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Assembly of Metal−Organic Frameworks from Large Organic and Inorganic Secondary Building Units: New Examples and Simplifying Principles for Complex Structures[△]

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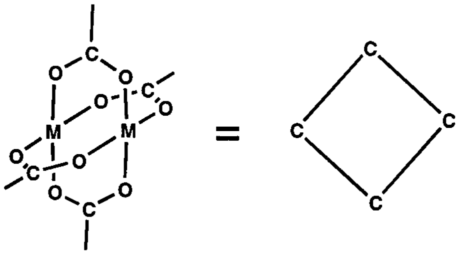
Abstract: The secondary building unit (SBU) has been identified as a useful tool in the analysis of complex metal−organic frameworks (MOFs). We illustrate its applicability to rationalizing MOF crystal structures by analysis of nine new MOFs which have been characterized by single-crystal X-ray diffraction. Tetrahedral SBUs in $Zn(ADC)_2 \cdot (HTEA)_2$ (MOF-31), $Cd(ATC) \cdot [Cd(H_2O)_6](H_2O)_5$ (MOF-32), and $Zn_2(ATB)(H_2O) \cdot (H_2O)_3(DMF)_3$ (MOF-33) are linked into diamond networks, while those of $Ni_2(ATC)(H_2O)_4 \cdot (H_2O)_4$ (MOF-34) have the structure of the Al network in $SrAl_2$. Frameworks constructed from less symmetric tetrahedral SBUs have the Ga network of $CaGa_2O_4$ as illustrated by $Zn_2(ATC) \cdot (C_2H_5OH)_2(H_2O)_2$ (MOF-35) structure. Squares and tetrahedral SBUs in $Zn_2(MTB)(H_2O)_2 \cdot (DMF)_6(H_2O)_5$ (MOF-36) are linked into the PtS network, which is the simplest structure type known for the assembly of these shapes. The octahedral SBUs found in $Zn_2(NDC)_3 \cdot [(HTEA)(DEF)(ClBz)]_2$ (MOF-37) form the most common structure for linking octahedral shapes, namely, the boron network in CaB_6. New structure types for linking triangular and trigonal prismatic SBUs are found in $Zn_3O(BTC)_2 \cdot (HTEA)_2$ (MOF-38) and $Zn_3O(HBTB)_2(H_2O) \cdot (DMF)_{0.5}(H_2O)_3$ (MOF-39). The synthesis, crystal structure, and structure analysis using the SBU approach are presented for each MOF.

Introduction

Considerable effort has been devoted to the assembly of extended frameworks from molecular building blocks due to the advantages such an approach offers for the design of materials.[1] However, controlling the orientation of building blocks in the solid state and thus prediction of the resulting structure remains a great challenge. We have found this to be especially true in our early efforts to build porous metal−organic frameworks (MOFs) from monodentate ditopic linkers such as 4,4′-bipyridine, where the flexible nature of the angles within the metal coordination sphere resulted in less predictable and more flexible framework topologies, ultimately leading to nonporous structures.[2]

We later focused on using multidentate carboxylate functionalities as they are known to be essential in chelating metal ions and locking their position into M−O−C clusters, **a**, which can act as *rigid* entities, referred to as secondary building units (SBUs).[3] Consideration of the overall shape adopted by the points of extension in an SBU (for example, the carboxylate carbon atoms forming a square SBU in **a**) is useful in predicting the topology of MOFs that would result from polymerizing these shapes with polytopic organic linkers.[4]



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[△] All crystal structures may be viewed and manipulated at http://www.umich.edu/~yaghigrp/structures.html.

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On a fundamental level, the use of both known and new metal−organic clusters as SBUs in the manner just illustrated represents an important component in the hierarchical description of complex structures. The successful application of this approach has had significant implications for the design of highly porous and robust MOF structures for which the rigidity of the SBUs made it possible to predict the topology.[5] Here we illustrate, using nine new MOFs assembled from a diverse set of large organic linkers and divalent transition metal ions, that this strategy can be generally applied to understanding, determining, and predicting new structure patterns and topologies of complex MOF structures. Although the compounds in this study have structures that offer promising host−guest chemistry and porosity, already investigated for other MOFs,[6] our main focus here will be on understanding the structural aspects relating to their construction from SBUs.

Experimental Section

Synthesis of MOFs, Abbreviations, and General Procedures. For easy reference, the crystallographic data for MOFs are listed in Table 1. The organic carboxylates used in this study are shown in Chart 1. The inorganic and organic SBUs identified in the crystal structures of MOF-31−39 including their respective spacers and structure topologies are summarized in Table 2. Unless otherwise indicated, all pore diameter values were obtained by considering the van der Waals radii of atoms making up the pores.

Typically, preparation of a MOF was performed by combining the metal(II) salt with the acid form of the organic carboxylate at room temperature under aerobic conditions or under solvo(hydro)thermal conditions in a closed stainless steel Parr Teflon-lined vessel (23 mL). In room-temperature syntheses, triethylamine was diffused into the solution mixture of reactants often in the presence of in mixed solvents. Preparations involving MOF-31 to MOF-37 were repeated at least three times and found to be fully reproducible. In contrast, the synthesis of MOF-38 and MOF-39 was found to be difficult to reproduce; nevertheless, the materials have been structurally characterized.

All metal salts, solvents, and the organic acids H_2ADC, H_3BTC, and H_2NDC were purchased from Aldrich Chemicals and used without further purification. The organic acids H_4MTB, H_4ATC, and H_4ATB were prepared, respectively, according to published procedures.[7−9] However, H_3BTB was prepared by combination of 1,3,5-tris(methylphenyl)benzene (1.0 g, 2.87 mmol), concentrated HNO_3 (1.5 mL), and water (6.0 mL) in a Parr Teflon-lined stainless steel vessel which was heated to 170 °C for 24 h to give 1.1 g of H_3BTB (86% yield).

Zn(ADC)$_2$·(HTEA)$_2$, MOF-31. Acetylenedicarboxylic acid (H_2ADC; 0.092 g, 0.80 mmol) and $Zn(NO_3)_2·6H_2O$ (0.118 g, 0.40 mmol) were dissolved in ethanol (20 mL) and placed in a vial that was then inserted in a larger vial containing triethylamine/ethanol (0.2 mL/4.0 mL). The

Table 1. Crystal and Structure Refinement Data for MOF-31−39[a]

