Supporting Information

Dative Boron-Nitrogen Bonds in Structural Supramolecular Chemistry: Multicomponent Assembly of Prismatic Organic Cages

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Content:

1. General:

2,4,6-Tri-(4-pyridyl)-1,3,5-triazine[1] was synthesized according to previously published procedures. Triphenylene, coronene, 4,5-dichlorocatechol, 4,4-biphenyldiboronic acid and 1,4-benzenediboronic acid were obtained from commercial sources. All solvents were dried using a solvent purification system from Innovative Technologies, Inc. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Combustion analysis was performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Elemental analysis of boron-containing compounds can be complicated by the formation of incombustible boron carbide residues during analysis.[2] This may lead to strong deviations in the carbon value, as such, only values for hydrogen and nitrogen are reported.

2. Synthesis of cage 1:

A solution of 1,4-benzenediboronic acid (0.45 mmol), 4,5-dichlorocatechol (0.90 mmol) and 2,4,6-tri-(4-pyridyl)-1,3,5-triazine (0.30 mmol) in a 2:1 toluene:THF mixture (90 mL) was heated under reflux for 4 h using a Dean Stark trap to remove water. The reaction mixture was cooled to room temperature and the orange precipitate was isolated by filtration and washed with pentane. Residual solvent was removed under vacuum. (276 mg, 94%) X-ray quality crystals were obtained by slow cooling of a concentrated 1,2-dichlorobenzene solution. Elemental anal. calc'd. for $C_{90}H_{48}B_6Cl_{12}N_{12}O_{12} \cdot 2C_6H_4Cl_2$: H 2.31 ; N 7.41. Found: H 2.72; N 7.45.

3. Synthesis of cage 2:

Cage **1** (5 μmol) and coronene (10 μmol) were heated in 1,2-dichlorobenzene (5 mL) until a clear solution was obtained. The solution was then cooled slowly in an oil bath. The resulting dark orange crystals were isolated by filtration and washed with pentane. (10.8 mg, 95%) X-ray quality crystals were obtained by slow cooling of a concentrated 1,2-dichlorobenzene solution. Elemental anal. calc'd. for $C_{114}H_{60}B_6Cl_{12}N_{12}O_{12}$: H 2.65; N 7.37. Found: H 2.59; N 7.05.

4. Synthesis of cage 3:

Cage **1** (5 μmol) and triphenylene (10 μmol) was heated in 1,2-dichlorobenzene (5 mL) until a clear solution was obtained. The solution was then cooled slowly in an oil bath. The resulting orange crystals were isolated by filtration and washed with pentane. (9.9 mg, 90 %) X-ray quality crystals were obtained by slow cooling of a concentrated 1,2-dichlorobenzene solution. Elemental anal. calc'd. for $C_{108}H_{60}B_6Cl_{12}N_{12}O_{12}$: H 2.74; N 7.61. Found: H 2.79; N 7.45.

5. Synthesis of cage 4:

A solution of 4,4-biphenyldiboronic acid (0.45 mmol), 4,5-dichlorocatechol (0.90 mmol) and 2,4,6-tri-(4-pyridyl)-1,3,5-triazine (0.30 mmol) in a 2:1 toluene:THF mixture (90 mL) was heated under reflux for 4 h using a Dean Stark trap to remove water. The reaction mixture was cooled to room temperature and the orange precipitate was isolated by filtration and washed with pentane. Residual solvent was removed under vacuum (206 mg, 62%). The orange precipitate (6.8 μmol) and triphenylene (40.8 μmmol) were heated in 1,2-dichlorobenzene (5 mL) until a clear solution was obtained. The solution was then cooled slowly in an oil bath. The resulting orange crystals were isolated by filtration and washed with pentane. (12.6 mg, 70 %) X-ray quality crystals were obtained by slow cooling of a concentrated 1,2-dichlorobenzene solution. Elemental anal. calc'd. for $C_{144}H_{84}B_6Cl_{12}N_{12}O_{12}$: H 3.17; N 6.30. Found: H 3.02; N 6.17.

