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Novel Metal–Organic Frameworks with Specific Topology from New Tripodal Ligands: 1,3,5-Tris(1-imidazolyl)benzene and 1,3-Bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)benzene

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Reactions of two new tripodal ligands 1,3,5-tris(1-imidazolyl)benzene (**4**) and 1,3-bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)benzene (**5**) with metal [Ag(I), Cu(II), Zn(II), Ni(II)] salts lead to the formation of novel two-dimensional (2D) metal–organic frameworks $[Ag_2(\mathbf{4})_2][p\text{-}C_6H_4(COO)_2]\cdot H_2O$ (**6**), $[Ag(\mathbf{4})]ClO_4$ (**7**), $[Cu(\mathbf{4})_2(H_2O)_2](CH_3COO)_2\cdot 2H_2O$ (**8**), $[Zn(\mathbf{4})_2(H_2O)_2](NO_3)_2$ (**9**), $[Ni(\mathbf{4})_2(N_3)_2]\cdot 2H_2O$ (**10**), and $[Ag(\mathbf{5})]ClO_4$ (**11**). All the structures were established by single-crystal X-ray diffraction analysis. Crystal data for **6**: monoclinic, $C2/c$, $a = 23.766(3)$ Å, $b = 12.0475(10)$ Å, $c = 13.5160(13)$ Å, $\beta = 117.827(3)°$, $Z = 4$. For compound **7**: orthorhombic, $P2_12_12_1$, $a = 7.2495(4)$ Å, $b = 12.0763(7)$ Å, $c = 19.2196(13)$ Å, $Z = 4$. For compound **8**: monoclinic, $P2_1/n$, $a = 8.2969(5)$ Å, $b = 12.2834(5)$ Å, $c = 17.4667(12)$ Å, $\beta = 96.5740(10)°$, $Z = 2$. For compound **9**: monoclinic, $P2_1/n$, $a = 10.5699(3)$ Å, $b = 11.5037(3)$ Å, $c = 13.5194(4)$ Å, $\beta = 110.2779(10)°$, $Z = 2$. For compound **10**: monoclinic, $P2_1/n$, $a = 9.8033(3)$ Å, $b = 12.1369(5)$ Å, $c = 13.5215(5)$ Å, $\beta = 107.3280(10)°$, $Z = 2$. For compound **11**: monoclinic $C2/c$, $a = 18.947(2)$ Å, $b = 9.7593(10)$ Å, $c = 19.761(2)$ Å, $\beta = 97.967(2)°$, $Z = 8$. Both complexes **6** and **7** are noninterpenetrating frameworks based on the (6, 3) nets, and **8**, **9** and **10** are based on the (4, 4) nets while complex **11** has a twofold parallel interpenetrated network with 4.8^2 topology. It is interesting that, in complexes **6**, **7**, and **11** with three-coordinated planar silver(I) atoms, each ligand **4** or **5** connects three metal atoms, while in the case of complexes **8**, **9**, and **10** with six-coordinated octahedral metal atoms, each ligand **4** only links two metal atoms, and another imidazole nitrogen atom of **4** did not participate in the coordination with the metal atoms in these complexes. The results show that the nature of organic ligand and geometric needs of metal atoms have great influence on the structure of metal–organic frameworks.

Introduction

In recent years, construction of organic−inorganic coordination polymeric complexes has attracted great attention from chemists owing to their potential as functional materials.[1] So far, considerable progress has been achieved in dominating the assembly and orientation of individual building blocks into structures with specific topologies and functions including ion/molecular recognition, selective guest inclusion, ion exchange, etc.[2] For example, some structural motifs formed by supramolecular arrays can, to a certain extent, be predicted by exploiting rigid bridging components, second building units (SBUs), and elaborately chosen and/or decorated metal salts to constrain the coordination geometry, etc.[3] Meanwhile, it is still a challenge to predict the exact structure of assembly products in crystal engineer-

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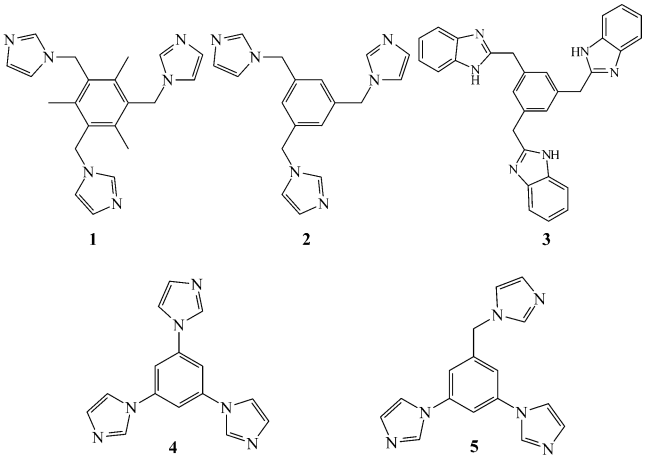
Chart 1. Schematic Drawing of Tripodal Ligands **1**−**5**



ing since the structure is controlled by the coordination preferences of transition metals, the nature of the organic building blocks, template, and solvent or even more subtle effects such as counteranions.[4] Hence, systematic research on this subject is crucial in understanding the control of structure and topology of metal−organic frameworks (MOFs).

In recent years, we and some other groups[5] have been developing a strategy using tripodal ligands with arene cores as building blocks. By employing a series of such tripodal ligands, for example 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (**1**), 1,3,5-tris(imidazol-1-ylmethyl)benzene (**2**), and 1,3,5-tris(benzimidazol-2-ylmethyl)benzene (**3**) (Chart 1), we aimed to investigate the influence of organic ligands on the formation of MOFs and obtained MOFs with specific topologies, such as individual three-dimensional (3D) cages, dumbbells, and two-dimensional (2D) honeycomb networks, and with interesting properties, for example, selective guest inclusion, anion exchange, etc.[6] According to this approach, we now expand this system with another two novel tripodal ligands, 1,3,5-tris(1-imidazolyl)benzene (**4**) and 1,3-bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)benzene (**5**). As shown in Chart 1, ligand **5** has a pendulous arm since there is a methylene group between the central benzene ring and terminal imidazole group, which makes ligand **5** have higher solubility than **4** in methanol, ethanol, and acetonitrile. The flexibility of **5** may lead to a great variety of structures when it interacts with metal salts. We report herein the reactions of **4** and **5** with metal [Ag(I), Cu(II), Zn(II), Ni(II)] salts and structural characterization of a range of 2D coordination MOFs.

