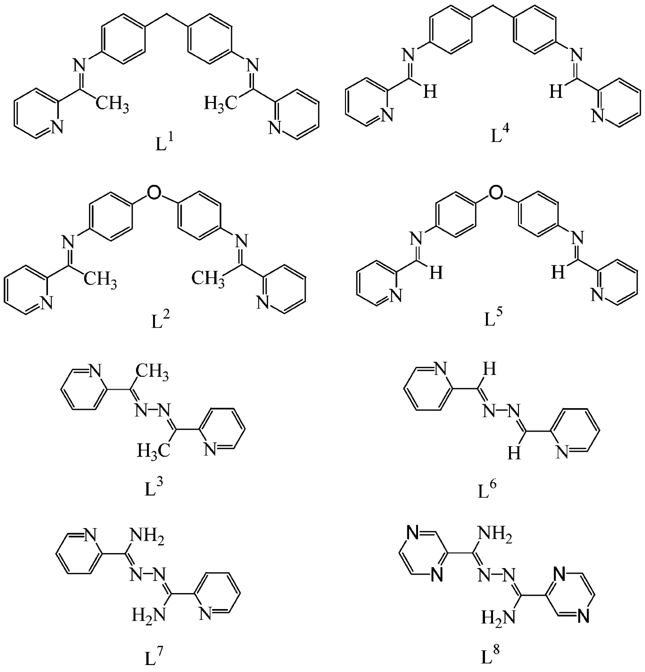
realize a supramolecular target structure as a synthetic chemist would use a neighboring or proximal group effect,[4] or to use intermolecular interacting inactive groups minimizing certain of various interaction types so that its individual feature is manifested more effectively, which resembles the group-protection of logic-directed organic synthesis.

In the absence of strong hydrogen donors and acceptors, aromatic compounds tend to self-assemble through $\pi-\pi$ interactions, C−H···π interactions, or both.[9,10] Such a tendency is so strong even in the presence of conventional hydrogen donors and acceptors that many synthons, even strong hydrogen bonded synthons, have limited predictions in the crystal packing based on aromatic molecules.[4] There is no doubt that the attempt to insulate and reduce certain $\pi-\pi$ intermolecular interactions from other interactions would increase the reliability and regularity of such synthons. The methyl group is steric exclusive and intermolecular interaction inactive in crystal packing. In our previous work involving helical architectures,[11] it was found that the spatial arrangement of the methyl group might effectively weaken the potential intramolecular and intermolecular interactions between aromatic rings, in both molecular formation and crystal packing. Therefore, it is expected that the existence of the methyl group as a side chain in aromatic backbones of helicands can sufficiently reduce potential intermolecular interactions in the crystal packing and make the geometrical features of other synthons exhibit more effectively.

On the other hand, helical architecture is one of the most investigated and best understood of metal−ligand coding edifices.[12−14] While the basic features of the design necessary to assemble such helices are now fairly well established, challenges in defining the precise conformation and molecular aggregation of the helical superstructure still remain. For a dinuclear triple helix, if two metal ions were linked by three identical, C_2-symmetric ligand strands, the resulting bimetallic cluster possibly has idealized D_3 symmetry.

Chart 1



However, from a crystallographic point of view, these symmetries have rarely been observed.[12c] It is postulated that the absence of ideal symmetry in the solid state would originate mainly from intermolecular interactions in the crystal packing or from the presence of side chains with a high degree of freedom precluding a rigorous application of the symmetry. In other words, if there were no obviously directional intermolecular interactions in crystal packing, crystallographic highly symmetric triple helicates should be generated.

To test this approach and the effect of the methyl group on crystal packing, we introduced methyl groups into systematic easy-to-prepare imine-based bis-bidentate ligands L,[4] L^5, and L^6 to obtain the ligands L^1, L^2, and L^3 (Chart 1) and constructed a series of metal helicates from pseudo-octahedral-coordinated metal ions such as cobalt(II), zinc(II), manganese(II), and so on. The ease of synthesis and high yield in a single-step reaction from commercial, inexpensive reagents has allowed us to systematically probe the effect of modifications to the ligand backbone through which we are attempting to control the precise topography, or micro-architecture, of the arrays.[15−17] Crystal structural analyses of these triple helicates clearly reveal that the existence of the methyl group in the side chains of aromatic ligands could effectively reduce the potential intermolecular $\pi-\pi$ interactions, and the side chain effect of the methyl group in crystal

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packing is robust enough to be exchanged from one network structure to another, which ensures that the formation of the crystallographic idealized symmetry of triple helicates could be general and predictable to a certain extent.

Experimental Section

Materials and Analyses. 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 240 analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 4000−400-cm^{-1} regions, ^{1}H NMR spectra on a DRX500 Bruker spectrometer at 298 K with TMS as internal standard, and ESI-MS (Electrospray Mass Spectra) on a LCQ system (Finnigan MAT, USA) with methanol as the mobile phase.

Preparation of ligand L^1. 4,4′-Diaminodiphenylmethane (1.0 g, 5.0 mmol) and 2-acetylpyridine (1.2 g, 10 mmol) were mixed in absolute methanol (25 mL) and refluxed for 4 h. When the solution was slowly evaporated to nearly dry under reduced pressure, yellow solids were obtained. The product (1.5 g, 3.7 mmol, yield 74%) was recrystallized from a methanol−ether mixture and dried under vacuum. Anal. Calcd for $C_{27}H_{24}N_4$: C, 80.2; H, 6.0; N, 13.8. Found: C, 80.3; H, 6.0; N, 13.8. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.66 (m, 2H, py), 8.26 (d, 2H, py), 7.89 (d, 2H, py), 7.48 (d, 2H, py), 7.22 (d, 2H, Ph), 6.96 (d, 2H, Ph), 6.76 (m, 2H, Ph), 6.63 (m, 2H, Ph), 3.83 (s, 2H, $-CH_2-$), 2.32 (s, 6H, $-CH_3$). IR (KBr, cm^{-1}): 3414 (ν_{C-H}), 1628, 1516, 1435 ($\nu_{C=C,C=N,C-N}$), 1288 (ν_{Ph-C}), 908, 811, 783 (δ_{C-H}).