	MOF-31	MOF-32	MOF-33	MOF-34	MOF-35	MOF-36	MOF-37	MOF-38	MOF-39
empirical formula[b]	$C_{16}H_{30}N_2O_8Zn$	$C_{14}H_{32}O_{18}Cd_2$	$C_{38}H_{44}O_{16}Zn_2$	$C_{14}H_{28}O_{16}Ni_2$	$C_{34}H_{47}O_{22}Zn_4$	$C_{40}H_{62}O_7Zn$	$C_{35}H_{41}N_2O_7ClZn$	$C_{33}H_{44}N_3O_{15.75}Zn_3$	$C_{55.5}H_{44}N_{0.5}O_{17}Zn_3$
formula wt	443.80	713.20	887.47	569.77	1069.20	720.27	702.52	930.86	1186.02
crystal size, mm	0.19 × 0.14 × 0.14	0.26 × 0.24 × 0.12	0.30 × 0.06 × 0.04	0.15 × 0.15 × 0.05	0.20 × 0.02 × 0.02	0.50 × 0.18 × 0.10	0.20 × 0.14 × 0.14	0.21 × 0.18 × 0.05	0.40 × 0.32 × 0.06
crystal system	cubic	cubic	orthorhombic	orthorhombic	orthorhombic	tetragonal	triclinic	tetragonal	orthorhombic
space group	$Pn(-3)m$	$P(-4)3m$	$Imma$	$P2_12_12_1$	$Pbca$	$P4_2/mmc$	$P(-1)$	$I4cm$	$Pnma$
T, K	158(2)	158(2)	23(2)	159(2)	158(2)	102(2)	158(2)	118(2)	158(2)
a, Å	10.8212(13)	13.4677(7)	19.561(6)	10.0656(3)	15.745(7)	11.722(5)	9.9518(8)	20.6571(7)	17.158(6)
b, Å	10.8212(13)	13.4677(7)	15.255(5)	11.1625(3)	16.907(7)	11.722(5)	11.5761(9)	20.6571(7)	21.591(7)
c, Å	10.8212(13)	13.4677(7)	23.404(7)	19.2011(2)	18.167(8)	23.740(14)	15.5562(12)	17.8400(6)	25.308(8)
α, deg	90	90	90	90	90	90	72.377(1)	90	90
β, deg	90	90	90	90	90	90	83.165(1)	90	90
γ, deg	90	90	90	90	90	90	84.326(1)	90	90
V, Å^3	1267.1(3)	2442.8(2)	6984(4)	2157.38(9)	4836(3)	3262(3)	1692.1(2)	7612.6(4)	9376(5)
Z	2	4	4	4	4	4	2	8	4
d_{calc}, g/cm^3 [c]	1.163	1.939	0.844	1.754	1.469	1.467	1.379	1.624	0.840
μ, mm^{-1}	2.373	1.822	0.728	4.013	2.033	8.100	0.855	3.882	0.802
reflcns collected	5111	25 227	14 526	9647	33 196	4574	12 232	17 901	79 244
unique reflctns	108	1000	1512	2941	3498	1002	4859	3082	8232
variables	24	84	145	233	287	110	418	263	400
$R1$, $wR2$, %	5.5, 6.5	5.90, 16.04	10.64, 32.10	2.9, 3.7	7.02, 21.59	10.18, 26.55	5.88, 15.65	4.2, 4.6	7.97, 24.14
goodness of fit	3.11	1.196	0.999	1.37	0.919	1.525	0.987	1.340	0.947

[a] All the data were collected by SMART CCD diffractometers with Mo Kα radiation (λ = 0.710 73 Å). [b,c] Based on crystal structure refinement. Due to disorder of guests in the pores, the empirical formulas in some cases may be different than those found using elemental microanalysis (see Supporting Information for details).

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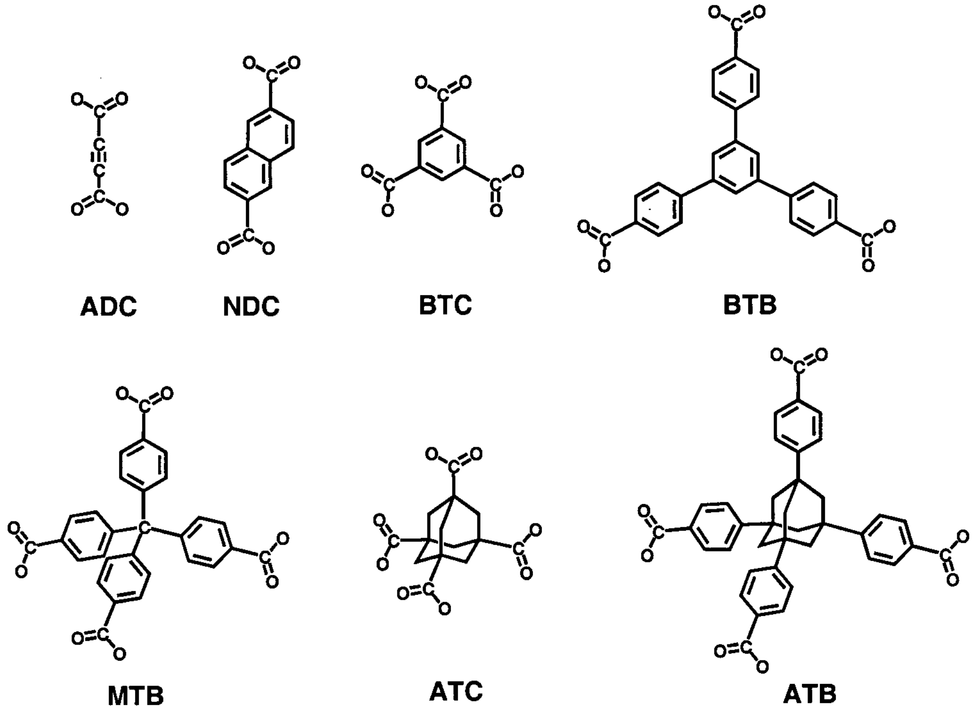
Chart 1. Organic Carboxylates Used in the Study[a]



[a] Key: ADC, acetylenedicarboxylate; BTC, benzenetricarboxylate; NDC, 2,6-naphthalenedicarboxylate; BTB, benzenetribenzoate; MTB, methanetetrabenzoate; ATC, adamantanetetracarboxylate; ATB, adamantanetetrabenzoate.

larger vial was sealed and left undisturbed for 21 days. The resulting colorless cubic crystals become opaque when exposed to air. This material is soluble in water, slightly soluble in methanol, and insoluble in ethanol, acetone, *N,N'*-dimethylformamide (DMF), and dimethyl sulfoxide. The crystals were filtered and washed with 3 × 10 mL ethanol and left to air-dry, yielding 0.077 g (40% based on H_2ADC). Anal. Calcd for $C_{20}H_{32}N_2O_8Zn$ = MOF-31: C, 48.64; H, 6.53; N, 5.67. Found: C, 46.46; H, 6.12; N, 5.06. FTIR (KBr, 3500−400 cm^{-1}): 3421 (br), 3245 (br), 3043 (br), 2984 (m), 2945 (m), 2815 (w), 2743 (m), 2684 (s), 2606 (w), 2496 (m), 1603 (vs), 1479 (m), 1433 (m), 1368 (vs), 1179 (m), 1075 (w), 1084 (m), 1016 (m), 872 (w), 781 (s), 683 (s).