Experimental Section

Materials and Measurements. All commercially available chemicals are of reagent grade and used as received without further purification. Ligands **4** and **5** were synthesized by same procedures reported for preparation of 1,3,5-tris(7-azaindol-1-yl)benzene using Ullmann condensation methods between 1,3,5-tribromobenzene or 1,3-dibromo-5-(imidazol-1-ylmethyl)benzene and imidazole.[2c] Solvents were purified by standard methods prior to use. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. Variable-temperature magnetic susceptibilities (75−300 K) of complexes **8** and **10** were measured on a CHAN-2000 Faraday magnetometer. Diamagnetic correction was made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{m}}T)^{1/2}$. Infrared (IR) spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr disks.

Caution. Perchlorate salts and azide salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Preparation of the Complexes. All procedures, for example synthesis and measurements, for silver(I) complexes were carried out in the dark.

$[Ag_2(4)_2][p\text{-}C_6H_4(COO)_2]\cdot H_2O$ (6). A solution of **4** (13.8 mg, 0.05 mmol) in methanol (15 mL) was carefully layered over an aqueous solution of freshly prepared $[Ag(Py)_2][p\text{-}C_6H_4(COO)_2]$ (Py = pyridine) (0.025 mmol mL^{-1}, 2 mL). Colorless crystals were isolated by filtration after several weeks. Yield 67%. Anal. Calcd for $C_{38}H_{30}Ag_2N_{12}O_5$: C, 48.02; H, 3.18; N, 17.68. Found: C, 47.97; H, 3.32; N, 17.54.

$[Ag(4)]ClO_4$ (7). The compound was prepared by the same method described for complex **6** using $[Ag(Py)_2]ClO_4$ (0.025 mmol mL^{-1}, 2 mL) instead of $[Ag(Py)_2][p\text{-}C_6H_4(COO)_2]$. Colorless crystals were isolated by filtration after several weeks. Yield 57%. Anal. Calcd for $C_{15}H_{12}AgClN_6O_4$: C, 37.25; H, 2.50; N, 17.38. Found: C, 37.28; H, 2.55; N, 17.39.

$[Cu(4)_2(H_2O)_2](CH_3COO)_2\cdot 2H_2O$ (8). A mixture of $Cu(CH_3COO)_2\cdot H_2O$ (10.0 mg, 0.05 mmol), **4** (26.7 mg, 0.1 mmol), and H_2O (10 mL) was kept in a Teflon liner autoclave at 100 °C for 24 h. After cooling to room temperature, blue platelike crystals were collected. Yield 64%. Anal. Calcd for $C_{34}H_{38}CuN_{12}O_8$: C, 50.65; H, 4.75; N, 20.85. Found: C, 50.67; H, 4.76; N, 20.73.

$[Zn(4)_2(H_2O)_2](NO_3)_2$ (9). A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (14.9 mg, 0.05 mmol), **4** (26.7 mg, 0.1 mmol), and H_2O (10 mL) was kept in a Teflon liner autoclave at 85 °C for 3 days. After cooling

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Table 1. Crystal Data and Refinement Results for Complexes **6**−**11**

	6	**7**	**8**	**9**	**10**	**11**
chemical formula	$C_{38}H_{30}Ag_2N_{12}O_5$	$C_{15}H_{12}AgClN_6O_4$	$C_{34}H_{38}CuN_{12}O_8$	$C_{30}H_{28}N_{14}O_8Zn$	$C_{30}H_{28}N_{18}O_2Ni$	$C_{16}H_{14}AgClN_6O_4$
fw	950.48	483.63	806.30	778.03	731.41	497.65
space group	$C2/c$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	23.766(3)	7.2495(4)	8.2969(5)	10.5699(3)	9.8033(3)	18.947(2)
b, Å	12.0475(10)	12.0763(7)	12.2834(5)	11.5037(3)	12.1369(5)	9.7593(10)
c, Å	13.5160(13)	19.2196(13)	17.4667(12)	13.5194(4)	13.5215(5)	19.761(2)
α, deg	90.00	90.00	90.00	90.00	90.00	90.00
β, deg	117.827(3)	90.00	96.5740(10)	110.2779(10)	107.3280(10)	97.967(2)
γ, deg	90.00	90.00	90.00	90.00	90.00	90.00
V, Å^3	3422.4(6)	1682.62(18)	1768.40(18)	1541.98(7)	1535.80(10)	3618.9(6)
Z	4	4	2	2	2	8
λ, Å	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107
D_{calcd}, g cm^{-3}	1.845	1.909	1.514	1.676	1.582	1.827
μ (Mo Kα), cm^{-1}	12.12	13.94	6.89	8.76	6.97	12.99
T, K	200	200	200	200	200	293
R^a/R_w^b	0.0325/0.0763	0.0394/0.0999	0.0396/0.0891	0.0308/0.0702	0.0283/0.0685	0.0509/0.1018

