Inorg. Chem. **2003**, *42*, 612–617

Inorganic Chemistry
Article

A Guest-Induced Assembly of a Molecular Box from Methylcobaloxime and 1, 4-Phenylenebisboronic Acid

Renata Dreos,* Giorgio Nardin, Lucio Randaccio,* Patrizia Siega, and Giovanni Tauzher

Dipartimento di Scienze Chimiche, Università di Trieste, via Licio Giorgieri 1,
34127, Trieste, Italy

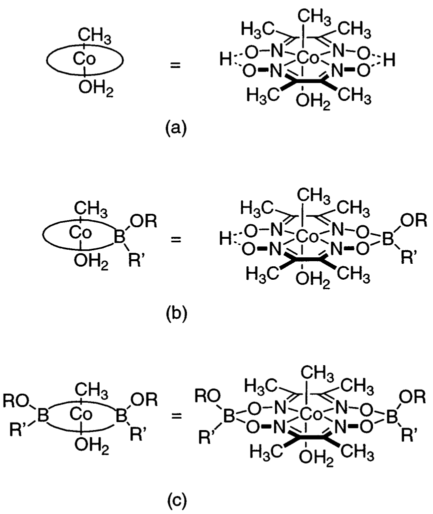
Received July 29, 2002

The guest-induced synthesis of a molecular box from methylaquacobaloxime and 1,4-phenylenebisboronic acid, with pyrazine (pz) as guest, is described. The resulting supramolecular species was characterized by X-ray structural analysis, ^{1}H and ^{13}C NMR spectroscopy, and low-resolution electrospray ionization (ES) mass spectrometry. The assembly was monitored by a time dependent ^{1}H NMR experiment, which showed that the guest thermodynamically drives the assembly of the host. The effectiveness of pyrazine in this role arises from its having both the correct geometry and a sufficiently low pK_a value. Several other ditopic ligands were tested, but none led to formation of an analogous product. However, a second supramolecular species was formed in the case of ethylenediamine (en). X-ray structural analysis and ^{1}H and ^{13}C spectroscopy revealed that this is closely related to the first, with a phenyl side removed and the pz bridge substituted by the en bridge.

Introduction

Supramolecular chemistry exploits noncovalent interactions to assemble large superstructures from molecular subunits in a rapid and reversible way.[1] Since these processes occur under thermodynamic control, many of these superstructures are not very stable, particularly in solution. The possibility of constructing molecular architectures linked by covalent bonds under thermodynamic control (dynamic covalent chemistry)[2] is therefore extremely appealing. Among the reversible reactions that lead to the formation of covalent bonds, the reaction of the cis diols of carbohydrates with boronic acids is well-known.[3] The reaction of boronic acids with the O···H···O moiety of methylaquabis(dimethylglyoximato)cobalt derivatives (methylaquacobaloximes, CH_3-$Co(DH)_2H_2O$, Chart 1a), to give mono- (Chart 1b) and diborylated (Chart 1c) cobaloximes, strongly resembles this interaction.[4]

Chart 1



Indeed, functionalized aromatic boronic acids have already been shown to efficiently direct the assembly of organocobaloximes, resulting in products of different nuclearity and geometry. The species formed appears to depend on the kind of phenyl ring functionalization. Thus, the reaction of methylaquacobaloxime with 3- and 4- pyridinylboronic acid gave a dinuclear "molecular parallelogram" (Scheme 1a)[5]

---

* Authors to whom correspondence should be addressed. E-mail: dreos@univ.trieste.it (R.D.); randaccio@univ.trieste.it (L.R.).

(1) Lehn, J. M. *Supramolecolar Chemistry*; VCH: Weinheim, 1995.

(2) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898.

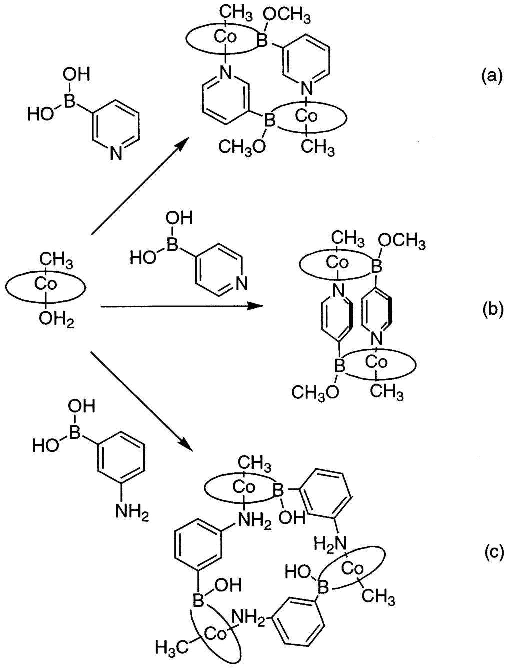
(3) For general reviews on boronic acid based saccharide receptors, see: (a) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1911. (b) James, T. D.; Linnane, P.; Shinkai, S. *Chem. Commun.* **1996**, 281.

