The Effect of the Steric Bulk of the Ligand on the Geometry of the Species Self-Assembled from Co^{III} Bis(dioximates) and Boronic Acids

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Keywords: Boronic acid / Cobalt / Dioximes / Self-assembly / Solid-state structures

The synthesis and characterization of the products of the reactions between the bis(diphenylglyoximato)cobalt(III) complexes $[Co(CH_3)(dpgH)_2L]$ [L = py or H_2O; $dpgH_2$ = bis(diphenylglyoxime)] and 4-pyridinylboronic acid (**1**) and 3-aminophenylboronic acid (**2**) are described. The crystals of both **1** and **2** are built up by dimeric units arranged on a crystallographic symmetry center, so that the 4-pyridinyl (in **1**) or the 3-aminophenyl residue (in **2**) of one moiety coordinates to the Co atom of the symmetry-related unit. ^1H NMR spectra show that both **1** and **2** are stable in solution in aprotic solvents: they do not dissociate and are not in equilibrium with species having different nuclearity. The geometry of **1** is very similar to that of the species assembled from the corresponding bis(dimethylglyoximato)cobalt(III) complex and 4-pyridinylboronic acid. On the contrary, the replacement of the methyls by phenyls prevents the trimeric arrangement previously found in the supramolecular species assembled from methylcobaloxime and 3-aminophenylboronic acid and leads to the dimeric species **2**.

Introduction

Organobis(dimethylglyoximato)cobalt(III) complexes $[Co(CH_3)(dmgH)_2L]$ [$dmgH_2$ = bis(dimethylglyoxime)], also known as organocobaloximes (Scheme 1), have been widely studied as vitamin B_{12} models.[1] Their derivatives with either one or both of the intramolecular O−H···O bridges replaced by organoboryl groups are well known and have recently been reviewed.[2] In the last few years organocobaloximes have also been shown to be good building blocks for the assembly of supramolecular systems by reaction with functionalised aromatic boronic acids.[3−5] The $B(OH)_2$ group of the boronic acid reacts with the oxime bridge of one cobaloxime molecule, with simultaneous coordination of the donor atom to the cobalt of another cobaloxime. Products of different nuclearity and geometry have been obtained depending on the boronic acid used as linker (Scheme 1). Thus, the reaction of methylcobaloxime with 4- and 3-pyridinylboronic acid (L^1 and L^2, respectively) gave a dinuclear "molecular box"[4] and a dinuclear "molecular parallelogram",[3] respectively, whereas reaction with 3-aminophenylboronic acid (L^3) gave a trinuclear molecular triangle (Scheme 2).[5]

The substitution of Co by Rh in the reaction with 3-aminophenylboronic acid produced a dramatic structural change, leading to an inorganic polymer (Scheme 3), although both the geometry and the coordination properties of the $[Rh(CH_3)(dmgH)_2L]$ and $[Co(CH_3)(dmgH)_2L]$ moieties are very similar. These results suggest that slight variations in the geometry of the building blocks can strongly affect the structure of the assembled polynuclear systems. Therefore, we decided to study the effect of the increase in steric hindrance of the metal complex by substituting either one or both of the methyl groups of the equatorial bis(dimethylglyoximato) ligand by a phenyl group (Scheme 1). The synthesis and characterization of the products of the reactions between the organobis(diphenylglyoximato)cobalt(III) complexes $[Co(CH_3)(dpgH)_2L]$ and L^1, L^2 and L^3 are discussed in this paper, whereas the results concerning the reactions of organobis(methylphenylglyoximato)cobalt(III) complexes $[Co(CH_3)(mpgH)_2L]$ will be reported elsewhere.

Results and Discussion

Synthesis

The starting complex for the synthesis of **1**, $[Co(CH_3)(dpgH)_2py]$, was synthesized as described previously.[6,7] In the synthesis of **2**, $[Co(CH_3)(dpgH)_2(H_2O)]$ was used instead of $[Co(CH_3)(dpgH)_2py]$ to facilitate the replacement of the axial ligand by the amine nitrogen of

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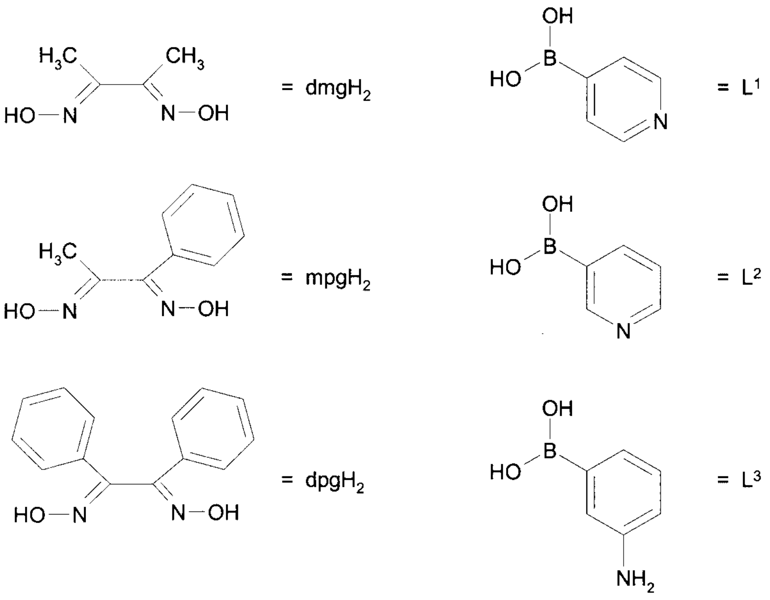
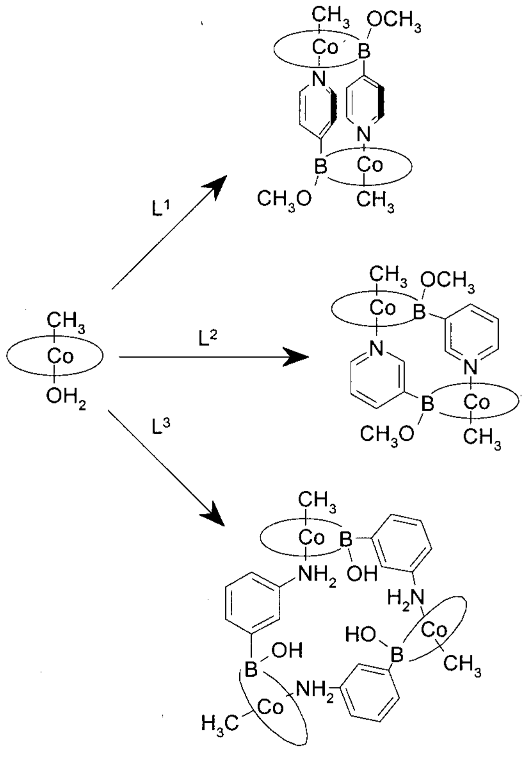
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200400314