$Cd(ATC)\cdot[Cd(H_2O)_6](H_2O)_5$, MOF-32. H_4ATC (0.048 g, 0.15 mmol), $Cd(NO_3)_2\cdot 4H_2O$ (0.120 g, 0.39 mmol), and aqueous NaOH solution (3 mL, 6 × 10^{-4} mmol) were added respectively to a vessel, which was sealed and heated to 180 °C at a rate of 5 °C/min for 60 h and then cooled to room-temperature at a rate of 2 °C/min. Octahedral colorless crystals of the product were formed and collected by filtration, yielding 0.10 g (91% yield based on H_4ATC). The product is stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, acetone, chloroform, and DMF. Anal. Calcd for $C_{14}H_{34}O_{19}Cd_2$ = MOF-33: C, 23.00; H, 4.65. Found: C, 22.99; H, 4.50. FT-IR (KBr, 4000−400 cm^{-1}): 3468 (br, s), 2954 (w), 1710 (w), 1559 (s), 1401 (m), 1348 (m), 1216 (w), 1118 (w), 723 (m).

$Zn_2(ATB)(H_2O)\cdot(H_2O)_3(DMF)_3$, MOF-33. H_4ATB (0.012 g, 0. 02 mmol), $ZnCl_2$ (0.020 g, 0.15 mmol), DMF (3 mL), C_2H_5OH (3 mL), and H_2O (2 mL) were added respectively to a vessel that was sealed and heated to 100 °C at a rate of 2 °C/min for 48 h and then cooled to room temperature at a rate of 1 °C/min. Needle-shaped colorless crystals of the product were formed and collected by filtration, yielding 0.012 g (57% yield based on H_4ATB). The product gradually turned opaque in air. Anal. Calcd for $C_{45}H_{57}O_{15}N_3Zn_2$ = MOF-32: C, 54.55; H, 5.51; N, 4.06. Found: C, 54.66; H, 5.34; N, 4.04. FT-IR (KBr, 4000−400 cm^{-1}): 3441 (br), 2934 (w), 2855 (w), 1657 (s), 1604 (s), 1552 (m), 1407 (s), 1381 (s), 1256 (w), 1183 (w), 1111 (w), 1012 (w), 867 (w), 762 (m), 723 (w).

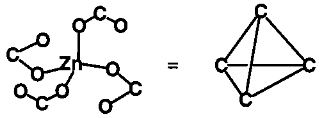
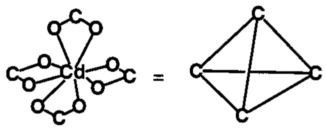
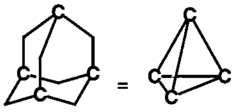
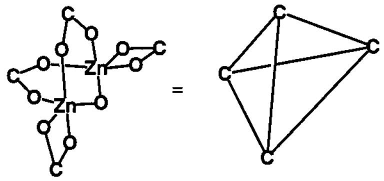
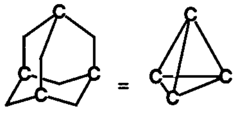
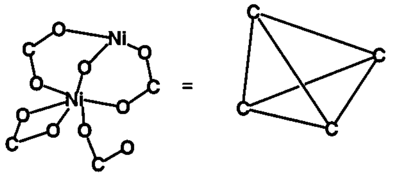
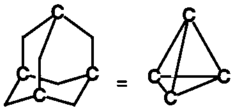
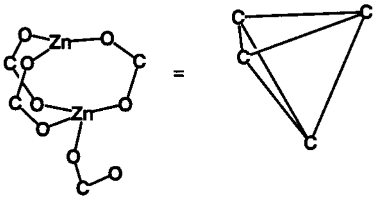
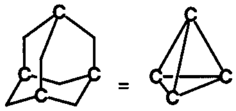
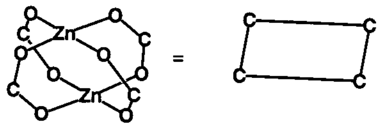
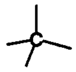
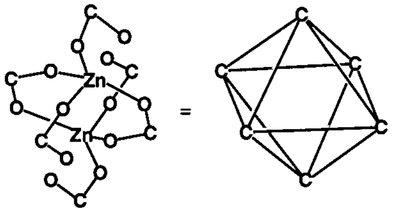
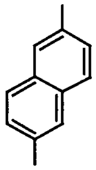
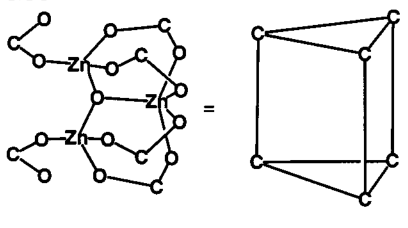
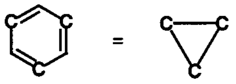
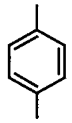
$Ni_2(ATC)(H_2O)_4\cdot(H_2O)_4$, MOF-34. H_4ATC (0.032 g, 0.10 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (0.070 g, 0.24 mmol), H_2O (1 mL), and aqueous NaOH solution (1 mL, 0.1 mmol) were added respectively to a vessel, which was sealed and heated to 180 °C at a rate of 5 °C/min for 40 h and then cooled to room temperature at a rate of 2 °C/min. Needle-shaped green crystals of the product were formed and collected by filtration, yielding 0.016 g (27% yield based on H_4ATC). The product is stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, acetone, chloroform, and DMF. Anal. Calcd for $C_{14}H_{28}O_{16}Ni_2$ = MOF-34: C, 29.51; H, 4.95. Found: C, 29.69; H, 4.70. FT-IR (KBr, 4000−400 cm^{-1}): 3428 (br), 2948 (w), 1611 (s), 1519 (s), 1414 (m), 1355 (m), 1229 (w), 1124 (w), 723 (m), 571 (w).

$Zn_2(ATC)\cdot(C_2H_5OH)_2(H_2O)_2$, MOF-35. A mixture of adamantanetetracarboxylic acid (H_4ATC) (0.047 g, 0.15 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.089 g, 0.30 mmol) in ethanol (10 mL) was placed in a 20-mL vial that was heated until all starting materials dissolved. This vial was inserted in a larger vial containing triethylamine (0.15 mL) and ethanol (4 mL). The larger vial was sealed and left undisturbed for 14 days to crystallize. The colorless crystals were filtered and washed with 3 × 10 mL ethanol and left to air-dry, yielding 0.068 g (78% based on H_4ATC). This material is insoluble in water and common organic solvents such as methanol, ethanol, acetone, acetonitrile, DMF, and dimethyl sulfoxide. Anal. Calcd for $C_{18}H_{28}O_{12}Zn_2$ = MOF-35: C, 38.12; H, 4.98; N, 0.00. Found: C, 38.18; H, 4.64; N, 0.10. FT-IR (KBr, 3500−400 cm^{-1}): 3401 (br), 2967 (m), 2868 (w), 1703 (sh), 1572 (s), 1460 (sh), 1407 (s), 1348 (s), 1216 (w), 1157 (w), 1091 (w), 1045 (w), 940 (w), 716 (m), 683 (sh), 565 (w), 505 (w).