(4) Dreos, R.; Nardin, G.; Randaccio, L.; Siega, P.; Tauzher, G.; Vrdoljak, V. *Inorg. Chem.* **2001**, *40*, 5536.

(5) Dreos, R.; Nardin, G.; Randaccio, L.; Tauzher, G.; Vuano, S. *Inorg. Chem.* **1997**, *36*, 2463.

10.1021/ic025909s CCC: $25.00

Scheme 1



and a “molecular box” (Scheme 1b),[4] respectively, whereas that with 3-aminophenylboronic acid gave a trinuclear molecular triangle[6] (Scheme 1c). In all cases the assembly occurs through the reaction of the $B(OH)_2$ group with the oxime bridge of one cobaloxime molecule, with simultaneous coordination of the nitrogen atom to the cobalt of another.

The use of a diboronic acid to link two organoaquacobaloxime units should allow formation of cyclic oligomers with the coordination positions inside the cavity occupied by water molecules, easily replaceable by suitable guests. Here we report the assembly of a dinuclear box by reaction of methylaquacobaloxime and 1,4-phenylenebisboronic acid, containing pyrazine as a guest molecule. Interestingly, the assembly does not occur in the absence of pyrazine, and, among the other tested ditopic ligands, only ethylenediamine allowed a partial assembling. Therefore, this is one of the relatively rare cases in which a specific guest induces the organization of the host itself.[7]

Experimental Section

General Information. NMR spectra were recorded on a JEOL EX-400 (^1H at 400 MHz and ^{13}C at 100.4 MHz) with TMS as internal standard. Electrospray mass spectra were recorded in positive mode by using an API 1 mass spectrometer (Perkin-Elmer) at 60 V cone voltage. $CH_3Co(DH)_2H_2O$ was prepared according to the literature.[8] All other reagents were reagent grade and used without further purification.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
formula	$C_{19.50}H_{30}B_2CoN_5O_7$	$C_{28.50}H_{59}B_2Co_2N_{10}O_{14}$
fw	527.03	905.34
T, K	293(2)	150(2)
λ, Å	0.71073	0.71073
cryst syst, space group	orthorhombic, *Pbca*	monoclinic, $P2_1/n$
a, Å	17.665(5)	12.986(2)
b, Å	15.695(3)	9.963(2)
c, Å	18.077(4)	33.280(4)
β, deg		91.13(2)
V, Å^3	5011.9(6)	4304.9(5)
Z, D_{calcd} Mg/m^3	8, 1.397	4, 1.397
μ, mm^{-1}	0.733	0.841
refinement meth	full-matrix least-squares on F^2	full-matrix least-squares on F^2
R indices $[I > 2\sigma(I)]^a$	R1 = 0.053, wR2 = 0.157	R1 = 0.065, wR2 = 0.182
R indices (all data)^a	R1 = 0.067, wR2 = 0.173	R1 = 0.077, wR2 = 0.191

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Synthesis. 1. 1,4-Phenylenebisboronic acid (55 mg, 0.33 mmol) was added to a methanolic solution (10 mL) of $CH_3Co(DH)_2H_2O$ (100 mg, 0.31 mmol). The solution was filtered, and after 1 h, 12 mg (0.15 mmol) of pyrazine was added. After 1 week, orange X-ray quality crystals of **1** were collected. Yield: (90 mg, 50%). ES-MS (CH_3OH): calcd for $C_{38}H_{54}B_4N_{10}O_{12}Co_2$ m/z^+ 1004.0018, found 1022.5 ($M^+ + H_2O$, 100%), 1005.5 (M^+). Anal. Calcd for $C_{38}H_{54}B_4N_{10}O_{12}Co_2{\cdot}H_2O{\cdot}CH_3OH$: C, 44.4; H, 5.74; N, 13.3. Found: C, 43.8; H, 5.51; N, 13.4. ^1H NMR (CD_3OD): 1.12 (6 H, s, axial CH_3), 2.60 (24 H, s, equatorial $C\mathit{H}_3$), 3.19 (12 H, s, $BOC\mathit{H}_3$), 6.42 (8 H, s, phenyl), 6.81 (4 H, s, pyrazine). ^{13}C NMR (CD_3OD): 12.15 ($\mathit{C}H_3C{=}NOB$), 49.11 ($O\mathit{C}H_3$), 132.17 (phenyl $\mathit{C}H$), 146.52 (pyrazine $\mathit{C}H$), 156.64 ($\mathit{C}{=}N$).