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **6**−**11**

	6		
Ag(1)−N(12)	2.164(2)	Ag(1)−N(52)	2.207(2)
Ag(1)−N(32)	2.386(2)		
N(12)−Ag(1)−N(52)	149.88(8)	N(12)−Ag(1)−N(32)	115.76(8)
N(52)−Ag(1)−N(32)	94.20(8)		
	7		
Ag(1)−N(52)	2.199(4)	Ag(1)−N(12)	2.225(4)
Ag(1)−N(32)	2.312(4)		
N(52)−Ag(1)−N(12)	137.41(14)	N(52)−Ag(1)−N(32)	124.37(14)
N(12)−Ag(1)−N(32)	98.15(14		
	8		
Cu(1)−N(12)	2.0130(15)	Cu(1)−N(32)	2.0359(14)
Cu(1)−O(4)	2.3958(15)		
N(12)−Cu(1)−N(32)	88.68(5)	N(12)−Cu(1)−O(4)	90.38(6)
N(32)−Cu(1)−O(4)	85.67(5)		
	9		
Zn(1)−N(12)	2.1375(14)	Zn(1)−N(32)	2.1491(14)
Zn(1)−O(1)	2.1880(13)		
N(12)−Zn(1)−N(32)	90.05(5)	N(12)−Zn(1)−O(1)	91.61(5)
N(32)−Zn(1)−O(1)	87.96(5)		
	10		
Ni(1)−N(32)	2.0963(12)	Ni(1)−N(12)	2.1055(12)
Ni(1)−N(1)	2.1457(13)		
N(32)−Ni(1)−N(12)	90.66(4)	N(32)−Ni(1)−N(1)	87.45(5)
N(12)−Ni(1)−N(1)	88.65(5)		
	11		
Ag(1)−N(5)	2.201(4)	Ag(1)−N(1)	2.265(4)
Ag(1)−N(3)	2.281(3)		
N(5)−Ag(1)−N(1)	133.02(13)	N(5)−Ag(1)−N(3)	122.10(13)
N(1)−Ag(1)−N(3)	103.90(13)		

to room temperature, colorless platelike crystals were collected. Yield 58%. Anal. Calcd for $C_{30}H_{28}N_{14}O_8Zn$: C, 44.26; H, 3.96; N, 24.09. Found: C, 44.28; H, 3.87; N, 24.08.

$[Ni(4)_2(N_3)_2]\cdot 2H_2O$ (10). A mixture of $Ni(CH_3COO)_2\cdot 4H_2O$ (14.4 mg, 0.05 mmol), NaN_3 (6.5 mg, 0.1 mmol), **4** (26.7 mg, 0.1 mmol), and H_2O (10 mL) was kept in a Teflon liner autoclave at 160 °C for 24 h. After cooling to room temperature, green platelike crystals were collected. Yield 43%. Anal. Calcd for $C_{30}H_{28}N_{18}O_2Ni$: C, 49.27; H, 3.86; N, 34.47. Found: C, 49.27; H, 4.02; N, 34.55.

$[Ag(5)]ClO_4$ (11). A solution of **5** (14.5 mg, 0.05 mmol) in methanol (15 mL) was carefully layered over an aqueous solution of freshly prepared $[Ag(NH_3)_2]ClO_4$ (0.025 mmol mL^{-1}, 2 mL). Colorless crystals were isolated by filtration after several weeks. Yield 40%. Anal. Calcd for $C_{16}H_{14}AgClO_4$: C, 38.62; H, 2.84; N, 16.89. Found: C, 38.42; H, 2.96; N, 16.95.

Crystallographic Analyses. The X-ray diffraction measurements for complexes **6**, **7**, **8**, **9**, and **10** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The data collection for complex **11** was made on a Bruker Smart Apex CCD with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods using SIR92[7] and expanded using Fourier techniques.[8] All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms except for those of water molecules were generated geometrically. Atoms O2, O3, and O4 of the perchlorate anion in complex **11** have two positions with the site occupancy factors of 0.63(3) and 0.37(3), respectively. The crystal parameters, data collection, and refinement results for compounds **6**−**11** are summarized in Table 1. Selected bond length and angles are listed in Table 2. Further details are provided in the Supporting Information.

Results and Discussion

Description of Crystal Structures. $[Ag_2(4)_2][p\text{-}C_6H_4(COO)_2]\cdot H_2O$ (6) and $[Ag(4)]ClO_4$ (7). The X-ray crystallographic analysis revealed that the asymmetric unit of complex **6** contains one molecule ligand **4**, one silver(I) cation, and half of a molecule of the paraphthalate anion (Figure 1a). Each silver(I) atom in complex **6** is coordinated by three N atoms of imidazole from three different **4** ligands. The Ag−N distances are ranging from 2.164(2) to 2.386(2) Å, and the coordination angles are varying from 94.20(8)° to 149.88(8)° (Table 2). The Ag1 atom locates within the plane formed by N12, N32, and N52A atoms (Figure 1a) with deviation less than 0.05 Å. On the other hand, each ligand **4** in turn links three Ag(I) atoms to generate an infinite 2D network structure based on (6, 3) nets as illustrated in Figure 1b. Three Ag(I) atoms and three **4** ligands (each **4** using two of the three arms connects two silver atoms) form a 30-membered macrocyclic ring through the Ag−N coordination bonds. In this macrometallacycle, the lengths of the