6. Single crystal X-ray analyses: Selected structure refinement details can be found in Table S1. Diffraction intensity data were collected using either Mo$K\alpha$ radiation on a four-circle kappa goniometer equipped with a Nonius-Bruker Apex II CCD or Cu$K\alpha$ radiation on a two-circle goniometer equipped with a STOE IPDS 2T image plate. Data were reduced by EvalCCD[3] or XRED.[4] Absorption corrections were applied to all data sets using either the semi-empirical[5] (**1**) or the analytical (**2**, **3** and **4**) method.[4] All structures were solved using conventional heavy atom methods and refined using full-matrix least-squares on F^2. The hydrogen atoms were placed in calculated positions using the riding model with $U_{iso} = aU_{eq}$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others). Refinement and geometrical calculations were carried out on all structures with SHELXTL.[6] For **1** and **2** the scattering contributions from some residual diffuse electron density (i.e. disordered solvent) were removed using the SQUEEZE routine in

PLATON.[7] In **2**, the anisotropic displacement parameters of all non-hydrogen atoms were refined with ISOR and SIMU restraints.

Table S1. Crystallographic data and structure refinement details for the cages.

	1	**2**	**3**	**4**
Empirical formula	$C_{90}H_{48}N_{12}O_{12}B_6Cl_{12}$	$C_{114}H_{60}N_{12}O_{12}B_6Cl_{12}$	$C_{108}H_{60}N_{12}O_{12}B_6Cl_{12}$	$C_{144}H_{84}N_{12}O_{12}B_6Cl_{12}$
Formula weight	1979.66	2280.00	2207.94	2664.58
Temperature / K	100(2)	298(2)	293(2)	270(2)
Wavelength / Å	0.71073	1.54186	1.54186	1.54186
Space group	*R*-3*c*	$P6_3$/m	*R*-3*c*	*R*-3*c*
Unit cell dimensions / Å	a = 13.4133(9)	a = 14.3139(9)	a = 13.5162(6)	a = 13.5417(3)
	b = 13.4133(9)	b = 14.3139 (9)	a = 13.5162(6)	b = 13.5417(3)
	c = 92.656(12)	c = 30.848(2)	c = 93.155(5)	c = 118.223(7)
	α = 90°	α = 90°	α = 90°	α = 90°
	β = 90°	β = 90°	β = 90°	β = 90°
	γ = 120°	γ = 120°	γ = 120°	γ = 120°
Volume / Å^3	14437(2)	5473.6(6)	14738.2(11)	18774.9(10)
Z	6	2	6	6
Calculated density / g cm^{-3}	1.366	1.383	1.493	1.414
Absorption coefficient / mm^{-1}	0.410	3.330	3.688	2.999
F(000)	6012	2316	6732	8172
Crystal size / mm	0.27 × 0.23 × 0.09	0.20 × 0.20 × 0.02	0.14 × 0.07 × 0.02	0.10 × 0.05 × 0.03
Measured θ range	3.047 to 20.030	2.87 to 47.96	2.85 to 51.88°	3.79 to 47.44°
Limiting indices	$-14 \le h \le 12$	$-12 \le h \le 12$	$-13 \le h \le 4$	$-12 \le h \le 12$
	$-14 \le k \le 14$	$-13 \le k \le 6$	$-9 \le k \le 13$	$-12 \le k \le 12$
	$-102 \le l \le 102$	$-25 \le l \le 23$	$-71 \le l \le 82$	$-107 \le l \le 100$
Reflections collected / unique	55409 / 2302	6112 / 1664	7164 / 1729	11423 / 1849
R_{int}	0.1313	0.1007	0.0890	0.1216
Data / restraints / parameters	2302 / 0 / 199	1664 / 360 / 248	1729 / 26 / 227	1849 / 0 / 281
Goodness of fit on F^2	1.264	0.796	0.809	1.059
R indices [$I \ge 2\sigma(I)$]	R_1 = 0.0761 wR_2 = 0.1394	R_1 = 0.0465 wR_2 = 0.1081	R_1 = 0.0459 wR_2 = 0.1195	R_1 = 0.0555 wR_2 = 0.1554
R indices (all data)	R_1 = 0.0900 wR_2 = 0.1452	R_1 = 0.0975 wR_2 = 0.1210	R_1 = 0.0763 wR_2 = 0.1307	R_1 = 0.0592 wR_2 = 0.1587
Final Fourier residuals	0.432 and −0.289 e Å^{-3}	0.197 and −0.163 e Å^{-3}	0.384 and −0.266 e Å^{-3}	0.344 and −0.273 e Å^{-3}

7. References:

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