2. 1,4-Phenylenebisboronic acid (20 mg, 0.12 mmol) was added to a methanolic solution (80 mL) of $CH_3Co(DH)_2H_2O$ (100 mg, 0.31 mmol). The solution was filtered, and 10 μL (0.15 mmol) of ethylendiamine was added after 1 h. The solution was left at 5 °C for 2 weeks. After partial evaporation of the solvent, orange crystals were collected. X-ray quality crystals were obtained by recrystallization in methanol at 5 °C. Yield: (64 mg, 50%). ES-MS (CH_3OH): calcd for $C_{28}H_{50}B_2N_{10}O_{10}Co_2$ m/z^+ 826.25, found 826.9. Anal. Calcd for $C_{28}H_{50}B_2N_{10}O_{10}Co_2{\cdot}0.5CH_3OH{\cdot}3.5H_2O$: C, 37.8; H, 6.57; N, 15.5. Found: C, 38.6; H, 6.25; N, 15.9. ^1H NMR (CD_3OD): 0.65 (6 H, s, axial $C\mathit{H}_3$), 1.37 (4H, m, $N\mathit{H}_2$), 1.80 (4H, m, $C\mathit{H}_2$), 2.20 (12H, s, equatorial $C\mathit{H}_3C{=}NOH$), 2.43 (12H, s, equatorial $C\mathit{H}_3C{=}NOB$), 3.30 (6H, s, $BOC\mathit{H}_3$), 7.20 (8H, s, phenyl). ^{13}C NMR (CD_3OD): 10.90 ($\mathit{C}H_3C{=}NOH$), 11.81 ($\mathit{C}H_3C{=}NOB$), 42.10 ($\mathit{C}H_2$), 49.13 ($O\mathit{C}H_3$), 132.26 (phenyl $\mathit{C}H$), 156.35($\mathit{C}{=}N$).

NMR Guest Binding Studies. In a typical experiment 5 mg of $CH_3Co(DH)_2H_2O$ was dissolved in 600 μL of CD_3OD, followed by addition of a 1:1 amount of 1,4-phenylenebisboronic acid and, after 1 h, of a 1:0.5 amount of the guest: pyrazine (pz), ethylenediamine (en), piperazine, 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-aminopyridine, azide, or SCN^-. Spectra were acquired at different times at room temperature.

X-ray Crystallographic Data Collection and Refinement of the Structures. Single plate crystals of **1** and prismatic crystals of **2** were grown as already reported in the Experimental Section. In the case of **2**, it was covered in Paratone oil and immediately mounted in the cold nitrogen stream of the diffractometer to prevent solvent loss. Crystal data and details of structure refinement are given in Table 1. The diffraction data were collected with a Nonius DIP 1030 H system using graphite-monochromated Mo Kα

---

(6) Dreos, R.; Nardin, G.; Randaccio, L.; Siega, P.; Tauzher, G. *Eur. J. Inorg. Chem.*, in press.

(7) For recent relevant examples: (a) Johnson, D. W.; Raymond, K. N. *Inorg. Chem.* **2001**, *40*, 5157. (b) Aoyagi, M.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 7457. (c) Hiraoka, S.; Fujita, M *J. Am. Chem. Soc.* **1999**, *121*, 10239. (d) Bilyk, A.; Harding, M. M. *Chem. Commun.* **1995**, 1697. (e) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649.

(8) Schrauzer, G. N. In *Inorganic Syntheses*; Parry, R., Ed.; McGraw Hill: New York, 1968; Vol. 11, p 61 ff.

radiation ($\lambda = 0.71070$ Å). For both structures a total of 30 frames were collected, using the xpress program,[9] over a hemisphere of reciprocal space with rotation of 6° about the ϕ axis. A MAC Science image plate (diameter = 300 mm) was used, and the crystal-to-plate distance was fixed at 90 mm. The determination of unit-cell parameters, integration of intensities, and data scaling were performed using MOSFLM and SCALA from the CCP4 program suite.[10] The structures were solved both by direct methods[11] and Fourier methods and refined by the least-squares method (on F^2).[12] In both structures all non-hydrogen atoms were refined anisotropically, except the solvent molecules (water and methanol) in **2**, which were treated isotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. A suite of programs[13] was also used in the geometrical and final calculation.