$Zn_2(MTB)(H_2O)_2\cdot(DMF)_6(H_2O)_5$, MOF-36. H_4MTB (0.020 g, 0.04 mmol), $Zn(NO_3)_2\cdot 4H_2O$ (0.053 g, 0.20 mmol), DMF (3 mL), C_2H_5OH (3 mL), and H_2O (2.4 mL) were added respectively to a vessel, which was sealed and heated to 70 °C at a rate of 2 °C/min for 72 h and then cooled to room temperature at a rate of 1 °C/min. Large colorless crystals of the product were formed and collected by filtration, yielding 0.030 g (63% yield based on H_4MTB). The product gradually turned opaque in air. Anal. Calcd for $C_{47}H_{72}O_{21}N_6Zn_2$ = MOF-36: C, 47.52; H, 6.06; N, 7.07. Found: C, 47.26; H, 5.80; N, 6.73. FT-IR (KBr, 4000−400 cm^{-1}): 3441 (br), 3065 (w), 2927 (w), 1657 (vs), 1611 (s), 1545 (m), 1414 (vs), 1117 (w), 1025 (m), 848 (w), 782 (m), 538 (w).

$Zn_2(NDC)_3\cdot[(HTEA)(DEF)(ClBz)]_2$, MOF-37. A mixture of 2,6-naphthalenedicarboxylic acid (H_2NDC; 0.040 g, 0.20 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.059 g, 0.20 mmol) was dissolved in *N,N'*-diethylformamide (DEF, 5 mL) and chlorobenzene (ClBz, 5 mL). This vial

Table 2. Schematic Description of Inorganic and Organic SBUs Including Linkers and Resulting Topologies for MOF-31−39

	Inorganic SBUs	Organic SBUs	Spacer	Topology
MOF-31		None		Augmented Diamond
MOF-32			None	Augmented Diamond
MOF-33				Decorated-Expanded Diamond
MOF-34			None	Decorated $SrAl_2$
MOF-35			None	Decorated $CaGa_2O_4$
MOF-36				Decorated-Expanded PtS
MOF-37		None		Decorated-Expanded CaB_6
MOF-38&39			None	Decorated 3,6-Network (MOF-38)
				Decorated-Expanded 3,6-Network (MOF-39)

was inserted in a larger vial containing DEF (2 mL), ClBz (2 mL), and triethylamine (0.15 mL). The larger vial was sealed and left undisturbed for 7 days to crystallize. The colorless crystals were filtered and washed with 3 × 10 mL of DEF and ClBz and left to air-dry, yielding 0.038 g (41% based on H_2NDC). This material is insoluble in water and common organic solvents such as methanol, ethanol, acetone, acetonitrile, DMF, and dimethyl sulfoxide. Anal. Calcd for $C_{70}H_{82}O_{14}N_4Cl_2Zn_2$ = MOF-37. C, 59.84; H, 5.88; N, 3.99. Found: C, 54.63; H, 5.54; 3.96. FT-IR (KBr, 3500−400 cm^{-1}): 3189 (br), 2981 (w), 2936 (w), 1670 (m), 1612 (s), 1586 (s), 1547 (m), 1501 (m), 1417 (vs), 1358 (s), 1267 (w), 1203 (w), 1118 (w), 929 (w), 794 (m), 651 (w), 592 (w), 482 (w).

$Zn_3O(BTC)_2$·$(HTEA)_2$ = MOF-38. A mixture of 1,3,5-benzenetricarboxylic acid (H_3BTC; 0.032 g, 0.15 mmol) and $Zn(NO_3)_2$·$6H_2O$ (0.080 g, 0.27 mmol) was dissolved in DMF (2 mL) and diluted with chlorobenzene (8 mL). Then a solution of triethylamine (0.06 mL) and

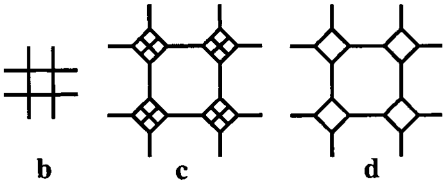
ClBz (5 mL) was allowed to diffuse slowly into the original mixture. After 2 weeks, colorless crystals were picked from the resulting crystalline solids. Repeated attempts to reproduce this synthesis were unsuccessful.

$Zn_3O(HBTB)_2(H_2O)\cdot(DMF)_{0.5}(H_2O)_3$ = MOF-39. H_3BTB (0.030 g, 0.07 mmol), $Zn(NO_3)_2\cdot 4H_2O$ (0.070 g, 0.27 mmol), DMF (3 mL), C_2H_5OH (3 mL), and H_2O (1 mL) were added respectively to a vessel, which was sealed and heated to 90 °C at a rate of 2 °C/min for 24 h and then cooled to room temperature at a rate of 1 °C/min. The solid was filtered, and the filtrate was placed in a 20-mL vial for several days. Small hexagonal crystals of the compound were mechanically separated from the resulting mixture.

Single-Crystal X-ray Diffraction Studies. Relevant parameters for data collection, structure solution, and refinement are assembled for MOF-31−39 in Table 1. Further details have been deposited as Supporting Information.

Results and Discussion

The structures of MOF-31−39 can be appreciated by considering that a vertex in a network, **b**, can be replaced by more than one vertex to give a *decorated* network, **c**, as it has been demonstrated for $In_{10}S_{18}^{6-}$ extended framework in which $In_{10}S_{18}^{10-}$ units occupy the position of 4-connected C atoms in the diamond network.[10] The new cluster of vertexes is referred to as a SBU. The special case when a vertex in an *n*-connected network is replaced by *n* vertexes is called *augmentation*, **d**.



Frameworks with large pores can be realized if vertexes in a network are spaced apart by longer links to give *expanded* structures. It is useful to keep in mind that polytopic organic links can also function as decorated and/or expanded vertexes to produce organic SBUs:[11] Thus, the 1,3,5-carbon atoms in BTC and in the central benzene ring of BTB (Table 2) decorate a 3-connected vertex, because these atoms form a triangular SBU that can be linked to other shapes. The 2-connected benzoate rings in BTB space apart the central benzene ring from the carboxylate carbon atoms; thus, BTB is considered an expanded version of BTC.

Our description of MOF-31−39 structures is facilitated by recognizing that the carboxylate carbon atoms in each structure represent *points of extension* in the same manner discussed for the paddle-wheel cluster in **a**. Thus, for a given MOF, the M−O−C cluster connectivity and the organic links are inspected and considered for determination of the shape of their respective SBUs—an important step in recognizing the topology of that MOF structure (Table 2). In this regard, we have recently emphasized that—for the assembly of frameworks from symmetric shapes—*only a small number of simple, high-symmetry structures will be of overriding general importance, and they would be expected to form most commonly*.[4] In this report, we show that this thesis coupled with the SBU strategy can be employed as a predictive tool especially in cases where specific SBUs can be designed and synthesized.