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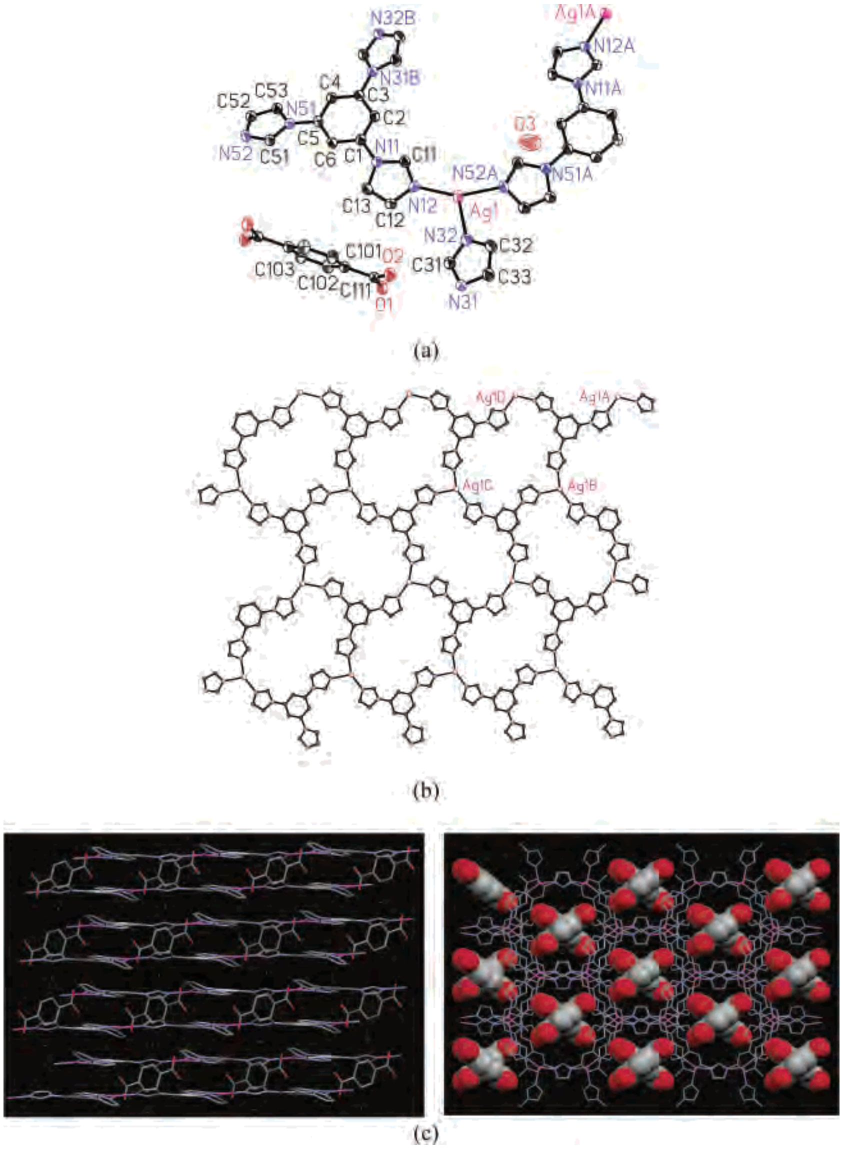

Figure 1. (a) Crystal structure of **6** with atom numbering scheme. The thermal ellipsoids are drawn at 50% probability, and hydrogen atoms were omitted for clarity. (b) 2D honeycomb network of **6** with 30-membered metallacycles. (c) Side (left) and top (right) views of crystal packing diagram of **6**.

edges are not equivalent, and the intermetallic separations of Ag1C···Ag1D, Ag1B···Ag1D, and Ag1B···Ag1C are 12.49, 11.88, and 12.05 Å, respectively.

The crystal packing diagram of **6** is shown in Figure 1c. It can be seen clearly that the 2D layers repeat in an ···ABAB··· stacking sequence (left) with open channels occupied by paraphthalate anions and water molecules (right). It is noteworthy that the paraphthalate anions and water molecules are sandwiched by each two adjacent layers, respectively. The distance between two layers separated by paraphthalate anions is 3.38 Å, and the one between two layers separated by water molecules is 3.34 Å. The 2D layers, paraphthalate anions, and water molecules are linked together by C−H···O and O−H···O hydrogen bonds to form a 3D structure (Figure S1). The data of hydrogen bonding are summarized in Table 3. The distance of 2.760(3) Å between the O atom of water and carboxylate O of paraphthalate indicates the formation of the O−H···O hydrogen bond although the hydrogen atoms of the water molecule could not be found.

In complex **6**, silver(I) atoms serve as trigonal nodes, and the formation of networks with (6, 3) topology is enhanced by using tripodal ligand **4** enclosing an angle about 120°. A previously reported three-coordinated silver(I) complex with the same (6, 3) topology is [Ag(TCB)](CF_3SO_3) (TCB = 1,3,5-tricyanobenzene).[1a] TCB is a strictly planar and rigid ligand, and there is no conformation variation of TCB. In contrast to TCB, ligand **4** can have different conformations defined by dihedral angles between the imidazole ring planes and the central benzene ring plane. In each 2D layer of complex **6**, the plane formed by silver(I) atoms and benzene ring planes are coplanar, while the imidazole ring planes deviate from the benzene ring planes with dihedral angles of 6.3°, 20.8°, and 26.0° in each ligand **4**. The dihedral angles between each two of three imidazole groups of ligand **4** in **6** are 26.3°, 26.6°, and 26.8°, respectively. In order to evaluate the influence of the anions on the structure of the complex, silver(I) perchlorate was used to react with **4** instead of silver(I) paraphthalate, and complex [Ag(**4**)]ClO_4 (**7**) was successfully isolated.

Table 3. Distances [Å] and Angles [deg] of Hydrogen Bonding for Complexes **6**−**11**[a]