Results

Synthesis and Structural Characterization of 1. Treatment of $CH_3Co(DH)_2H_2O$ with slightly less than a 1:1 amount of 1,4-phenylenebisboronic acid in methanol followed, after 1 h, by addition of pyrazine at room temperature led to the formation of **1** (Figure 1a). Addition of pyrazine after a shorter time, before the formation of a sufficient amount of monoborylated species, caused the immediate precipitation of the already known $[CH_3Co(DH)_2]_2$ μ-pz,[14] very insoluble in methanol, which was identified by ^1H NMR. Such precipitation prevents further reactions. If pyrazine was not added to the solution of methylaquacobaloxime and 1,4-phenylenebisboronic acid, X-ray quality crystals of methylaquacobaloxime with a molecule of diboronic acid inserted in the O···H···O moiety, **3**, precipitated from the solution (Figure 2).[15]

The molecule of **1** may be described as an open centrosymmetric rectangular box with two opposite faces made by the diborylated cobaloxime units and by two phenyl groups (Figure 1a). The box is filled by the planar pz ligand, nearly parallel to the phenyl faces (at a mean distance of 3.27 Å) and bridging the Co atoms in one axial position, the other being occupied by the CH_3 group. The crystallographic symmetry center lies in the baricenter of the pz ligand. The pz ligand is forced to be oriented above the five-membered rings of the equatorial moiety. Consequently, the two rings are bent toward the CH_3 group and their mean planes make an α angle of 10.7(3)°. The Co atoms, 6.873(1) Å apart, are pulled slightly inside the box, being displaced by 0.081(1) Å out of the four N equatorial mean plane toward the axial N5 donor. The coordination bond lengths and angles are given in Table 2. The axial Co−C and the equatorial Co−N distances are within the range reported for analogous methylcobalt derivatives having similar equatorial ligands, derived from cobaloximes by substitution of the oxime bridge with either BF_2 or BPh_2 bridges.[16] The axial Co−pz distance of 2.045(2) Å is significantly shorter than the Co−py

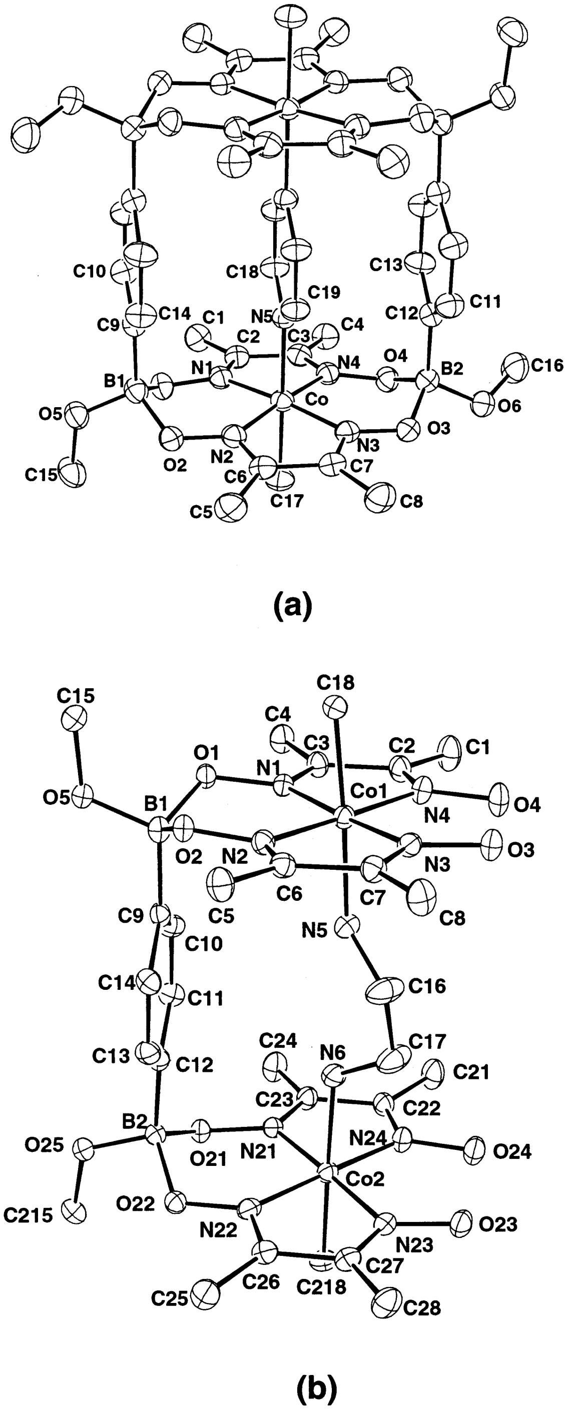


Figure 1. (a) ORTEP drawing (thermal ellipsoid, 30% probability) and labeling scheme for the non-hydrogen atoms of **1**. (b) ORTEP drawing (thermal ellipsoid, 30% probability) and labeling scheme for the non-hydrogen atoms of **2**.

---

[9] Schierbeek, B. *Nonius*; Delft: The Netherlands, 1998.

[10] Collaborative Computational Project, Number 4. *Acta Crystallogr.* **1990**, *46A*, 467.