In the discussion that follows, we analyze nine new MOF structures to reveal how organic and inorganic SBUs play a crucial role in the application of these principles to the design and synthesis of MOFs. We will also show that SBUs with less symmetric and uncommon shapes can lead to new structure types.

Tetrahedral Frameworks. Copolymerization of ADC with Zn^{2+} gives MOF-31 whose crystal structure is constructed from tetrahedral zinc centers linked by acetylene units (Table 2, Figure 1a−c). Each zinc is bound in a disordered monodentate fashion to four different ditopic ADC linkers to give two interpenetrating diamond networks with triethylammonium (HTEA) counterions (not shown) filling pores of 8 Å diameter. Although this is a simple structure, its description using SBUs is illustrative: The four carboxylate C atoms in each $Zn(CO_2)_4$ unit represent a tetrahedral inorganic SBU (Figure 1b) that augments the C vertex in the diamond network, while the acetylene (C≡C) links space apart such SBUs to give an augmented−expanded interpenetrating framework (Figure 1c).

When adamantane is used instead of acetylene, a framework (MOF-32) with inorganic and organic SBUs is produced (Table 2, Figure 1d−f). Here, the relatively larger size of Cd^{2+} compared to Zn^{2+} allows for the carboxylates to bind in a bidentate fashion. Thus, each cadmium center is connected to four carboxylates of four independent ATC links (Figure 1d). Note that the adamantane represents an organic tetrahedral SBU and the carboxylate carbons of each $Cd(CO_2)_4$ unit encompass an inorganic tetrahedral SBU (Figure 1e). These SBUs are linked to each other by sharing vertexes to produce an augmented diamond network (Figure 1f). Interpenetration is not observed here because the shortest distance across the pores (4 Å) is significantly lower than the diameter of an adamantane unit (7 Å), which would be required to fit in that space for interpenetration to be possible. Instead, the void space is filled by one $Cd(H_2O)_6^{2+}$ counterion and five free water molecules per formula unit.

ATC can be functionalized to produce its expanded analogue ATB, which when copolymerized with Zn^{2+} gives (MOF-33), a network that again has the diamond topology (Table 2, Figure 1g−i). In this structure, each pair of Zn atoms is bridged by a water and two carboxylates that bind in a dimonodentate fashion (Figure 1g). Each Zn center is further linked by one bidentate carboxylate to produce a complex cluster arrangement in which consideration of only the carboxylate carbon atoms reveals that it is a tetrahedral SBU (Figure 1h). In contrast to MOF-32, this SBU is spaced from the tetrahedral adamantane SBU by 2-connected benzene units to give a decorated−expanded structure of 2-interpenetrating frameworks having several channels of 5 × 9 $Å^2$ dimension that are filled with three water and three DMF molecules per formula unit (Figure 1i).

Although the shapes of SBUs in MOF-31 and 32 and thus their diamond topology were not unexpected, prediction of the inorganic SBU in MOF-33 would have been more challenging; nevertheless, being able to recognize it as a tetrahedral SBU allows rationalization of the resulting structure.

Analysis of MOF-34 and -35 structures using the SBU approach showed that they have two common tetrahedral networks, namely, the networks of the Al atoms in $SrAl_2$ and the Ga atoms in $CaGa_2O_4$, respectively (Table 2, Figure 2).[12] Both compounds were prepared by linking ATC with either Ni^{2+}

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(10) (a) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145−1147. (b) Li, H.: Eddaoudi, M.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 6096−6097.

(11) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021−1023. The idea of using extended groups to expand nets was clearly recognized in the work of Kinoshita, Y.; Matsubara, I.; Higuchi, T.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1221, and is extensively discussed by Wells, A. F. *Three-Dimensional Nets and Polyhedra*, Wiley: New York, 1977. Other examples are to be found in ref 1.

(12) O'Keeffe, M.; Hyde, B. G. *Crystal Structures. I. Patterns and symmetry*; Mineralogical Society of America: Washington, DC, 1996.