Preparation of Complexes $[Co_2L^1_3][BF_4]_4$ (1), $[Zn_2L^1_3][BF_4]_4$ (2), and $[Mn_2L^1_3][BF_4]_4$ (3). The ligand L^1 (0.12 g, 0.30 mmol) and $M(BF_4)_2$ (0.20 mmol) [M = Co (**1**), Zn (**2**), and Mn (**3**)] were mixed in ethanol (25 mL), and after half an hour of stirring, the white precipitate obtained was filtered off, washed with ethanol, and dried under vacuum. **1**: Anal. Calcd for $C_{81}H_{72}N_{12}B_4F_{16}Co_2$: C, 58.0; H, 4.3; N, 10.0. Found: C, 58.1; H, 4.3; N, 9.9. IR (KBr, cm^{-1}): 3428 (ν_{C-H}), 1625, 1597, 1515, 1440, 1375, 1319 ($\nu_{C=C,C=N,C-N}$), 1084 (ν_{B-F}), 871, 829, 781, 747 (d_{C-H}). **2**: Anal. Calcd for $C_{81}H_{72}N_{12}B_4F_{16}Zn_2$: C, 57.5; H, 4.3; N, 9.9. Found: C, 57.5; H, 4.4; N, 9.8. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 8.62 (m, 2H, py), 8.20 (d, 2H, py), 7.97 (m, 2H, py), 7.60 (d, 2H, py), 7.36 (d, 2H, Ph), 7.05 (d, 2H, Ph), 6.82 (s, 2H, Ph), 6.58 (d, 2H, Ph), 3.95 (t, 2H, $-CH_2-$), 2.30 (s, 6H, $-CH_3$). IR (KBr, cm^{-1}): 3425 (ν_{C-H}), 1628, 1594, 1514, 1439, 1372, 1314 ($\nu_{C=C,C=N,C-N}$), 1065 (ν_{B-F}), 869, 828, 782, 745 (δ_{C-H}). **3**: Anal. Calcd for $C_{81}H_{72}N_{12}B_4F_{16}Mn_2$: C, 58.2; H, 4.3; N, 10.1. Found: C, 58.3; H, 4.4; N, 10.0. IR (KBr, cm^{-1}): 3419 (ν_{C-H}), 1634, 1595, 1503, 1439, 1373, 1315 ($\nu_{C=C,C=N,C-N}$), 1084 (ν_{B-F}), 871, 817, 785, 747 (δ_{C-H}). Crystals suitable for X-ray diffraction determination were grown by slow diffusion of diethyl ether into acetontrile solutions, respectively.

Preparation of Ligand L^2. Bis(4-aminophenyl) ether (1.0 g, 5.0 mmol) and 2-acetylpyridine (1.2 g, 10 mmol) were mixed in methanol (25 mL) and refluxed for 4 h. When the solution was slowly evaporated to nearly dry under reduced pressure, yellow solids were obtained. The product (1.70 g, 4.2 mmol, yield 84%) was recrystallized from a methanol−ether mixture and dried under vacuum. Anal. Calcd for $C_{26}H_{22}N_4O\cdot H_2O$: C, 73.6; H, 5.7; N, 13.2. Found: C, 73.7; H, 5.8; N, 13.3. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.65 (d, 2H, Py), 8.24 (d, 2H, Py), 7.89 (dt, 2H, Py), 7.48 (t, 2H, Py), 6.94−6.82 (dd, 4H, Ph), 6.82−6.71 (dd, 4H, Ph), 2.35 (s, 6H, $-CH_3$). IR (KBr, cm^{-1}): 3444 (ν_{C-H}), 1634, 1588, 1509, 1493, 1435, 1361 ($\nu_{C=C,C=N,C-N}$), 1231 (ν_{Ph-O}), 872, 843, 784, 749 (δ_{C-H}).

Preparation of Complexes $[Co_2L^2_3][BF_4]_4$ (4), $[Zn_2L^2_3][BF_4]_4$ (5), and $[Mn_2L^2_3][BF_4]_4$(6). The ligand L^2 (0.12 g, 0.30 mmol) and $M(BF_4)_2$ (0.20 mmol) [M = Co (**4**), Zn (**5**), and Mn (**6**)] were dissolved in ethanol (25 mL), and after half an hour of stirring, the gray yellow solid (0.12 g, 0.07 mmol, yield 70%) obtained was filtered off and dried under vacuum. **4**: Anal. Calcd for $C_{78}H_{66}B_4F_{16}N_{12}O_3Co_2\cdot 3H_2O$: C, 53.9; H, 4.2; N, 9.7. Found: C, 53.9; H, 4.6; N 9.9. IR (KBr, cm^{-1}): 3422 (ν_{C-H}), 1619, 1595, 1493, 1440, 1376, 1317 ($\nu_{C=C,C=N,C-N}$), 1243 (ν_{Ph-O}), 1059 (ν_{B-F}), 878, 817, 784, 746 (δ_{C-H}). **5**: Anal. Calcd for $C_{78}H_{66}B_4F_{16}N_{12}O_3Zn_2\cdot 3H_2O$: C, 53.5; H, 4.1; N, 9.6. Found: C, 53.3; H, 4.0; N, 9.3. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 8.72 (t, 2H, Py), 8.21 (d, 2H, Py), 7.99 (m, 2H, Py), 7.64 (t, 2H, Py), 7.08−6.53 (m, 8H, Ph), 2.64−2.26 (m, 6H, $-CH_3$). IR (KBr, cm^{-1}): 3423 (ν_{C-H}), 1626, 1596, 1494, 1441, 1376, 1315 ($\nu_{C=C,C=N,C-N}$), 1245 (ν_{Ph-O}), 1058 (ν_{B-F}), 878, 816, 785, 746 (δ_{C-H}). **6**: Anal. Calcd for $C_{78}H_{66}B_4F_{16}N_{12}O_3Mn_2\cdot 3H_2O$: C, 54.1; H, 4.2; N, 9.7. Found: C, 54.4; H, 4.1; N, 9.5. IR (KBr, cm^{-1}): 3419 (ν_{C-H}), 1625, 1594, 1493, 1437, 1374, 1313 ($\nu_{C=C,C=N,C-N}$), 1244 (ν_{Ph-O}), 1059 (ν_{B-F}), 871, 817, 785, 752 (δ_{C-H}). Recrystallization of the complexes from an acetonitrile solution by diffusion of diethyl ether afforded crystals from which we confirmed the structure by X-ray crystallography.