D−H···A[b]	distance (D···A)	D−H−A	angle (D−H−A)
	6		
C2−H1···O1#1	3.336(4)	C2−H1−O1#1	175
C11−H4···O1#1	3.267(4)	C11−H4−O1#1	172
C12−H5···O2	3.317(3)	C12−H5−O2	163
C31−H7···O2	3.228(4)	C31−H7−O2	172
C51−H10···O3#2	3.184(4)	C51−H10−O3#2	163
C53−H12···O2#3	3.261(3)	C53−H12−O2#3	170
O3···O1#4	2.760(3)		
	7		
C4−H2···O2#5	3.195(6)	C4−H2−O2#5	124
C6−H3···O3#6	3.281(5)	C6−H3−O3#6	130
C11−H4···O1#6	3.426(7)	C11−H4−O1#6	146
C11−H4···O3#6	3.313(6)	C11−H4−O3#6	156
C31−H7···O2#7	3.237(6)	C31−H7−O2#7	159
C32−H8···O2#8	3.489(6)	C32−H8−O2#8	172
C33−H9···O1#9	3.341(5)	C33−H9−O1#9	168
C51−H10···O3#8	3.398(5)	C51−H10−O3#8	159
C53−H12···O2#10	3.351(5)	C53−H12−O2#10	156
	8		
O3−H16···O2	2.807(2)	O3−H16−O2	175
O3−H17···O1#11	2.815(2)	O3−H17−O1#11	169
O4−H18···O1	2.836(2)	O4−H18−O1	165
O4−H19···N52#12	2.846(2)	O4−H19−N52#12	174
C2−H1···O2#13	3.262(2)	C2−H1−O2#13	154
C4−H2···O3#14	3.402(2)	C4−H2−O3#14	162
C11−H4···O1	3.201(2)	C11−H4−O1	176
C33−H9···O3#13	3.273(2)	C33−H9−O3#13	148
	9		
O1−H13···O12#15	2.796(2)	O1−H13−O12#15	171
O1−H14···O13	2.972(2)	O1−H14−O13	173
C2−H1···O11#16	3.482(2)	C2−H1−O11#16	157
C4−H2···O11#17	3.337(2)	C4−H2−O11#17	167
C11−H4···N52#18	3.418(3)	C11−H4−N52#18	144
C31−H7···O11	3.268(2)	C31−H7−O11	137
C51−H10···O11#17	3.326(2)	C51−H10−O11#17	165
C53−H12···O13#19	3.145(3)	C53−H12−O13#19	149
	10		
O1−H13···N1	2.978(2)	O1−H13−N1	164
O1−H14···N3#20	2.877(2)	O1−H14−N3#20	170
C11−H4···O1	3.274(2)	C11−H4−O1	142
C31−H7···N52#21	3.328(2)	C31−H7−N52#21	136
C51−H10···O1	3.450(2)	C51−H10−O1	165
	11		
C6−H6···O4	3.164(17)	C6−H6−O4	161
C7−H7A···O3#22	3.441(11)	C7−H7A−O3#22	162
C7−H7B···O1#23	3.453(6)	C7−H7B−O1#23	149
C13−H13···O2#22	3.334(15)	C13−H13−O2#22	153
C14−H14···O3#24	3.349(13)	C14−H14−O3#24	149

[a] Symmetry transformation used to generate equivalent atoms: #1, $^{1}/_{2} - x, -^{1}/_{2} + y, ^{3}/_{2} - z$; #2, $-^{1}/_{2} + x, -^{1}/_{2} + y, z$; #3, $x, -1 + y, z$; #4, $^{1}/_{2} - x, ^{1}/_{2} - y, 1 - z$; #5, $^{1}/_{2} + x, ^{1}/_{2} - y, 1 - z$; #6, $1 + x, y, z$; #7, $-x, -^{1}/_{2} + y, ^{1}/_{2} - z$; #8, $-^{1}/_{2} - x, 1 - y, -^{1}/_{2} + z$; #9, $^{1}/_{2} + x, ^{1}/_{2} - y, -z$; #10, $-x, ^{1}/_{2} + y, ^{1}/_{2} - z$; #11, $^{3}/_{2} - x, ^{1}/_{2} + y, ^{3}/_{2} - z$; #12, $^{3}/_{2} - x, -^{1}/_{2} + y, ^{3}/_{2} - z$; #13, $^{5}/_{2} - x, -^{1}/_{2} + y, ^{3}/_{2} - z$; #14, $^{1}/_{2} + x, ^{1}/_{2} - y, ^{1}/_{2} + z$; #15, $^{3}/_{2} - x, -^{1}/_{2} + y, ^{3}/_{2} - z$; #16, $1 - x, -y, 1 - z$; #17, $^{1}/_{2} + x, -^{1}/_{2} - y, -^{1}/_{2} + z$; #18, $2 - x, -1 - y, 1 - z$; #19, $x, -1 + y, z$; #20, $^{1}/_{2} - x, ^{1}/_{2} + y, ^{1}/_{2} - z$; #21, $-^{1}/_{2} + x, ^{1}/_{2} - y, -^{1}/_{2} + z$; #22, $1 - x, 1 - y, -z$; #23, $-^{1}/_{2} + x, ^{3}/_{2} - y, -^{1}/_{2} + z$; #24, $^{3}/_{2} - x, ^{3}/_{2} - y, -z$. [b] D = donor; A = acceptor.

As exhibited in Figure 2a, complex **7** has same coordination mode and (6, 3) topology as those of complex **6** as already described. The 2D layers of **7** also repeat in an ···ABAB··· stacking sequence. The perchlorate anions occupy the vacancy among the 2D layers (Figure 2b) and link the 2D layers together through the C−H···O hydrogen bonds (Table 3). However, there are substantial differences between the two complexes **6** and **7** due to the different counterions. First, they crystallize in different crystal systems. Complex **6** has a monoclinic $C2/c$ space group, while **7** is orthorhombic with space group of $P2_12_12_1$. It is noteworthy that complex **7** crystallizes in a chiral space group. Such difference between complexes **6** and **7** is considered to be caused by the symmetry and size of the anions. The dicarboxylate anion in **6** is at the symmetric center. The macrocyclic ring in **6** is planar (Figure 1c) while the corresponding ring in **7** is bent (Figure 2b). The anions restrict the conformation of the macrocycle which determines the crystal packing. Another important difference between **6** and **7** is the conformation of the imidazole groups of ligand **4**. The dihedral angles between each two of three imidazole groups of ligand **4** in **7** are 30.1°, 37.3°, and 55.5°, and the dihedral angles between each imidazole group and central benzene ring are 24.8°, 38.3°, and 41.9°, respectively, which are much larger than the corresponding dihedral angles in complex **6**. As a result of such conformational difference, in contrast to the near planar 2D layers of **6** (Figure 1c), the 2D layers in **7** are corrugated, and the silver(I) atoms in each layer are not coplanar as shown in Figure 2b. There are two silver(I) planes with a separation of 1.33 Å in each layer of **7**. The intermetallic distances in one layer of Ag1A···Ag1B, Ag1A···Ag1C, and Ag1B···Ag1C (Figure 2a) are 12.28, 13.25, and 10.17 Å, respectively, and the distance between two adjacent layers is 3.62 Å which is larger than that in complex **6**. The results show that in this system with a rigid ligand the anions do not affect the structure of the backbone but have influence on the conformation of the ligand and crystal packing.