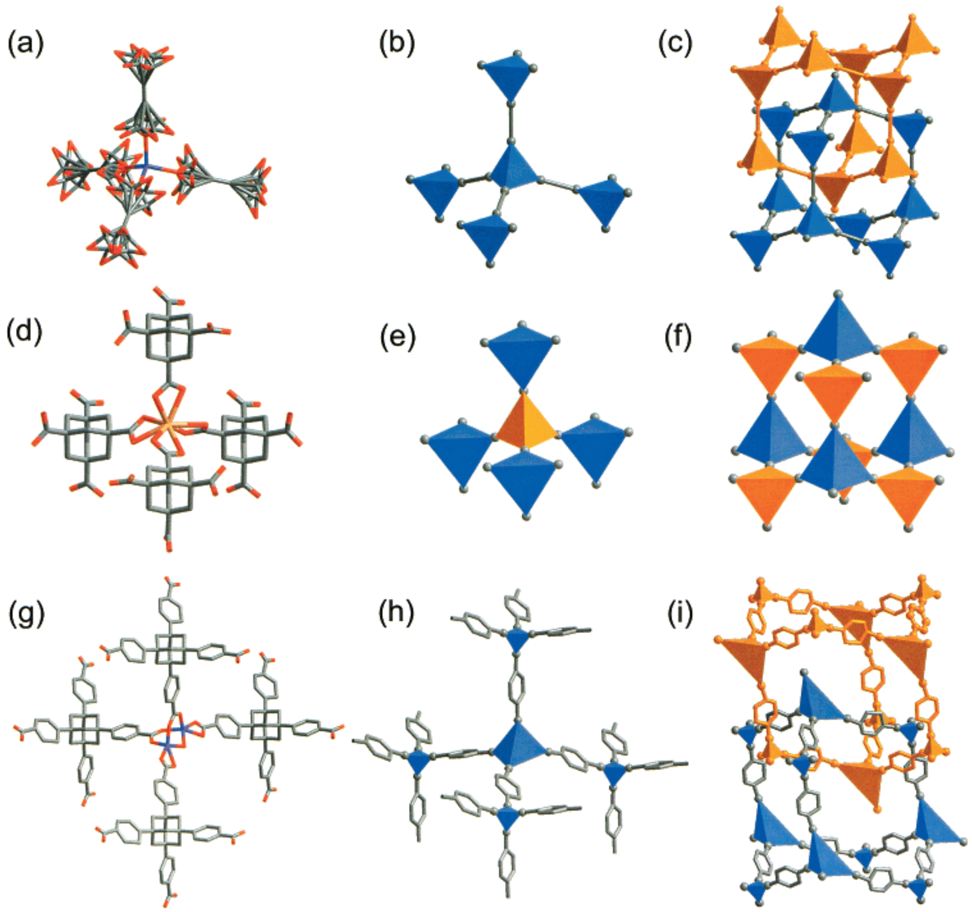

Figure 1. Structures of MOF-31−33: $Zn(ADC)_2 \cdot (HTEA)_2$ (MOF-31) showing tetrahedral zinc (blue) centers with disordered carboxylates of the acetylene links (a), tetrahedral SBUs formed by carboxylate carbon atoms (gray spheres) which are connected by acetylene bonds (gray rods) (b) to produce two interpenetrating diamond frameworks (c); $Cd(ATC) \cdot [Cd(H_2O)_6](H_2O)_5$ (MOF-32) having cadmium (orange) centers with bidentate carboxylates of ATC (d) resulting in tetrahedral inorganic (orange) and organic (blue) SBUs (e) that share vertexes in a diamond network (f); $Zn_2(ATB)(H_2O) \cdot (H_2O)_3(DMF)_3$ (MOF-33), ATB bind to zinc (blue) to give a complex Zn−O−C cluster arrangement (g) in which the carboxylate carbon atoms and the adamantane units respectively form large and small tetrahedral SBUs (blue) (h) and assemble into two interpenetrating diamond frameworks (i). Atomic coordinates from single-crystal data were used to produce each diagram. Carboxylate carbon atoms were used to define the vertexes of all polyhedra representing the SBUs. Oxygen atoms are represented in red.

(MOF-34) or Zn^{2+} (MOF-35) to produce frameworks based on linking of the tetrahedral adamantane SBU with dimeric metal carboxylate clusters. In MOF-34, two Ni centers are bridged by a water oxygen and two carboxylates that are bound in a dimonodentate fashion (Figure 2a). An additional two carboxylates are bound (one in a bidentate and the other in a monodentate fashion) to only one of the Ni centers. The other Ni center instead has an additional three terminal water ligands. We follow the reasoning expressed above in order to understand the topology of the MOF-34 framework: The carboxylate carbon atoms are vertexes to a tetrahedral SBU composed of $Ni_2(CO_2)_4$ and the adamantane represents the other SBU (Figure 2b). These SBUs are linked together to form a 4-connected network that represents a decorated version of the Al network in the $SrAl_2$ structure (Figure 2c)—an arrangement that supports a 3-D channel system of 5×8 Å^2 dimension in which four water molecules reside as guests.

On the other hand, the dimeric clusters in MOF-35 are composed of two Zn centers that are bridged by three carboxylates bound in a dimonodentate fashion with one Zn having an additional monodentate carboxylate, while the other Zn is bound by an additional ethanol as a terminal ligand (Figure 2d). Again, the carboxylate C atoms form a tetrahedral SBU that shares its vertexes with the adamantane tetrahedral SBU (Figure 2e) and give a decorated form of the network defined by Ga in $CaGa_2O_4$ (Figure 2f). One ethanol and two water guests per formula unit occupy internal diameter cavities of 5 Å in diameter.

The formation of these simple nets ($SrAl_2$ and $CaGa_2O_4$) rather than that of diamond, which has higher symmetry, is related, at least in part to the fact that the SBU itself has less than the full tetrahedral symmetry. Ultimately, attempts at *a priori* prediction of the network adopted by assembled SBUs will have to take into account the symmetry of the SBUs and of the links. Indeed, the deliberate construction of low-symmetry components is a way of encoding the information necessary to produce more complex structures.

In addition, to the three examples of common 4-connected networks discussed above, there are at least two more simple and commonly occurring networks that are expected from assembly of tetrahedra; these are the sodalite network and the boron network of CrB_4, which to our knowledge, have not yet been reported for MOFs. However, we have recently prepared indium sulfide porous crystals with supertetrahedral SBUs that assemble into decorated sodalite and CrB_4 networks as well as the decorated diamond network.[10a,b]

Assembly of Square and Tetrahedra SBUs. The PtS network is expected to be formed from the assembly of square and tetrahedral shapes (see below).[4] Indeed, MTB and Zn^{2+} were used to assemble the structure of MOF-36 in which there is

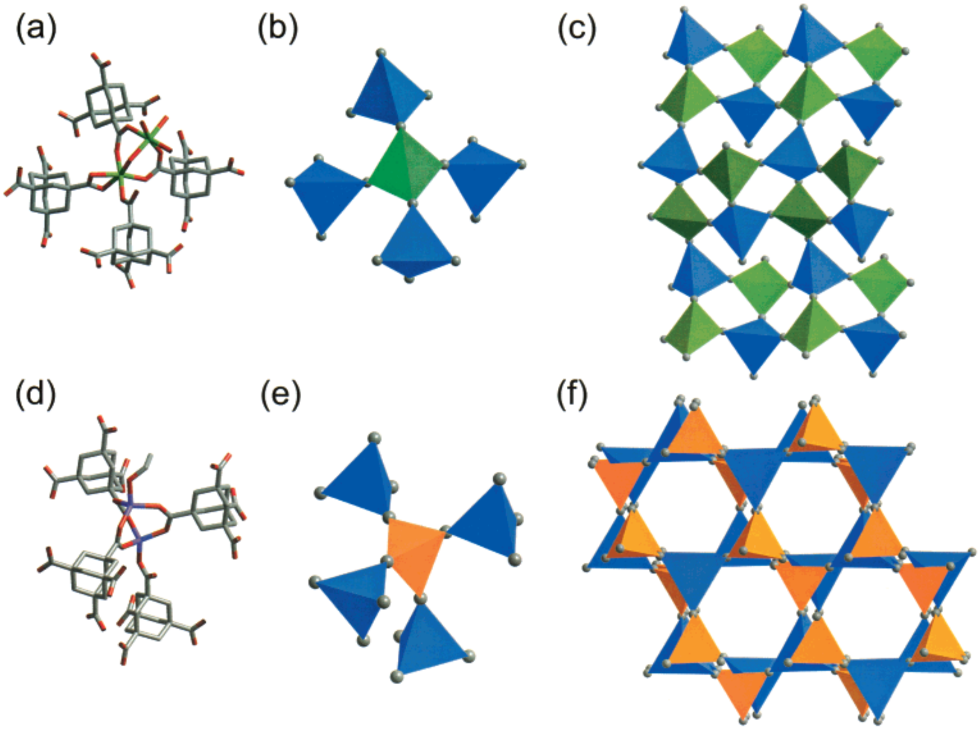

Figure 2. Structures of $Ni_2(ATC)(H_2O)_4{\cdot}(H_2O)_4$ (MOF-34) (a−c) and $Zn_2(ATC){\cdot}$ $(C_2H_5OH)_2(H_2O)_2$ (MOF-35) (d−f). All drawing conditions are the same as in Figure 1 with Ni in green, and the extended structures of MOF-34 (c) and MOF-35 (f) are shown along their [010].