[11] SIR92−A program for crystal structure solution. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

[12] Sheldrick, G. M. SHELXL97−*Programs for Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1998.

[13] Farrugia, L. J. *Appl. Crystallogr.* **1999**, *32*, 837.

[14] Gupta, B. D.; Qanungo, K. *J. Organomet. Chem.* **1998**, *557*, 243.

[15] Single prismatic crystals of **3** were collected from the reaction mixture. Diffraction data on a DIP 1030 ($\lambda = 0.71073$ Å) at 150 K. $C_{15}H_{31}B_2CoN_4O_{11}$, fw = 523.99, triclinic, space group $P\bar{1}$, $a = 8.853(3)$ Å, $b = 11.865(4)$ Å, $c = 12.866(4)$ Å, $\alpha = 106.24(2)°$, $\beta = 111.20(2)°$, $\gamma = 97.83(2)°$, $V = 1166.4(7)$ Å^3, $Z = 2$, $D_{calc} = 1.492$ Mg/m^3. Total reflections collected 7638, unique 4677 (R(int) = 0.0448). Final R1 = 0.0511, wR2 = 0.1364. R1 = 0.0463, wR2 = 0.1327 for 4125 with $I > 2\sigma(I)$.

[16] Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327−376.

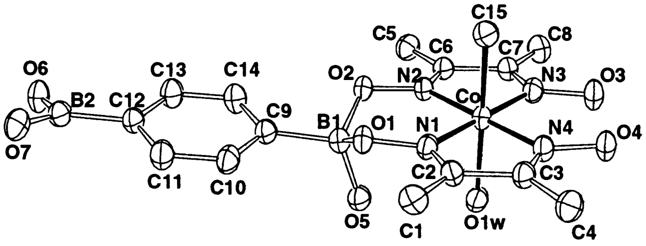


Figure 2. ORTEP drawing (thermal ellipsoid, 50% probability) and labeling scheme for the non-hydrogen atoms of **3**. Selected bond distances (Å): Co−N(1), 1.878(2); Co−N(2), 1.880(2); Co−N(3), 1.874(2); Co−N(4), 1.882(2); Co−O(1W), 2.0712(18); Co−C(15), 1.998(3).

Table 2. Coordination Bond Distances (Å) and Angles (deg) for **1** and **2**

	1	2	
Co−N1	1.866(3)	1.866(3)	1.878(3)
Co−N2	1.870(3)	1.860(3)	1.860(4)
Co−N3	1.875(3)	1.872(3)	1.878(3)
Co−N4	1.866(3)	1.859(4)	1.867(4)
Co−N5 (N6)	2.045(2)	2.063(4)	2.072(4)
Co−C17 (C18)	2.008(3)	1.981(5)	1.996(5)
N1−Co−N2	97.6(1)	98.3(1)	97.7(1)
N1−Co−N3	174.9(1)	176.8(2)	177.4(2)
N1−Co−N4	82.3(1)	82.0(1)	81.2(1)
N1−Co−N5 (N6)	92.1(1)	90.3(1)	91.2(1)
N1−Co−C17 (C18)	87.5(1)	86.8(2)	88.2(2)
N2−Co−N3	82.3(1)	81.6(1)	81.9(1)
N2−Co−N4	175.1(1)	178.3(2)	177.6(2)
N2−Co−N5 (N6)	92.6(1)	93.2(2)	92.9(2)
N2−Co−C17 (C18)	87.2(1)	85.9(2)	88.8(2)
N3−Co−N4	97.4(1)	98.0(1)	99.1(1)
N3−Co−N5 (N6)	93.0(1)	93.0(1)	91.4(2)
N3−Co−C17 (C18)	87.4(1)	90.0(2)	89.2(2)
N4−Co−N5 (N6)	92.3(1)	88.5(2)	89.3(2)
N4−Co−C17 (C18)	87.9(1)	92.5(2)	89.0(2)
N5 (N6)−Co−C17 (C18)	179.5(1)	176.7(1)	178.2(2)

distances, trans to CH_3, reported to be in the range 2.106(3)−2.119(4) Å for the above-cited analogous methyl derivatives. However, the Co−pz distance is within the range 2.042(2)−2.068(7) Å, reported in several complexes with similar equatorial ligands and the Me−Co−1-MeIm (1-MeIm = 1-methylimidazole) axial fragment.

The ^1H NMR spectrum of **1** in CD_3OD shows only five signals as a consequence of the high symmetry of the complex. The aromatic protons of both pyrazine and boronic acid are shifted remarkably upfield in comparison with the free compounds, due to the shielding effect of the facing aromatic rings. The NOESY spectrum shows cross-peaks between these protons, confirming their spatial proximity. The axial methyl resonates downfield, as is generally found for cobaloximes with two boryl bridges.[17] The signal at 3.19 ppm is assigned to the OCH_3 on boron, arising from the esterification of B(OH) in methanol. The ES-MS spectrum in methanol shows the main peak at $m/z+$ 1022.5, corresponding to **1** plus one water molecule. The above results indicate that **1** is stable in CD_3OD solution.