Preparation of Ligand L^3. The ligand L^3 was synthesized according to the literature method.[18]

Preparation of Complexes $[Co_2L^3_3][BF_4]_4$ (7), $[Zn_2L^3_3][BF_4]_4$ (8), $[Ni_2L^3_3][BF_4]_4$ (9), and $[Cu_2L^3_3][BF_4]_4$ (10). The ligand L^3 (0.14 g, 0.6 mmol) and $M(BF_4)_2$ (0.4 mmol) [M = Co (**7**), Zn (**8**), Ni (**9**), and Cu (**10**)] were mixed in ethanol (15 mL), and after an hour of stirring the white solid (0.21 g, 0.18 mmol, yield 88%) obtained was filtered off, washed with ethanol (20 mL) and Et_2O (5 mL), and dried under vacuum. **7**: Anal. Calcd for $C_{42}H_{42}B_4F_{16}N_{12}Co_2$: C, 42.8; H, 3.6; N, 14.2. Found: C, 42.9; H, 3.8; N, 14.5. IR (KBr, cm^{-1}): 3388.5 (ν_{C-H}), 1618.4, 1594.9, 1476.5, 1441.0, 1374.8, 1331.5 ($\nu_{C=C\ C=N,C-N}$), 1083.7 (ν_{B-F}), 774.8, 740.5. **8**: Anal. Calcd for $C_{42}H_{42}B_4F_{16}N_{12}Zn_2$: C, 42.3; H, 3.6; N, 14.1. Found: C, 42.3; H, 3.7; N, 13.9. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 2.30 (s, 6H, CH_3), 7.54 (t, 2H, py), 7.88 (t, 2H, py), 8.18 (d, 2H, py), 8.67 (d, 2H, py). IR (KBr, cm^{-1}): 3422.2 (ν_{C-H}), 1622.5, 1596.1, 1568.3, 1466.1, 1439.4, 1375.6, 1330.3 ($\nu_{C=C,C=N,C-N}$), 1083.9 (ν_{B-F}), 777.9, 742.4. **9**: Anal. Calcd for $C_{42}H_{42}B_4F_{16}N_{12}Ni_2$: C, 42.8; H, 3.6; N, 14.3. Found: C, 42.8; H, 3.6; N, 14.1. IR (KBr, cm^{-1}): 3422.6 (ν_{C-H}), 1622.3, 1591.4, 1566.3, 1469.9, 1437.6, 1369.0, 1321.7 ($\nu_{C=C,C=N,C-N}$), 1083.9 (ν_{B-F}), 783.9, 746.2. **10**: Anal. Calcd for $C_{42}H_{42}B_4F_{16}N_{12}Cu_2$: C, 42.4; H, 3.6; N, 14.1. Found: C, 42.5; H, 3.3; N, 14.1. IR (KBr, cm^{-1}): 3421.9 (ν_{C-H}), 1583.2, 1560.4, 1467.9, 1443.5, 1318.8 ($\nu_{C=C,C=N,C-N}$), 1083.8 (ν_{B-F}), 775.4, 749.4. Crystals suitable for X-ray diffraction determination were grown by slowly evaporating acetonitrile solutions at room temperature.

Crystallographic Studies. Parameters for data collection and refinement of complexes **1**−**10** are summarized in Tables 1−3. Intensities were collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic Mo Kα radiation (l = 0.71073

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Table 1. Crystallographic Data for Complexes **1**−**3**^{a}

	1	**2**	**3**
mol formula	$C_{81}H_{72}N_{12}B_4F_{16}Co_2$	$C_{81}H_{72}N_{12}B_4F_{16}Zn_2$	$C_{81}H_{72}N_{12}B_4F_{16}Mn_2$
M	1678.61	1691.49	1670.63
cryst syst	hexagonal	hexagonal	hexagonal
space group	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$
a/Å	10.61(1)	10.61(2)	10.68(2)
b/Å	10.61(1)	10.61(2)	10.68(2)
c/Å	40.83(5)	41.12(1)	41.05(8)
V/Å^3	3982.6(7)	4009.5(2)	4058.8(1)
Z	2	2	2
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	0.506	0.687	0.399
no. of reflns measd	18909	18887	19022
no. of unique reflns	2360	2366	2401
R_{int}	0.0833	0.0546	0.0614
R_1	0.0667	0.0615	0.0672
wR_2	0.1381	0.1850	0.1983

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [F_o^2 + 2F_c^2]/3$.

Table 2. Crystallographic Data for Complexes **4**−**6**^{a}

	4	**5**	**6**
mol formula	$C_{78}H_{66}B_4Co_2F_{16}N_{12}O_3$	$C_{78}H_{66}B_4F_{16}N_{12}O_3Zn_2$	$C_{78}H_{66}B_4F_{16}Mn_2N_{12}O_3$
M	1684.53	1697.41	1676.55
cryst syst	hexagonal	hexagonal	hexagonal
space group	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$
a/Å	10.5469(8)	10.5469(8)	10.6183(18)
b/Å	10.5469(8)	10.5469(8)	10.6183(18)
c/Å	40.909(4)	40.909(4)	40.843(10)
V/Å^3	3941.0(6)	3941.0(6)	3988.0(14)
Z	2	2	2
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	0.515	0.702	0.409
no. of reflns measd	18742	18935	18840
no. of unique reflns	2332	2339	2361
R_{int}	0.086	0.094	0.111
R_1	0.073	0.056	0.064
wR_2	0.169	0.135	0.172

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [F_o^2 + 2F_c^2]/3$.

Table 3. Crystallographic Data for Complexes **7**−**10**^{a}

	7	**8**	**9**	**10**
mol formula	$C_{42}H_{44}B_4Co_2F_{16}N_{12}O$	$C_{42}H_{46}B_4F_{16}N_{12}O_2Zn_2$	$C_{42}H_{42}B_4F_{16}N_{12}Ni_2$	$C_{42}H_{42}B_4Cu_2F_{16}N_{12}$
M	1197.99	1228.88	1179.54	1189.2
cryst syst	cubic	cubic	cubic	cubic
space group	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$	$Pa\bar{3}$
a/Å	21.982(3)	22.0634(8)	21.980(3)	21.973(3)
V/Å^3	10622(2)	10740.3(7)	10619(2)	10609(2)
Z	8	8	8	8
T/K	293(2)	293(2)	293(2)	293(2)
μ/mm^{-1}	0.727	0.997	0.809	0.902
no. of reflns measd	87312	53539	73910	80385
no. of unique reflns	3109	3150	2338	3110
R_{int}	0.128	0.025	0.168	0.087
R_1	0.076	0.062	0.077	0.072
wR_2	0.194	0.065	0.194	0.185

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [F_o^2 + 2F_c^2]/3$.