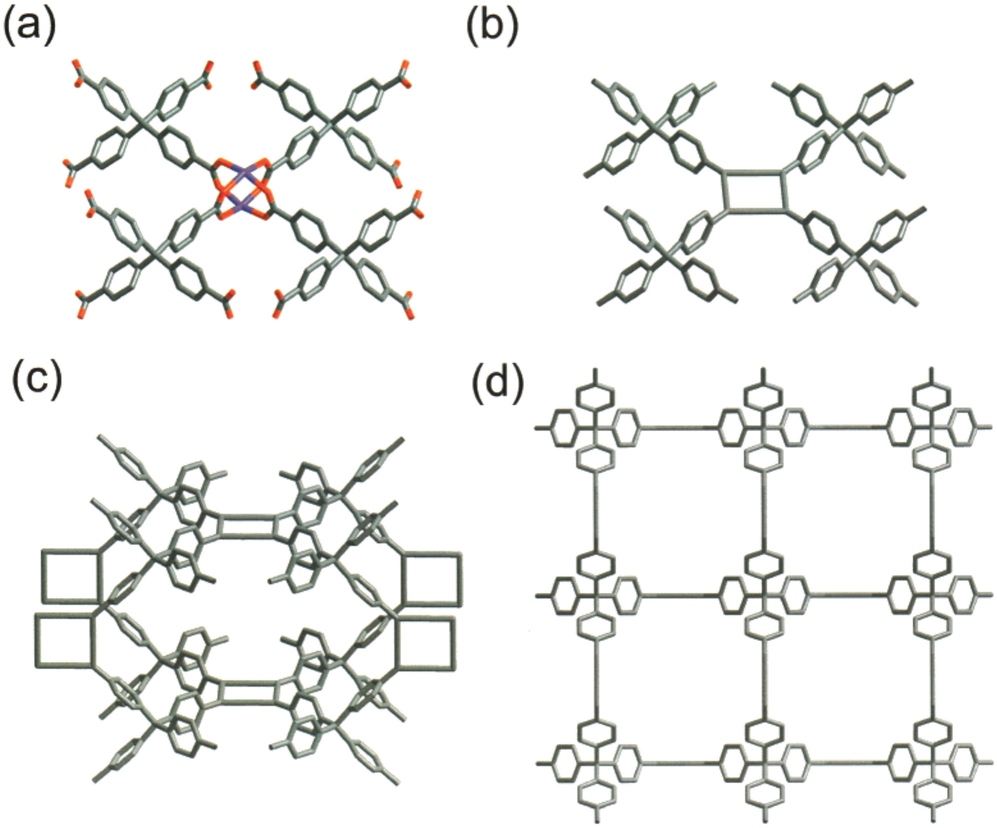

Figure 3. Structure of $Zn_2(MTB)(H_2O)_2{\cdot}(DMF)_6(H_2O)_5$ (MOF-36). All drawing conditions are the same as in Figure 1 with axial water ligands not shown on zinc atoms, carboxylate carbon atoms are represented in cylinder mode rather than spheres, and the extended structure (d) shown along the [001] where the edges of overlapping squares appear as lines between MTB.

only one SBU (Table 2, Figure 3): the paddle-wheel cluster in which a zinc dimer is bridged by four dimonodentate carboxylates with water ligands occupying the axial positions on Zn (not shown, Figure 3a). Thus, the central C of MTB can be considered the S vertex, and the square composed of the carboxylate C atoms at the corners of the SBU decorates the Pt positions in PtS (Figure 3b,c). The benzene units space apart the vertexes to give an overall decorated−expanded PtS network

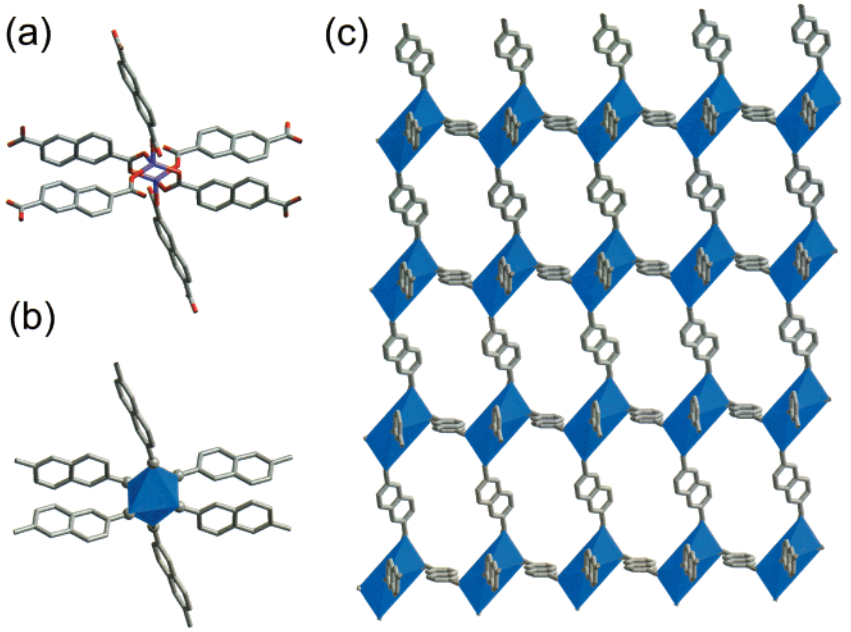

Figure 4. Structure of $Zn_2(NDC)_3 \cdot [(HTEA)(DEF)(ClBz)]_2$ (MOF-37). All drawing conditions are the same as in Figure 1 with the extended structure (c) shown along the [010] and the craboxylate carbon atoms are not shown as spheres.