^{1}H NMR Study of the Assembly of 1. The self-assembly process of **1** was monitored by time dependent ^1H NMR experiments (Figure 3). After the addition of a 1:1 amount of 1,4-phenylenebisboronic acid to a solution of $CH_3Co(DH)_2H_2O$ in CD_3OD (pD about 8), the spectra of the solution showed several singlets in the range 0.0−1.2 ppm (axial methyls) and couples of singlets in the range 2.2−2.5 ppm (equatorial methyls). The splitting of the signals of the equatorial methyls suggests the formation of species containing one boryl bridge (Figure 3b). The concentrations of these species increase with time (Figure 3c).

The addition of pyrazine in a ratio of 0.5:1, about 1 h after the addition of the boronic acid, increased the complexity of the spectra, because of the formation of species with axially coordinated pyrazine (Figure 3d,e). One set of signals, whose integration ratio was constant with time, was immediately apparent among the others. The set consists of one singlet in the range of the axial methyls (1.09 ppm, 3H), two singlets in the range of the equatorial methyls (2.34 and 2.53 ppm, 6H each), and two singlets in the aromatic range (6.59 and 7.41 ppm, 2H each). The low-field shift of the axial methyls and the two singlets for the equatorial methyls suggest the insertion of one boryl bridge.[4] The high-field shift of both the pyrazine and the phenyl signals suggests that the two aromatic rings are facing and shield each other. This spectral pattern is in agreement with a dinuclear species with two cobaloxime units bound by a molecule of diboronic acid and a pyrazine (similar to **2**, see below). This species can be considered a "precursor" of the thermodynamically more stable **1**. The concentration of this species decreased with time, while the signals of **1**, which appeared about a half-hour after the addition of pyrazine, increased in intensity. After some days **1** was the prevailing species in solution (Figure 3g,f). The proposed reaction mechanism for the formation of **1** is reported in Scheme 2.

^1H NMR spectra showed that **1** also formed by reaction of the dimer $[CH_3Co(DH)_2]_2$ μ-pz dissolved in $CDCl_3/CD_3OD$ (50%) with 1,4-phenylenebisboronic acid in a ratio of 1:1, and from a solution of **3** in CD_3OD upon addition of pyrazine in a ratio of 1:0.5. In both cases, the preliminary formation of the "precursor" species occurred. On the other hand, solutions containing only $CH_3Co(DH)_2H_2O$ and 1,4-phenylenebisboronic acid did not show the formation of a unique species even using longer reaction times. Attempts to remove the guest from **1** by protonation of pyrazine required very acidic pH values, owing to the low pK_a value of pyrazine (0.6).[18] Under these conditions the removal of the guest led to the destruction of the host.

Synthesis and Stuctural Characterization of $[CH_3Co(DH)(DB)(OCH_3)(1,4\text{-}Ph)(OCH_3)(DB)CoCH_3](\mu\text{-en})$, 2. Initially, the synthesis of **2** was carried out under experimental conditions similar to those employed for **1**, with slightly less than a 1:1 amount of 1,4-phenylenebisboronic acid with respect to methylcobaloxime. As the only product

---

(17) (a) Asaro, F.; Dreos, R.; Nardin, G.; Pellizer, G.; Peressini, S.; Randaccio, L.; Siega, P.; Tauzher, G.; Tavagnacco, C. *J. Organomet. Chem.* **2000**, *601*, 114. (b) Dreos, R.; Geremia, S.; Nardin, G.; Randaccio, L.; Tauzher, G.; Vuano, S. *Inorg. Chim. Acta* **1998**, *272*, 74. (c) Asaro, F.; Dreos, R.; Geremia, S.; Nardin, G.; Pellizer, G.; Randaccio, L.; Tauzher, G.; Vuano, S. *J. Organomet. Chem.* **1997**, *548*, 211. (d) Dreos, R.; Tauzher, G.; Vuano, S.; Asaro, F.; Pellizer, G.; Nardin, G.; Randaccio, L.; Geremia, S. *J. Organomet. Chem.* **1995**, *505*, 135.

(18) Goldacre, R.; Albert, A.; Phillips, J. *J. Chem. Soc.* **1948**, 2240.