Å), using SMART and SAINT[19a] 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.[19b] 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 complexes **4**−**6**, the spacer groups (including the benzene rings and oxygen atom) were refined disorder. The benzene ring exhibits 2-fold positional disordered. The s.o.f. (site occupancy factor) of atoms in each part is fixed at 0.5. The s.o.f. of the oxygen atom is also fixed at 0.5. To stabilize the refinement, thermal parameters on adjacent atoms in disordered moieties were restrained to be similar.

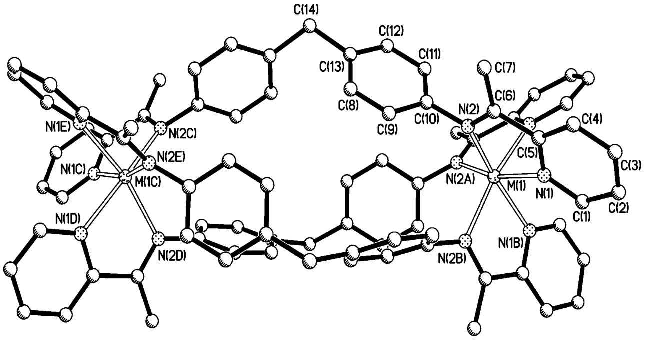

Figure 1. Molecular structure of the triple helicates for complexes **1**−**3** with hydrogen atoms and anions omitted for clarity.

For complexes **1**−**6**, the BF_4^- anions occupied the 3-fold positions with the s.o.f. of each boron atom fixed at $^1/_3$. The fluorine atoms were also refined disordered into two parts with the s.o.f. of fluorine atoms in the 3-fold position fixed at $^1/_6$, and the s.o.f. of other atoms fixed at 0.5. For complexes **7**−**10**, the fluorine atoms in tetrafluoroborates were also refined disordered into two parts with the s.o.f. of fluorine atoms in the 3-fold position fixed at $^1/_6$, and the s.o.f. for other atoms fixed at 0.5. To assist the refinement, several restraints were applied: (1) all B−F or Cl−O bonds were restrained to be similar and (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar.

Results and Discussion

Crystal Structures of Complexes 1−3. Ligand L^1 was obtained in good yield by simply mixing 4,4′-diaminodiphenylmethane and 2-acetylpyridine in a methanol solution. Interaction of 3 equiv of ligand and 2 equiv of $Co(BF_4)_2$, $Zn(BF_4)_2$, or $Mn(BF_4)_2$ in ethanol resulted in the formation of helicates $[M_2L^1_3]$ (M = Co (**1**), Zn (**2**), Mn (**3**)) in 70−80% yields. Elemental analyses are consistent with the formation of complexes of the form $[M_2L^1_3][BF_4]_4$. Crystal structure analyses reveal that complexes **1**−**3** are isostructural (Figure 1) and each consists of two six-coordinated M^{II} ions chelated and bridged by three L^1 groups. The M···M separations are similar [ca. 11.5 Å on average] and the molecules are in a triple-helix conformation with crystallographic D_3 symmetry. One-sixth of the triple helicate is found in an asymmetry unit with the metal ion occupying the crystallographic 3-fold axial special position and the methylene carbon atom occupying the crystallographic 2-fold axial special position. While the mean-square line passing through the metal ions of the helix shows a crystallographic 3-fold symmetry axis, three crystallographic 2-fold symmetries perpendicular to the helical axis are found through the methylene carbon atoms of the ligands. Each metal center is bound to three pyridylimine units inthe *fac* configuration

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(19) (a) *SMART* and *SAINT*, Area Detector Control and Integration Software; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996. (b) Sheldrick, G. M. *SHELXTL* V5.1, Software Reference Manual; Bruker AXS, Inc.: Madison, WI, 1997.

Table 4. Selected Bond Distances (Å) and Angles (deg) of Complexes **1**−**6**[a]

1		**2**		**3**	
Co(1)−N(2)	2.113(4)	Zn(1)−N(2)	2.140(3)	Mn(1)−N(2)	2.216(4)
Co(1)−N(1)	2.138(4)	Zn(1)−N(1)	2.193(3)	Mn(1)−N(1)	2.263(4)
N(2)−Co(1)−N(2)	101.2(2)	N(2A)−Zn(1)−N(2)	101.0(1)	N(2)−Mn(1)−N(2A)	102.7(1)
N(2A)-Co(1)−N(1)	167.4(2)	N(2A)−Zn(1)−N(1)	165.6(1)	N(2A)−Mn(1)−N(1)	163.2(1)
N(2)−Co(1)−N(1)	75.8(2)	N(2)−Zn(1)−N(1)	75.5(1)	N(2)−Mn(1)−N(1)	72.7(1)
N(1A)−Co(1)−N(1)	92.0(2)	N(2B)−Zn(1)−N(1)	93.5(1)	N(1A)−Mn(1)−N(1)	91.3(1)
N(2B)−Co(1)−N(1)	91.4(2)	N(1A)-Zn(1)−N(1)	90.6(1)	N(2B)−Mn(1)−N(1)	94.1(1)

4		**5**		**6**	
Co(1)−N(2)	2.106(5)	Zn(1)−N(2)	2.137(4)	Mn(1)−N(2)	2.212(4)
Co(1)−N(1)	2.129(5)	Zn(1)−N(1)	2.184(4)	Mn(1)−N(1)	2.243(4)
N(2)−Co(1)−N(2A)	100.9(2)	N(2)−Zn(1)−N(2A)	101.1(1)	N(2)−Mn(1)−N(2A)	102.8(1)
N(2)−Co(1)−N(1A)	167.5(2)	N(2A)−Zn(1)−N(1)	165.7(2)	N(2A)−Mn(1)−N(1)	163.1(2)
N(2)−Co(1)−N(1)	76.1(2)	N(2)−Zn(1)−N(1)	75.7(2)	N(2)−Mn(1)−N(1)	72.6(2)
N(2A)−Co(1)−N(1)	91.7(2)	N(2B)−Zn(1)−N(1)	93.2(2)	N(1A)−Mn(1)−N(1)	91.3(1)
N(1A)−Co(1)−N(1)	91.7(2)	N(1A)−Zn(1)−N(1)	90.5(1)	N(2B)−Mn(1)−N(1)	94.1(1)