Complexes $[Cu(4)_2(H_2O)_2](CH_3COO)_2 \cdot 2H_2O$ (8), $[Zn(4)_2(H_2O)_2](NO_3)_2$ (9), $[Ni(4)_2(N_3)_2] \cdot 2H_2O$ (10). In contrast to the three-coordinated silver(I) atoms in complexes **6** and **7**, metal atoms such as Cu(II), Zn(II), and Ni(II) are usually six-coordinated when they react with organic ligands with N donors. In order to evaluate the role of metal atoms with different geometric requirements in crystal engineering of organic−inorganic hybridized compounds,[9] reactions of **4** with various metal salts were carried out, and the results of Cu(II), Zn(II), and Ni(II) complexes are described here. Similar cell parameters of complexes **8**, **9**, and **10** (Table 1) indicate that they have an analogous structure. Therefore, only the structure of complex **8**, as a typical example, is described here in detail.

In complex **8**, each Cu(II) atom is six-coordinated and has a slightly distorted octahedral coordination environment with four N atoms at the equatorial plane from four different **4** ligands and two O atoms from two water molecules with the coordination angles varying from 85.67(5)° to 180° and bond lengths of Cu1−N12 = 2.0130(15) Å, Cu1−N32B = 2.0359(14) Å, and Cu1−O4 = 2.3958(15) Å (Table 2 and Figure 3a). Two coordinated water molecules are at the opposite direction of the Cu(II)

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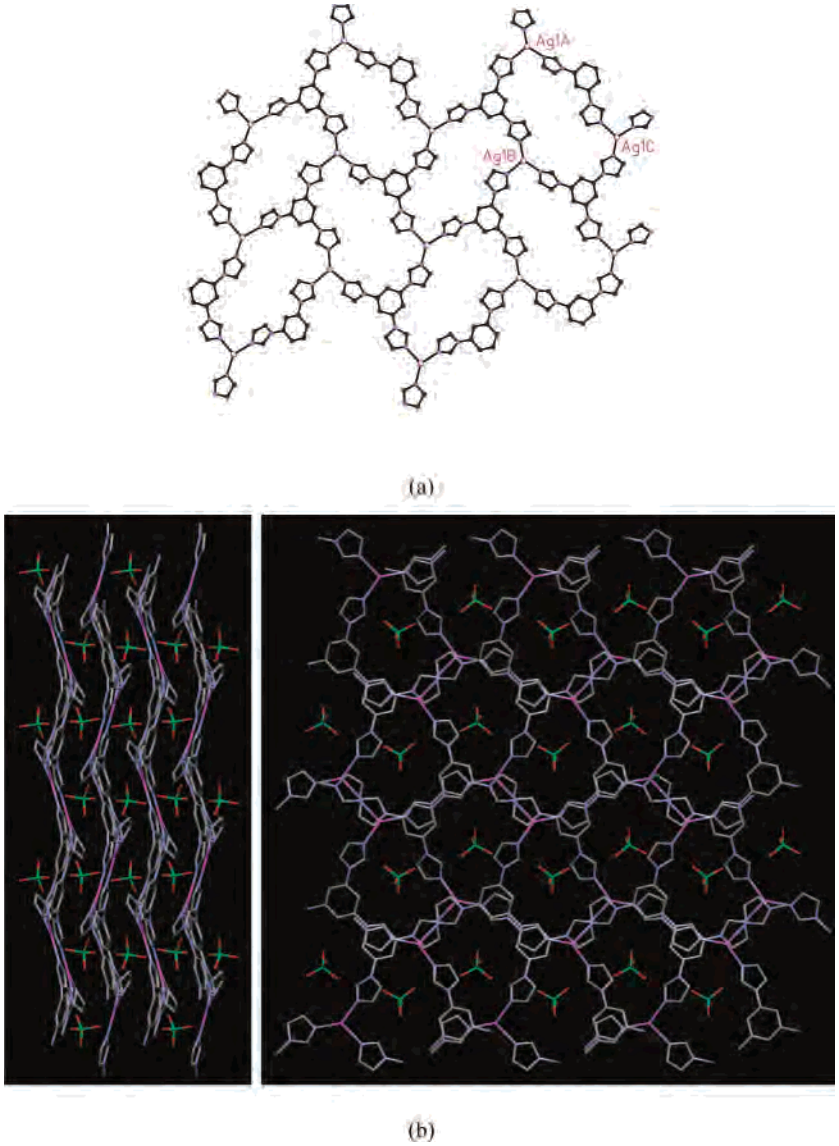

(a)

(b)

Figure 2. (a) 2D honeycomb network of **7** with 30-membered metallacycles. (b) Side (left) and top (right) views of crystal packing diagram of **7**.

atoms. It is noteworthy that the acetate anions did not coordinate to the Cu(II) atoms in complex **8** while, in the reported complex $[Cu_3(\mathbf{1})_2(CH_3COO)_6]\cdot H_2O$ obtained by reaction of $Cu(CH_3COO)_2\cdot H_2O$ with ligand **1**, the acetate anions coordinated to the Cu(II) atoms.[6d] In the case of complex **10**, the coordinated water molecules are replaced by azide anions, and the complex is neutral with one Ni(II) atom and two azide anions. It is interesting that each ligand **4** in **8** coordinates to two Cu(II) atoms rather than three, and the third imidazole group does not participate the coordination. Namely, **4** acts as a three-connecting ligand in **6** and **7**, and as a two-connecting (bridging) one in **8**. As shown in Figure 3a, four Cu(II) atoms (e.g., Cu1, Cu1A, Cu1C, and Cu1E) and four molecules of ligand **4** form a 40-membered macrocyclic ring which is further linked by Cu–N bonds to give a 2D network structure. The intermetallic distance in one layer of Cu1···Cu1A = Cu1A···Cu1C (Figure 3a) is 11.09 Å.