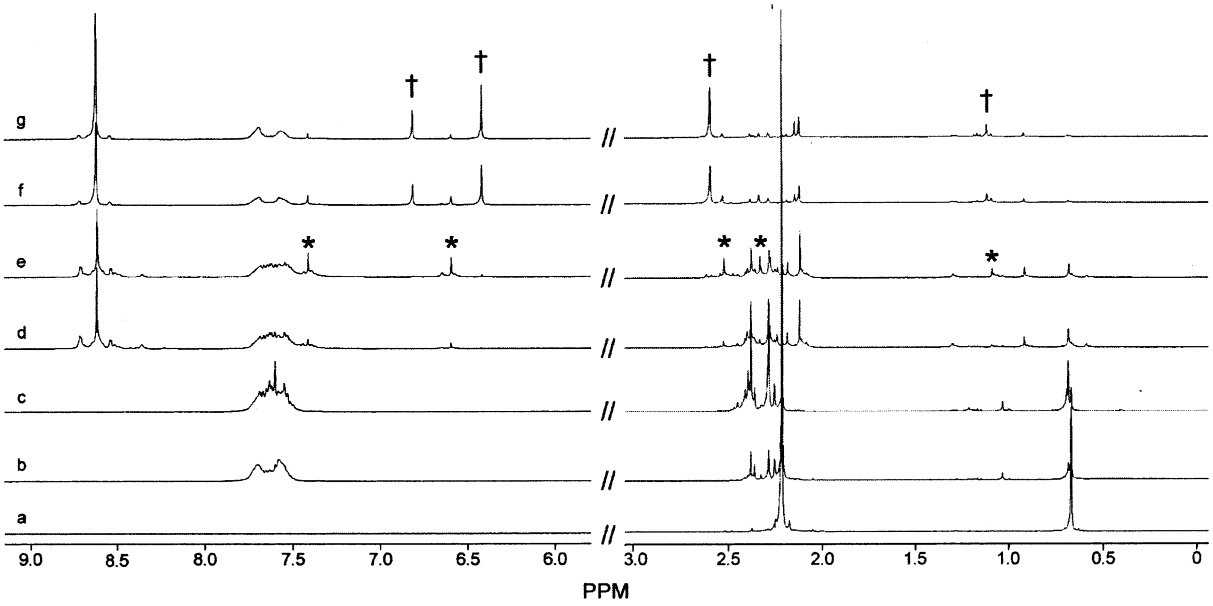
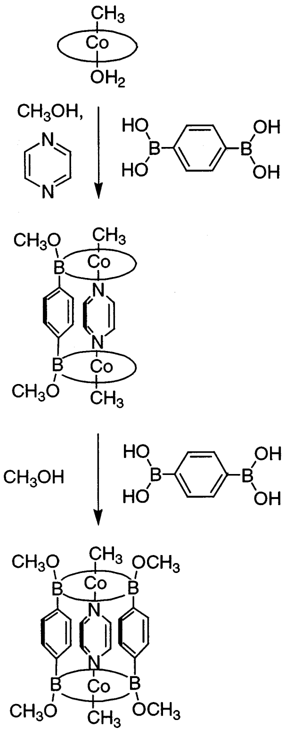


Figure 3. Monitoring of the guest-induced self-organization of **1** by ^{1}H NMR: (a) 30 mM solution of $CH_3Co(DH)_2H_2O$ in CD_3OD (pD about 8); (b) immediately after the addition of a 1:1 amount of 1,4-phenylenebisboronic acid; (c) after 45 min; (d) immediately after the addition of a 1:0.5 amount of pz; (e) after 45 min; (f) after 2 days; (g) after 10 days. The signals of **1** are marked with a dagger and those of the "precursor" (see text) with an asterisk.

Scheme 2. Proposed Reaction Mechanism for the Formation of **1**[a]



[a] The first step involves the formation of the "precursor", the second step the closure of the box.

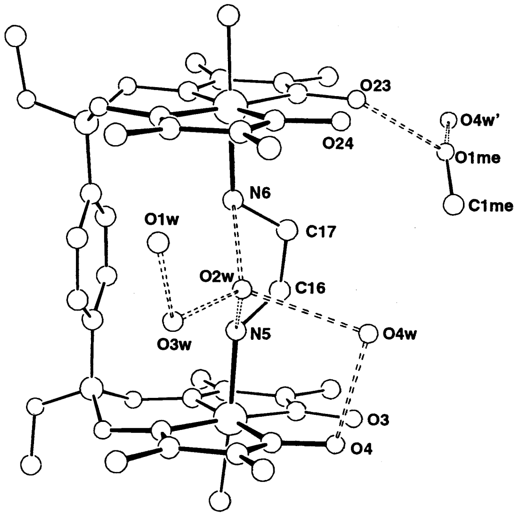


Figure 4. Scheme of the hydrogen bonds (dotted lines) involving **2** and water and methanol molecules.

recovered was **2**, contaminated by impurities of 1,4-phenylenebisboronic acid which are difficult to remove, the synthesis was repeated using half the amount of acid. A time dependent ^{1}H NMR experiment showed that the formation of **2** is almost complete after 2 days, but good X-ray quality crystals could be obtained only after 2 weeks at 5 °C.