[a] Symmetry code A: $2 - y, 1 + x - y, z$. Symmetry code B: $1 - x + y, 2 - x, z$.

attaining a C_3 pseudooctahedral coordination geometry with three equivalent metal−N (CH═N) bonds and three equal metal−N (pyridyl) bonds, respectively. Coordination to the metal center to form the ideal D_3-symmetric helix causes the interannular twisting among the pyridine and benzene rings. Bond lengths and angles are all in common ranges (Table 4).

It is interesting to find that no obviously intermolecular $\pi-\pi$ interactions were found relative to the pyridine rings and benzene rings, for the shortest interhelical atom···atom separation involving the pyridine and benzene rings is longer than 4.0 Å, which is the upper limit of the common distances for $\pi-\pi$ interactions between two aryl rings.[14b,20] As an alternative, the shortest interhelical atom···atom separation of these crystal structures relative to the carbon atom of the methyl group is found to be 3.68 Å, which is in agreement with the distance of a weak CH/π interaction between CH (soft acids) and π groups (soft bases) first advocated by Nishio.[21] However, it should be noted that this contact plays an important role in weakening the potential $\pi-\pi$ interactions between the aryl rings. In this case, it is reasonable to speculate that the methyl group is the essential factor determining the helicates formed in crystallographic ideal D_3 symmetry.

Since the helicates are ionic species, their molecular packing is essentially directed by weak electrostatic interaction driven by BF_4^- anions. Although the electrostatic compression in these cases is preferential to make the intermolecular interactions stronger than that between neutral systems,[22] it seems that these interactions do not reduce the idealized D_3 symmetry of the helicates reported here. Like most of triple helicates, parallel to their C_3 helical axis, the molecules tend to align themselves giving the densest packing and leaving sufficient space in cavities for the counteranions. As in the crystal packing of chain molecules,[23] the helicates form layers of hexagonal close-packed cylindrical molecules, which lead to the hexagonal AB close-packed arrangement (Figure 2).

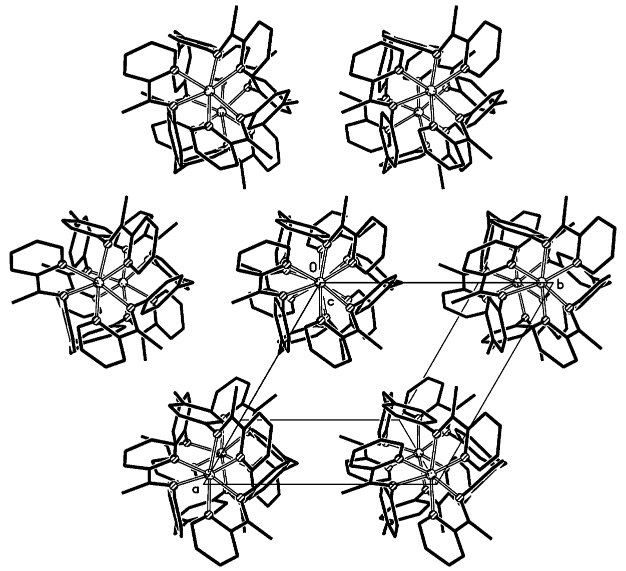

Figure 2. Hexagonal packing of triple helical species **1**−**3** along the M···M axis.

Crystal Structures of Complexes 4−**6.** To further understand the factors influencing the triple helicates formation and crystallographic conformations extensively, ligand L^2 was also used to react with the cobalt(II), zinc(II), or manganese(II) for assembling possible crystallographic D_3 symmetric triple helicates. Interaction of ligand L^2 with $Co(BF_4)_2$, $Zn(BF_4)_2$, or $Mn(BF_4)_2$ in a 3:2 ratio in ethanol solution resulted in the formation of precipitates $[M_2L_3]$ (M = Co, (**4**), Zn (**5**), Mn (**6**)). Elemental analyses are consistent with the formation of the helicates of the form $[M_2L_3][BF_4]_4$. ESI-MS in acetonitrile−methanol solution shows one strong

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(21) (a) Nishio, M. *Kagaku No Ryoiki* **1977**, *31*, 998. (b) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201. (c) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/p interaction, Evidence, Nature and Consequences*; John Wiley & Sons: New York, 1998.

(22) (a) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **2000**, *33*, 601. (b) Braga, D.; Novoa, J. J.; Grepioni, F. *New J. Chem.* **2001**, *25*, 226.

(23) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press Inc.: London, UK, 1973.

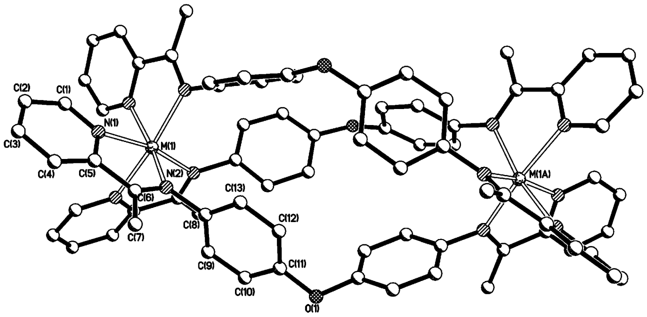

Figure 3. Molecular structure of the triple helicates for complexes **4**−**6** with hydrogen atoms and anions omitted for clarity.