In complex **8**, the uncoordinated N atom of imidazole of ligand **4** forms an O–H···N hydrogen bond with the coordinated water molecule from the adjacent layer to link the 2D networks to generate a 3D framework (Figure S2). The acetate anions occupy the voids between the 2D layers (Figure 3b) and are bound to the framework through (water) O–H···O (acetate) and C–H···O (acetate) hydrogen bonds (Table 3 and Figure S2). Crystallographic study reveals that the structures of complexes **8**, **9**, and **10** are very similar concerning the coordination mode, network structure, and crystal packing despite the wide variety of the metal center and anions. The results indicate that the structures of assemblies are mainly depending on the geometric requirement of metal ions but are not influenced significantly by the anions and metal atoms in this system.

Complex $[Ag(\mathbf{5})]ClO_4$ (11). Three imidazole groups are connected to the central benzene group directly through the C–N bonds in ligand **4**, so it can be referred to as a rigid organic ligand. In the previously reported ligands **1**, **2**, and **3**, there is one methylene group between each imidazole and central benzene group. Thus, they are flexible ligands and can adopt different conformations when they interact with

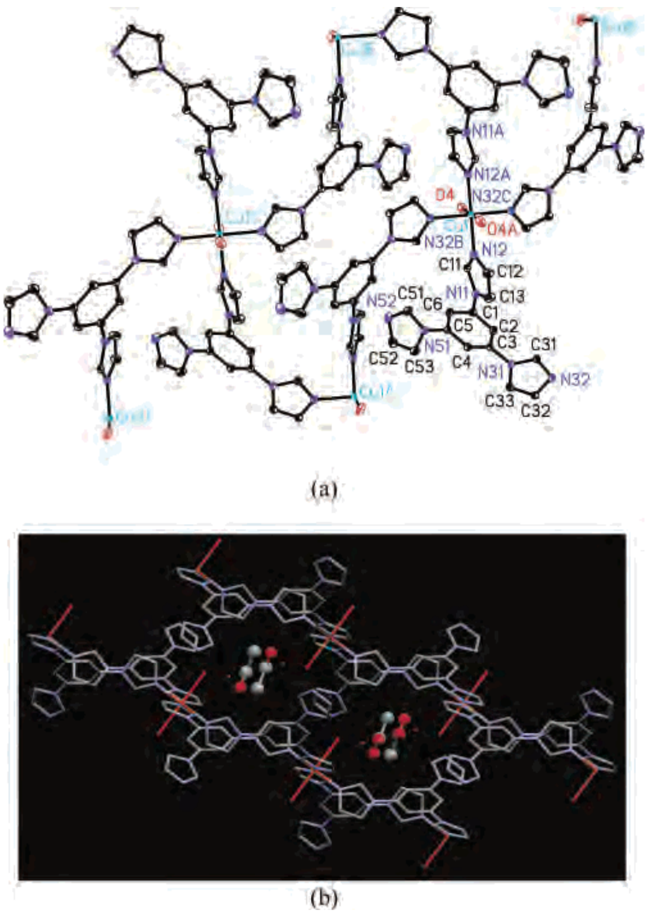

Figure 3. (a) Top view of 2D network structure of complex **8** with atom numbering scheme. The thermal ellipsoids are drawn at 50% probability, and hydrogen atoms and acetate anions were omitted for clarity. (b) Crystal packing diagram of **8**.

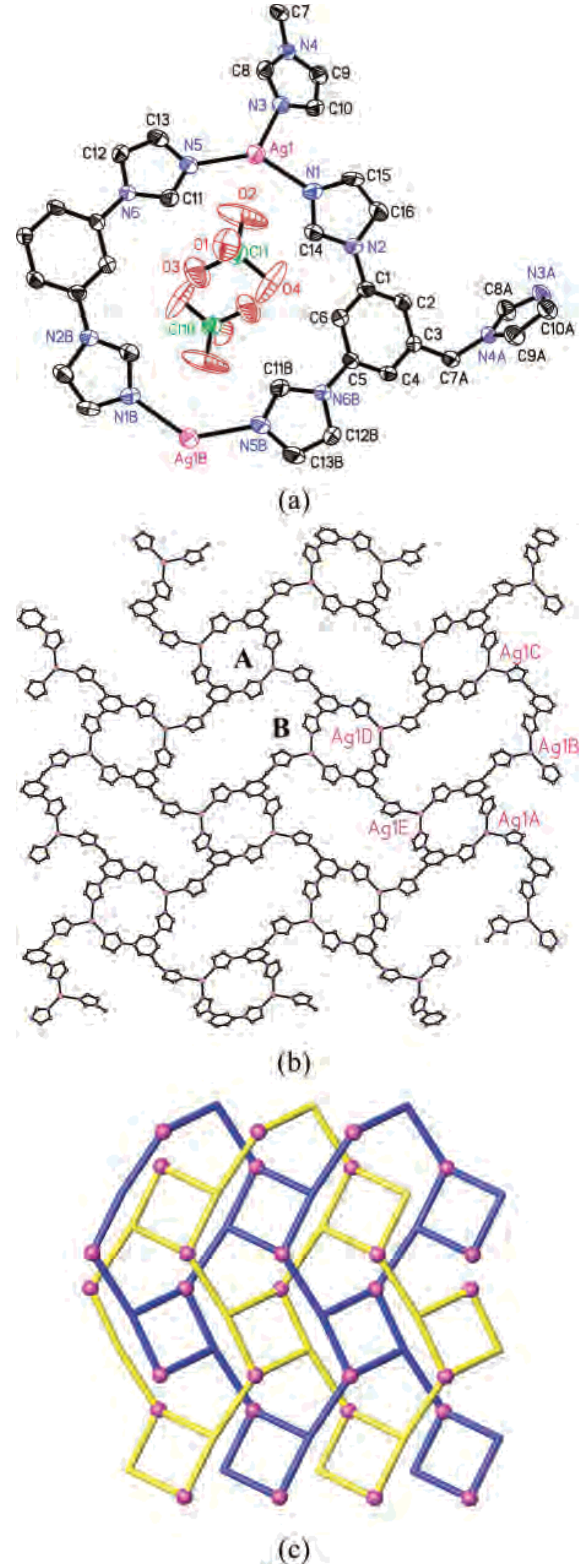

Figure 4. (a) Crystal structure of **11** with atom numbering scheme. The thermal ellipsoids are drawn at 50% probability, and hydrogen atoms were omitted for clarity. (b) 2D network with 20- and 44-membered metallacycles in **11**. (c) Parallel interpenetration of two 4.8^2 nets in **11**. The red circles represent silver atoms.

metal ions.[6] In order to further investigate the influence of the flexibility of ligands on the formation of MOFs, we introduced one flexible arm in ligand **5** by insertion of one methylene group between the imidazole and central benzene group. A twofold parallel interpenetrated network **11** with 4.8^2 topology was obtained by reaction of **5** with silver perchlorate.