The structure of **2,** shown in Figure 1b, may be described as related to that of **1**, in which a phenyl side is removed and the pz bridge is substituted by an en bridge, between Co atoms 7.037(1) Å apart. The B···B distance of 6.105(4) Å is essentially equal to that of 6.105(6) Å found in **1**. The en bridge is characterized by a torsion angle about the C−C bond of 36.4(8)°, which is oriented away from the phenyl bridge (Figure 1b). The conformation of the en bridge appears to be dictated by the H-bond formation of both the NH_2 groups with the water molecule O2W, which lies between the peripheries of the two equatorial moieties (Figure 4). O2W in turn is involved in a network of H-bonds with other solvent molecules, as shown in Figure 4. The Co atoms are displaced out of the 4-N equatorial donor plane by 0.040(2) Å toward the N axial donor and, correspondingly, the two five-membered equatorial rings in each equatorial unit bend toward the CH_3 axial ligand, making α angles of 3.4(1)° and 1.7(2)°, respectively.

The coordination bond lengths and angles are given in Table 2. No marked difference is detected between the chemically equivalent distances and angles, which do not differ from those found in **1**, if the axial distances are excepted. In fact, in **2** the Co−CH_3 mean distance of 1.989(5) Å appears to be slightly shorter than that of 2.008(3) Å in **1**, whereas the axial Co−N mean distance of 2.068(4) Å in **2** is only slightly longer the that of 2.045(2) Å in **1**. The former value is surprisingly short for a Co−N(sp^3) distance compared with the axial Co−N(sp^2) distance in **1**. In fact, in methyl cobaloximes with trans NH_2Ph and anisidine,[19] the Co−N axial distances are 2.129(1) and 2.118(2) Å, respectively. However, the Co−pz distance (2.045(2) Å) is only slightly shorter when compared to that of 2.068(3) Å in methylcobaloxime pyridine.[16] The difference of about 0.8 Å may be due to the electronic cis influence of the equatorial ligand and to the different nature of the axial amine.

The ^1H NMR spectra of **2** recorded in CD_3OD show one singlet for the axial methyl (0.65 ppm), two singlets for the equatorial methyls (2.20 and 2.43 ppm), one singlet for the OCH_3 arising from the esterification of B(OH) (3.30 ppm), and one singlet for the protons of the 1,4-phenylenebisboronic acid (7.20 ppm). If the spectra are recorded immediately after the dissolution of the complex, the NH_2 and the CH_2 protons appear as multiplets at 1.37 and 1.80 ppm, respectively. After some days, the signal of NH_2 disappears and the signal of CH_2 ppm becomes a singlet, because of the loss of coupling with NH_2. This result suggests that the strong hydrogen bonds involving the NH_2 protons are relatively persistent in solution and slow the exchange with the solvent. The upfield shift of the CH_2 protons relative to the free ligand (2.66 ppm) is due to the shielding effect of the phenyl.

Role of the Guest Molecule in the Self-Assembly of the Host. The above results show that pyrazine is not included in a preformed box, after assembly from methycobaloxime and bisboronic acid, but rather thermodynamically drives the assembly process. To probe the role of the guest in the formation of the host, several ditopic ligands (ethylenediamine, piperazine, DABCO, 4-aminopyridine, azide, SCN^-) have been used and the process has been monitored by ^1H NMR spectroscopy. None of them proved to be effective, and ethylenediamine only allowed the formation of **2**, even if the X-ray structure of **2** does not show apparent geometrical reasons that prevent the closure of the box. Therefore, the action of pyrazine seems quite specific.

The effectiveness of pyrazine probably arises from its having both a correct geometry and a sufficiently low pK_a value. Indeed, it has been shown[4] that the reaction of boronic acids with the O•••H•••O moiety of bis(dimethylglyoximato) derivatives requires a neutral medium, in order to allow the formation of a hydroxyboronate species, containing a tetrahedral boron, and the release of a water molecule. At these pH values the pyrazine is still in the basic form and may coordinate efficiently the Co atoms. Furthermore, a favorable $\pi-\pi$ stacking interaction between the aromatic rings could stabilize **1**.

Acknowledgment. This work was supported by MIUR (PRIN MM03185591) and by CNR, Agenzia 2000 (Rome). We thank Dr. F. Hollan for recording mass spectra and Dr. N. Hickey for the English supervision.

Supporting Information Available: One crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025909S

---

(19) Geremia, S.; Mari, M.; Randaccio L.; Zangrando, E. *J. Organomet. Chem.* **1991**, *408*, 95.