peak corresponding to $[Co_2L^2{}_3]^{4+}$ (*m*/*z* 334.4), consistent with formation of a triple helical structure. The presence of the only intensive $[Co_2L^2{}_3]^{4+}$ species indicates that this species has high stability in solution. ESI-MS spectra also exhibit three prominent signals centered at *m*/*z* 337.8, 407.3, and 477.9 for **2** corresponding to $[Zn_2L^2{}_3]^{4+}$, $[HL^2]^+$, and $[Zn_2L^2{}_3(BF_4)]^{3+}$ and *m*/*z* 332.5, 407.3 and 637.1 corresponding to $[Mn_2L^2{}_3]^{4+}$, $[HL^2]^+$, and $[MnL^2{}_3]^{2+}$, respectively. The base peaks at *m*/*z* 337.8 and 332.5 correspond to the most abundant ion $[Zn_2L^2{}_3]^{4+}$ and $[Mn_2L^2{}_3]^{4+}$ with isotopic peaks separated by 0.25, which confirmed the 4+ charge borne by the cations. The peaks at *m*/*z* 407.3 result from a singly charged species $[HL^2]^+$. The presence of the $[Zn_2L^2{}_3]^{4+}$ and $[Mn_2L^2{}_3]^{4+}$ species indicates the formation of triple-helical structures. An Additional peak that results from the association with BF_4^- was observed at *m*/*z* 477.9 and ascribed to $[Zn_2L^2{}_3(BF_4)]^{3+}$. The associations between the cationic helicates and various counteranions are very common in ESI-MS and have been tentatively attributed to electrostatic interactions.[24]

Crystal structural analyses of complexes **4**−**6** confirm the formation of triple helicates in crystallographic idealized D_3 symmetry as those of complexes **1**−**3** (Figure 3). Complexes **4**−**6** are also isostructural and each consists of two six-coordinated M^{II} ions chelated and bridged by three L^2. The M···M separations are ca. 11.5 Å on an average. Only one-sixth of the triple helicate is found in an asymmetry unit with the metal ions occupying the crystallographic 3-fold axis special position. Bond lengths and angles are both unremarkable (Table 4). Coordination to the metal center to form the ideal D_3-symmetric helix causes the interannular twisting among the pyridine and benzene rings. To achieve the idealized D_3 symmetry, the benzene ring exhibits 2-fold positional disorder, and its scattering power is represented by two "half-rings".

Similarly, no obvious interhelical $\pi-\pi$ interactions were found involving the pyridine rings and benzene rings, for the interhelical atom···atom separations relative to the pyridine and benzene rings are all longer than 4.0 Å, which is also longer than the common distances for $\pi-\pi$ interactions between two aryl rings. As an alternative, the shortest interhelical atom···atom separation of these three crystal structures related to the carbon atoms of the methyl groups is found to be 3.68 Å, which is in agreement with the distance of a weak interaction involving the methyl group.

Table 5. Selected Crystallographic Data of Related Complexes

ligand	metal complexes	cryst syst	space group
L^1	$[Zn_2L^1{}_3][BF_4]_4$	hexagonal	$P\bar{3}c1$
	$[Co_2L^1{}_3][BF_4]_4$	hexagonal	$P\bar{3}c1$
	$[Mn_2L^1{}_3][BF_4]_4$	hexagonal	$P\bar{3}c1$
L^4	$[Zn_2L^4{}_3][ClO_4]_4$[16b]	monoclinic	$C2/c$
	$[Ni_2L^4{}_3][BF_4]_4$[15c]	monoclinic	$C2/c$
L^2	$[Co_2L^2{}_3][BF_4]_4$	hexagonal	$P\bar{3}c1$
	$[Zn_2L^2{}_3][BF_4]_4$	hexagonal	$P\bar{3}c1$
	$[Mn_2L^2{}_3][BF_4]_4$	hexagonal	$P\bar{3}c1$
L^5	$[Co_2L^5{}_3][BF_4]_4$[17b]	monoclinic	Cc
	$[Ni_2L^5{}_3][BF_4]_4$[17b]	monoclinic	Cc

Crystal engineering is defined as the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding on the design of a new solid with the desired physical and chemical properties.[25] Above we have demonstrated the syntheses and crystal structures of six novel crystallographic idealized D_3 symmetric triple helicates. Contrasted with the helical complexes from the related ligands L^4 and L^5, it is clear that (Table 5) the methyl group is an essential factor in controlling the symmetry of the helices, and this synthon is robust enough to be exchanged from one network structure to another, which ensures generality and predictability of crystallographic ideal symmetry to a certain extent.

Crystal Structures of Complexes 7−10. To test that the methyl group in the side chain is a supramolecular synthon in controlling the crystal packing, we also examined the crystal structures of triple helicates derived from ligand L^3. To date, only two triple helicates derived from L^3 have been structurally characterized by Sheldrick et al.[26] and Hannon et al.[27] The crystal structure of $[Co_2L^3{}_3][(ZnCl_4)(ZnCl_3{\cdot}H_2O)_2{\cdot}4H_2O]$[26] is determined in space group $P2_1/n$ since there are classical O−H···O, O−H···Cl hydrogen bonds which causes its departure from crystallographic idealized C_3 symmetry. It seems that the absence of ideal symmetry would originate mainly from intermolecular interactions such as hydrogen bonds in the crystal packing. We believe that by choosing the appropriate counteranions to reduce the potential intermolecular hydrogen bonds, the helicates should be crystallized in crystallographic D_3 symmetry, or at least should be formed in C_3 symmetry if the ligand is considered not to have C_2 symmetry. Reaction of L^3 with $Zn(BF_4)_2$ or $Co(BF_4)_2$ or $Ni(BF_4)_2$ or $Cu(BF_4)_2$ in a 3:2 ratio in ethanol solution resulted in the formation of precipitates. Elemental analyses indicate the formation of complexes of the formula $[M_2L^3{}_3][BF_4]_4$ (M = Co (**7**), Zn (**8**), Ni (**9**), Cu (**10**)). Crystal structure analyses of complexes **7**−**10** have unequivocally confirmed that these complexes are isostructural crystal-

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Table 6. Selected Bond Distances (Å) and Angles (deg) of Complexes **7**−**10**