As shown in Figure 4a, each silver(I) atom in complex **11** is coordinated by three N atoms from three different **5** ligands. Because of the presence of one flexible arm, ligand **5** can coordinate to the metal center comfortably to meet the geometric requirement of Ag(I). As a result, the three Ag−N bond lengths in **11** are essentially equal to each other (Ag1−N5 = 2.201(4) Å, Ag1−N1 = 2.265(4) Å, Ag1−N3 = 2.281(3) Å), and the N−Ag−N coordination angles are much closer to 120° than those in complexes **6** and **7** (Table 2).

There is only one kind of 30-membered macrocycle in complexes **6** and **7**. However, as illustrated in Figure 4b, each ligand **5** links three Ag(I) atoms to generate a 2D network structure with two different metallacycles A and B. In A, four arms without methylene groups from two **5** ligands connect two Ag(I) atoms to form a 20-membered ring with a Ag···Ag (e.g., Ag1A···Ag1E in Figure 4b) distance of 9.52 Å. In B, four **5** ligands, each using two of their two arms, link four Ag(I) atoms to form a 44-membered ring with intermetallic distances of Ag1B···Ag1C

= Ag1D⋯Ag1E = 11.31 Å and Ag1B⋯Ag1E = Ag1C⋯Ag1D = 14.56 Å. Accordingly, each 20-membered ring is surrounded by four 44-membered rings, and each 44-membered ring neighbors upon four 20-membered rings and four 44-membered rings. Thus, the 2D network of **11** can be regarded as a 4.8^2 topology.[10,11]

In contrast to the frequent occurrence of network interpenetrating in coordination polymers with (6, 3) topology,[12] the interpenetration of 4.8^2 networks are not well-known yet.[10] In complex **11**, two independent 4.8^2 networks are interpenetrating each other in a parallel fashion, still making an infinite 2D network structure (Figure 4c). Flexible ligand **5** makes its Ag(I) complex **11** possible to interpenetrate each other, while Ag(I) complex **7** with rigid ligand **4** could not. In complex **11**, the 44-membered ring is large enough to include a 20-membered ring from another sheet. In addition, the corrugation of the 2D sheets, caused by the flexible arm of **5**, is also essential for the parallel interpenetration. The dihedral angles between the imidazole without the methylene group and central benzene ring are 21.3° and 35.0°. The one between the imidazole with the methylene group and central benzene ring is 96.1°, which implies that the imidazole of the flexible arm is nearly perpendicular with the central benzene ring (Figure 4a). The perchlorate anions locate at a vacancy of a 20-membered ring (Figure 4a) and connect to the framework through C−H⋯O hydrogen bonds (Table 3).

Properties. The magnetic behavior of the paramagnetic compounds **8** and **10** was measured over the temperature range from 70 to 300 K. The observed magnetic moments of 1.63 and 3.00 μ_B at 300 K per molecule of **8** and **10** are close to the spin only values of 1.73 and 2.83 μ_B, respectively. Furthermore, both effective moments remain almost unchanged over the measured temperature range for **8** and **10**. The results indicate that there is practically no magnetic interaction between the neighboring metal atoms in these two complexes due to the long intermetallic distance as revealed by X-ray analysis.

The anion-exchange properties of the complexes were investigated by procedures described previously.[6a,e,f] It was found that the paraphthalate anions in complex **6** could not be exchanged by other anions. However, the perchlorate anions in complexes **7** and **11** can be exchanged by nitrate and tetrafluoroborate anions, respectively. For example, after complex **11** was exchanged with aqueous sodium tetrafluoroborate solution, the IR spectrum of the exchanged product exhibited characteristic bands of the tetrafluoroborate anion at 1143, 1118, and 1084 cm^{-1}, which are different from those of the original **11** at 1118, 1090, and 1066 cm^{-1} as observed in the anion-exchange of cagelike complexes.[6a]

Conclusions

Six 2D coordination polymers with 1,3,5-tris(1-imidazolyl)benzene (**4**) and 1,3-bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)benzene (**5**) have been prepared and structurally characterized. The structures of **6** and **7** have a similar 2D honeycomb framework with (6, 3) topology, in which the three-coordinated silver center serves as a trigonal node. In complexes **8**−**10**, the metal centers are all six-coordinated, and the backbones are based on (4, 4) nets. The topological difference between complexes **6**, **7**, and **8**−**10** is attributed to the different geometric needs of metal atoms. The results of structural analysis of complexes **6**−**10** with rigid ligand **4** reveal that their structures are mainly depending on the geometric requirement of the metal ions but are not influenced by the counteranions greatly. The reaction of $AgClO_4$ with ligand **5** with a flexible arm yields complex **11** with an unexpected 4.8^2 framework, in which the silver center is also three-coordinated and serves as trigonal node as same as the one in **7**. MOFs **7** and **11** with different topologies were obtained by reactions of $AgClO_4$ with **4** and **5**, respectively. Such a difference was caused by the introduction of one methylene group between the imidazole and central benzene groups in **5**, and the results show that the nature of the organic ligand has a great influence on the self-assembly process of MOFs.

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Supporting Information Available: X-ray crystallographic file, in CIF format, and crystal packing diagrams with hydrogen bonds of **6** (Figure S1) and **8** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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