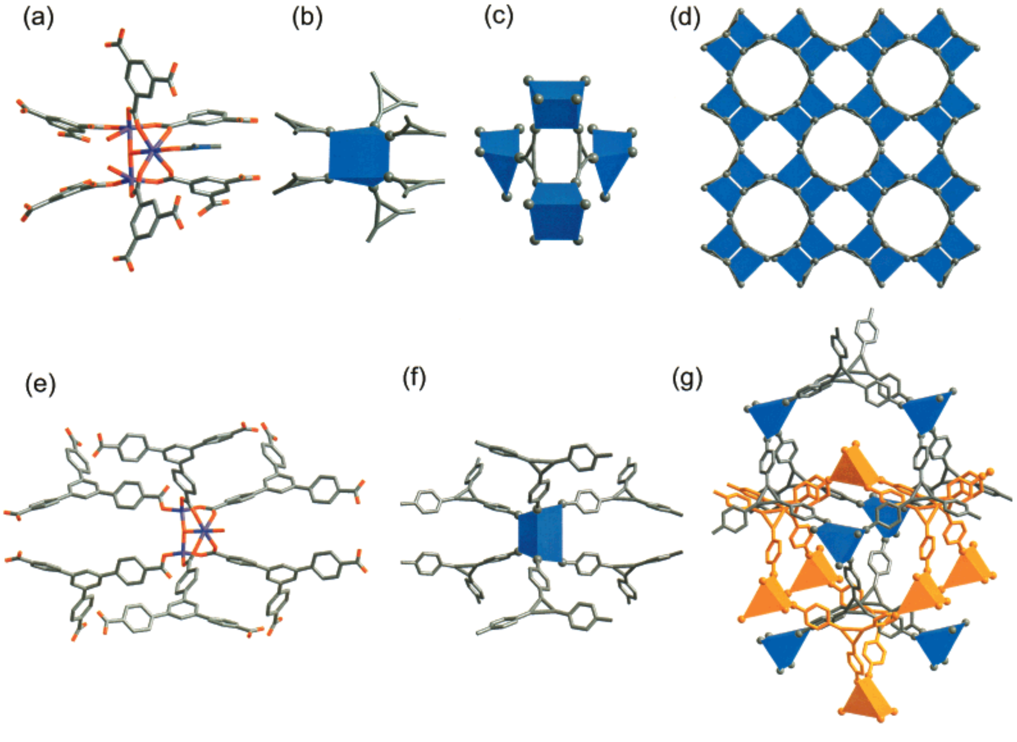

Figure 5. New structure types for the assembly of trigonal prisms and triangles. Structures of $Zn_3O(BTC)_2 \cdot (HTEA)_2$ (MOF-38) and $Zn_3O(HBTB)_2$-$(H_2O) \cdot (DMF)_{0.5}$ $(H_2O)_3$ (MOF-39). All drawing conditions are the same as in Figure 1 with one DMF and two water terminal ligands shown (a), and one water terminal ligand in (e). The extended structure of MOF-38 (d) shown along [001].

with 3-D pores of 5 × 5 Å^2 dimension (Figure 3d) that are filled with five water and six DMF guests per formula unit.

A fully decorated PtS network was previously found in MOF-11 in which tetrahedral adamantane (from ATC) and square Cu−paddle-wheel SBUs were assembled to decorate the tetrahedral and square sites, respectively.[13a] In both MOF-11 and MOF-36 it was possible to construct their frameworks by *design* for two reasons: (a) we used synthetic conditions that yield the paddle-wheel arrangement, and (b) the PtS network is the only one available for the assembly of square and tetrahedral building blocks with all links related by symmetry.

A Framework from Octahedral SBUs. Copolymerization of Zn^{2+} with NDC gives MOF-37 (Table 2, Figure 4), which has a framework constructed from dimeric Zn centers that are bridged by two carboxylates bound in dimonodentate fashion (Figure 4a). Each Zn also is bound by an additional two

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(13) (a) Chen, B.; Eddaoudi, M.; Reineke, T. M.; Kampf, J. W.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc*. **2000**, *122*, 11559−11560. (b) Li, H.; Davis, C. E.; Groy, T. L.; Kelley, D. G.; Yaghi, O. M. *J. Am. Chem. Soc*. **1998**, *120*, 2186−2187.

monodentate carboxylates—an arrangement where the carboxylate C atoms form an SBU with an octahedral shape (Figure 4b). These octahedra are spaced apart by the long NDC links to give a decorated primitive cubiclike framework (Figure 4c) having the boron network in CaB_6 (carboxylate C atoms replace the B atoms).[4,12] This framework supports a 3-D channel system of 6 × 13 Å^2 dimension filled with two HTEA, two DEF, and two ClBz guests per formula unit (Figure 4c). Analogous frameworks having this topology have been reported with other linkers such as BDC (MOF-3 and -5) and 1,4-diazodibenzoate (MOF-9).[5b,13b,14] Again we note that this structure represents the simplest possibility for joining octahedra by equivalent links.

New Structure Types Assembled from Triangles and Trigonal Prisms. Trigonal prismatic geometry is uncommon for metal ions in extended networks;[12] however, using BTC and its expanded derivative BTB, we have been able to access frameworks constructed from SBUs having this geometry. Both MOF-38 and -39 have structures based on Zn_3O clusters in which each of two Zn centers is bound by two bridging dimonodentate and one monodentate carboxylates (Table 2, Figure 5). The remaining Zn center is bound by a total of four bridging dimonodentate carboxylates. The only difference between the clusters is that in MOF-38 there are three terminal ligands (two water and one DMF, each bound to different Zn), while in MOF-39 there is only one terminal ligand (one water bound to the unique Zn center); so in MOF-38 the Zn_3O cluster consists of two ZnO_4 tetrahedra and a ZnO_6 octahedron sharing a common corner, while in MOF-39 the cluster consists of two ZnO_5 trigonal prisms and a ZnO_6 octahedron sharing a common corner (Figure 5a,e).

In both structures, the carboxylate C atoms are at the vertexes of a trigonal prism SBU (Figure 5b,f), and in MOF-38, the corners of these prisms are linked by six different BTC linkers (triangular SBUs) to give a 3,4 network or a decorated 3,6-connected network (Figure 5c). The structure arrangement illustrated for MOF-38 in which trigonal prism dimers are bridged by BTC (Figure 5d) is repeated in the structure of MOF-39; however, in the latter, they assemble into an isomeric structure (Figure 5g) in which the prisms and triangles are spaced apart by 2-connected benzene units again to produce a 3,4 network or a decorated−expanded 3,6 network. As expected, the use of BTB as an expanded analogue of BTC allows for two identical networks to interpenetrate. As far as we are aware, the 3,6 nets that form the basis for these structures have not been described before, but we note that, as far as we are aware, very little attention was previously devoted to nets based on trigonal prismatic coordination. Both nets represent simple solutions to the problem of linking together trigonal prisms and triangles—an arrangement that does not appear to be possible with all links being the same (related by symmetry). It is interesting that in both cases the frameworks are polar (the triangular faces of the trigonal prisms have the same orientation) although in MOF-39 the interpenetrating nets have opposite polarity and the structure is centrosymmetric.

Conclusions

Analysis of metal−organic framework structures using the SBU approach provides new and simplifying principles to what otherwise are complex structures. The analysis of MOF-31−39 using this approach, coupled to our thesis on the predominance of simple extended structures obtained by the assembly of symmetric building blocks, illustrates a useful tool for understanding and designing structures. Symmetrical and simple M−O−C SBUs such as tetrahedra in MOF-31 and -32 and squares and tetrahedra in MOF-35 are easier to make predictably, and they lead to predictable geometries. In contrast, the formation of less symmetrical (complex) SBUs such as in MOF-33, -34, and -36 is difficult to predict, but they lead to one of a small group of expected topologies. Complex SBUs with uncommon geometries lead to previously unobserved topologies as in MOF-38 and -39. The fact that SBUs have the flexibility to be of any connectivity, size, composition, and stereochemistry promises the design and synthesis of a wide diversity of functional MOFs.

Acknowledgment. The National Science Foundation support to M.O'K. (DMR-9804817) and O.M.Y. (DMR-9980469) is gratefully acknowledged.

Supporting Information Available: Crystallographic data, bond lengths, and angles for MOF-31−39. This material is available free of charge via the Internet at http://pubs.acs.org.

JA010825O

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[14] Reineke, T. M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc*. **2000**, *122*, 4843−4844.