7[a]		**8**[a]		**9**[b]		**10**[a]	
Co(1)−N(1)	2.091(4)	Zn(1)−N(1)	2.080(3)	Ni(1)−N(1)	2.057(6)	Cu(1)−N(1)	2.081(4)
Co(1)−N(2)	2.114(4)	Zn(1)−N(2)	2.190(3)	Ni(1)−N(2)	2.088(6)	Cu(1)−N(2)	2.149(4)
Co(2)−N(3)	2.128(4)	Zn(2)−N(3)	2.208(3)	Ni(2)−N(3)	2.081(6)	Cu(2)−N(3)	2.159(4)
Co(2)−N(4)	2.085(5)	Zn(2)−N(4)	2.086(3)	Ni(2)−N(4)	2.064(6)	Cu(2)−N(4)	2.067(5)
N(1)−Co(1)−N(1A)	100.1(2)	N(1)−Zn(1)−N(1A)	102.5(1)	N(1)−Ni(1)−N(1A)	98.7(2)	N(1)−Cu(1)−N(1A)	100.8(2)
N(1)−Co(1)−N(2)	76.2(2)	N(1)−Zn(1)−N(2)	75.0(1)	N(1)−Ni(1)−N(2)	77.5(2)	N(1)−Cu(1)−N(2)	76.0(2)
N(1)−Co(1)−N(2A)	95.1(2)	N(1)−Zn(1)−N(2A)	95.6 (1)	N(1)−Ni(1)−N(2A)	94.7(2)	N(1)−Cu(1)−N(2A)	95.1(2)
N(1)−Co(1)−N(2B)	164.8(2)	N(1)−Zn(1)−N(2B)	161.8(1)	N(1)−Ni(1)−N(2B)	166.5(2)	N(1)−Cu(1)−N(2B)	164.2(2)
N(2)−Co(1)−N(2A)	89.3(2)	N(2)−Zn(1)−N(2A)	87.3(1)	N(2)−Ni(1)−N(2A)	89.8(2)	N(2)−Cu(1)−N(2A)	88.7(2)
N(3)−Co(2)−N(4)	75.7(2)	N(3)−Zn(2)−N(4)	74.6(1)	N(3)−Ni(2)−N(4)	77.0(2)	N(3)−Cu(2)−N(4)	75.8(2)
N(3)−Co(2)−N(3A)	88.9(2)	N(3)−Zn(2)−N(3A)	86.0(1)	N(3)−Ni(2)−N(3A)	89.9(2)	N(3)−Cu(2)−N(3A)	88.1(2)
N(3)−Co(2)−N(4A)	94.2(2)	N(3)−Zn(2)−N(4A)	94.2(1)	N(3)−Ni(2)−N(4A)	94.3(2)	N(3)−Cu(2)−N(4A)	94.4(2)
N(3)−Co(2)−N(4B)	164.2(2)	N(3)−Zn(2)−N(4B)	160.5(1)	N(3)−Ni(2)−N(4B)	166.2(2)	N(3)−Cu(2)−N(4B)	163.6(2)
N(4)−Co(2)−N(4A)	101.6(2)	N(4)−Zn(2)−N(4A)	104.7(1)	N(4)−Ni(2)−N(4A)	99.5(2)	N(4)−Cu(2)−N(4A)	101.9(2)

[a] Symmetry code A: *z*, *x*, *y*. Symmetry code B: *y*, *x*, *z*. [b] Symmetry code A: $-0.5 + z$, $0.5 - x$, $1 - y$. Symmetry code B: $-0.5 - y$, $1 - z$, $0.5 + z$.

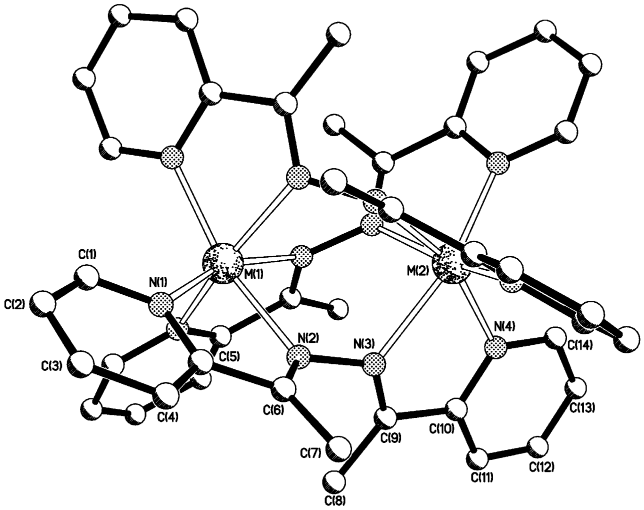

Figure 4. Molecular structure of the triple helicates for complexes **7**−**10** with hydrogen atoms and anions omitted for clarity.

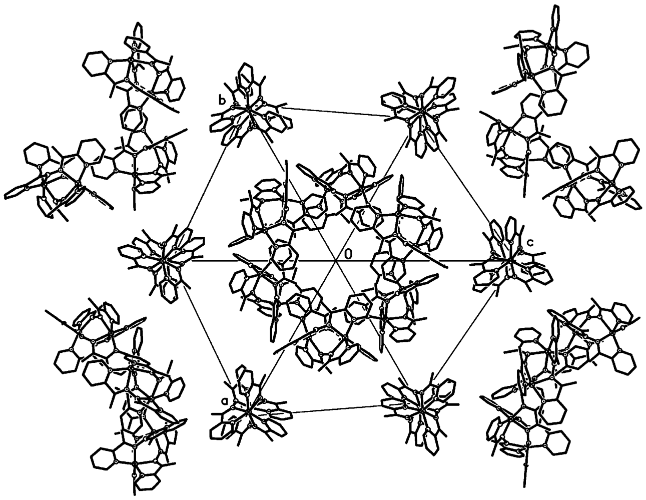

Figure 5. Hexagonal packing of triple helical species **7**−**10** along the M⋯M axis.

lographic C_3 symmetric triple helicates (Figure 4). These complexes all crystallize in the cubic crystal system with space group $Pa\bar{3}$ and only one-third of the triple helicate is found in an asymmetry unit of each complex. The metal ions occupy the crystallographic 3-fold axial special positions with similar M⋯M separations [ca. 3.75 Å for **7**, 3.96 Å for **8**, 3.68 Å for **9**, and 3.81 Å for **10**], and the mean-square line passing through the metal ions of the helix shows a crystallographic 3-fold symmetry. Each metal center is bound to three pyridylimine units in *fac* configuration to attain a C_3 pseudooctahedral geometry with three equivalent metal−N (pyridyl) and metal−N (CH═N) bonds (Table 6). Interestingly, It is worth noting that the Cu−N separations have a relatively narrow range (2.07−2.16 Å), indicating the Jahn−Teller effect of the d^9 electronic configuration of copper(II) observed commonly in copper(II) complexes[28] disappears. It is suggested that the disposition of the binding sites in the ligand is the more important factor than the stereoelectronic preference of the metal ions in directing the course of the assembly of the resulting triple-helical complexes in the present systems. Bond lengths and angles are in the common ranges (Table 6). Coordination to the metal centers forces the two pyridyl rings to twist around the N−N bond and the logical consequence is the formation of triple-helical arrays.

Detailed structural analyses reveal that no obvious intermolecular interactions are found in the crystal packing of complexes **7**−**10**, for the shortest intermolecular atom⋯atom separation in all complexes related to the pyridine ring and the methyl carbon atom is at least 3.9 Å. According to above analyses, it seems that the existence of methyl groups might minimize the potential directional intermolecular interactions, and the absence of the obviously directional intermolecular interactions in the crystals should cause the helicates to depart from idealized C_3 symmetry.

Table 7 shows the triple helicates derived from ligand L^3 and the related ligands,[26,27,29−32] it is clear that in the presence of the methyl group, the helicates preferentially form idealized C_3 symmetry as shown in the solution, except for the silver triple helicate.[27] The silver(I) triple helicate itself

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Table 7. Selected Crystallographic Data of Related Complexes

ligand	metal complexes	cryst syst	space group
L^3	$[Zn_2L^3_3][BF_4]_4$	cubic	$Pa\bar{3}$
	$[Co_2L^3_3][BF_4]_4$	cubic	$Pa\bar{3}$
	$[Ni_2L^3_3][BF_4]_4$	cubic	$Pa\bar{3}$
	$[Cu_2L^3_3][BF_4]_4$	cubic	$Pa\bar{3}$
	$[Co_2L^3_3][(ZnCl_4)(ZnCl_3{\cdot}H_2O)_2{\cdot}4H_2O]$[26]	monoclinic	$P2_1/n$
	$[Ag_2L^3_3][PF_6]_2$[27]	monoclinic	$C2/c$
L^6	$[Cd_2L^6_3][ClO_4]_4$	monoclinic	$P2_{1/c}$
	$[Ni_2L^6_3][BF_4]_4$[29]	monoclinic	$P2_{1/c}$
	$[Co_2L^6_3][BF_4]_4$[33]	monoclinic	$P2_{1/c}$
	$[Zn_2L^6_3][BF_4]_4$	monoclinic	$P2_{1/c}$
	$[Fe_2L^6_3][PF_6]_4$[27]	orthorhombic	Fdd_2
L^7	$[Mn_2L^7_3][ClO_4]_4$[30a]	monoclinic	$C2/c$
	$[Fe_2L^7_3][NO_3]_4$[30a]	cubic	$Pa\bar{3}$
	$[Co_2L^7_3][NO_3]_6$[30a]	trigonal	$R\bar{3}c(h)$
	$[Ni_2L^7_3][Ni(H_2O)_6][NO_3]_6$[30a]	trigonal	$R\bar{3}c$
	$[Zn_2L^7_3][ZnBr_4]_2$[30b]	triclinic	$P\bar{1}$
L^8	$[Fe_2L^8_3][NO_3]_4$[30a]	monoclinic	$P2/n$
	$[Ni_2L^8_3][ClO_4]_4$[30b]	monoclinic	$P2_1/n$
	$[Cu_2L^8_3][ClO_4]_4$[30b]	monoclinic	$P2_1/c$

does not have the potential to exhibit C_3 symmetry even in solution for the three ligands are not equivalent at all. With regard to other similar systems in which the methyl group in the side chain is substituted by the amino group,[30] the triple helicates from ligand L^7 also have the possibility to crystallize in idealized D_3 symmetry. Although the factors controlling the molecular packing are not discussed in detail, it can be seen from the crystal structures that the presence of high symmetry might be raised from the absence of strong directional intermolecular interactions. However, the Mn(II) and Zn(II) complexes from L^7 packed in $C2/c$ and $P\bar{1}$ space groups, respectively, in which no C_3 molecular symmetry was found due to the hydrogen bonds involving the amino group. And for the same reason, no D_3 or C_3 symmetric helicates were found in complexes from ligand L^8. In comparison, the intermolecular interaction inactive methyl group is better than the amino group to ensure the generality and predictability of forming crystallographically idealized symmetric helicates, since the methyl group cannot support strong hydrogen bonds. High symmetric architectures were also found in T_d symmetric M_4L_6 pyramidal complexes in which the methyl group also presented as a side chain.[31]

The above results indicate that a substituent group (especially, methyl groups) in the side chain could effectively reduce the potential directional $\pi-\pi$ interactions between aromatic groups. And such a structural unit could be considered as a supramolecular synthon to control crystal packing. That means that if we introduce the methyl group into the functional systems containing aromatic groups, it is predicted that these systems should be packed in the fashion in which $\pi-\pi$ interactions weakened to a certain degree. However, it should also be noted that in some cased the presence of hydrogen bonds completely disrupted the ability of methyl groups to facilitate high symmetry. These results demonstrated that the aggregation of molecules obviously relies on a variety of weaker intermolecular interactions and controlls the delicate balance between all weak interactions. If one were to assign significance to supramolecular synthons on the basis of specific interaction strengths, these synthons might not rank very high.

Conclusion

In summary, we have successfully constructed a series of idealized symmetric triple helicates in which the methyl group acts as a supramolecular synthon to minimize the potential $\pi-\pi$ interactions between the aromatic groups of the backbone of helicands and leads the helicates formed in crystallographic idealized symmetry as those existed in solution. These results also demonstrated that although the interactions involving the methyl group are very weak, their effect on molecular structure and crystal packing could just be as predictable as the effect of the classical hydrogen bonds and strong $\pi-\pi$ interactions. To understand the factors controlling the self-assembly of helicates in crystallographic D_3 symmetry is essential in expanding the field of metal supramolecuar chemistry into the development of new supramolecular systems and devices.[32] The designing of ligands suitable to modify the inter- and intramolecular interactions provides a possible synthetic route for artificially controlling crystal engineering. Although these complexes are very classical triple-stranded helicates, the observation of crystallographic D_3 symmetry in the solid state is a remarkable event.

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Supporting Information Available: X-ray crystallographic data (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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