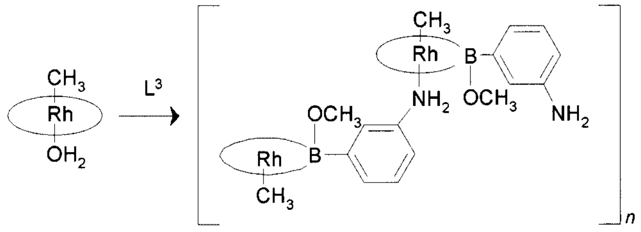


Scheme 1



Scheme 2

the boronic acid. It has previously been shown that the products of the reactions of methylcobaloxime with L^1, L^2 and L^3 are strongly pH dependent,[4,5] because the boronic acids are zwitterionic species.[8] Indeed, the formation of the supramolecular species occurs by reaction of the complex with either the neutral or the zwitterionic form of the boronic acid.[4] The macroscopic pK_a values of the first and the second deprotonation are, respectively, 3.83 and 8.2 for L^1,[4] 4.0 and 8.2 for L^2,[8] and 4.56 and 9.14 for L^3.[5]



Scheme 3

Therefore the reactions were carried out within these pH ranges also in the present case. X-ray quality crystals of **1** and **2** were obtained from the reaction with L^1 and L^3, after one week and after four days, respectively. Only complicated mixtures of products were obtained from the reaction with L^2, despite several attempts carried out at different pH values and in different solvents, and they were not further characterized.

It should be noted that the reaction time for the formation of **1** and **2** is substantially longer than that required for the assembly of the corresponding systems starting from cobaloximes. This effect may be due to both electronic and to steric effects. In fact, the electron-withdrawing power of the phenyls decreases the electron density on the oxime oxygens with respect to cobaloximes and hinders the electrophilic attack of the sp^2-hybridized B atom of the boronic acid. Furthermore, the steric hindrance of the phenyls may also make the approach of L both to the oxime bridge and to the axial coordination position more difficult.

X-ray Crystal Structures

The crystal structure of $[Co(CH_3)(dpgH)\{dpgB(OMe)(4\text{-}Py)\}]_2$ (**1**) is built up from dimeric units arranged on a crystallographic symmetry center in such way that the 4-pyridinyl residue of one unit axially coordinates the Co atom of the symmetry-related unit (Figure 1). Four MeOH and two H_2O molecules were also located in the unit cell, all with half-occupancy factor. A series of H-bonds are formed between water and methanol [O1w···O7Me = 2.929 Å; O1w···O6Me = 2.422 Å] and between methanol and the B-methoxide residue [O6Me···O5 = 2.735 Å]. The dimer can be considered a rectangular box with the two equatorial moieties and the two pyridinyl groups as ideal sides. The Co···Co distance is 7.605(1) Å, whereas the Co···B distance is 3.240(4) Å, Co···B1 is 6.510(4) Å and the Co−B−Co′ and B−Co−B1 angles are 96.7(1)° and 82.9(9)°, respectively. The geometry of the dimer is very close to that found in $[Co(CH_3)(dmgH)\{dmgB(OMe)(4\text{-}Py)\}]_2$ (**1′**) in which the corresponding distances and angles are 7.592(3) Å, 3.20(1) Å, 6.51(1) Å, 97.1° and 82.9°, respectively (Scheme 4).[4] As in **1′**, the pyridinyl ligand is nearly perpendicular to the Co_2B_2 mean plane (85.4°) and oriented in such way as to nearly bisect the five-membered ring of the equatorial moiety. The two pyridinyl rings, related by a symmetry center, are nearly face to face at a distance of 3.38 Å (3.30 Å in **1′**).[4] The latter orientation of the axial planar ligand is typical of the iminocobaloximes (Costa's models)[1] and of bis(diphenylborylated) cobaloximes,[9–11] whereas the axial ligand is rotated by about 90° in the monomeric complexes $[CoR(dpgH)_2py]$ with R = CH_3,[6] CH_2SiMe_3,[7] CH_2CMe_3,[7] and CF_3,[7] where the pyridine ligand bisects the O···O vectors of the diphenylglyoximate ligands.

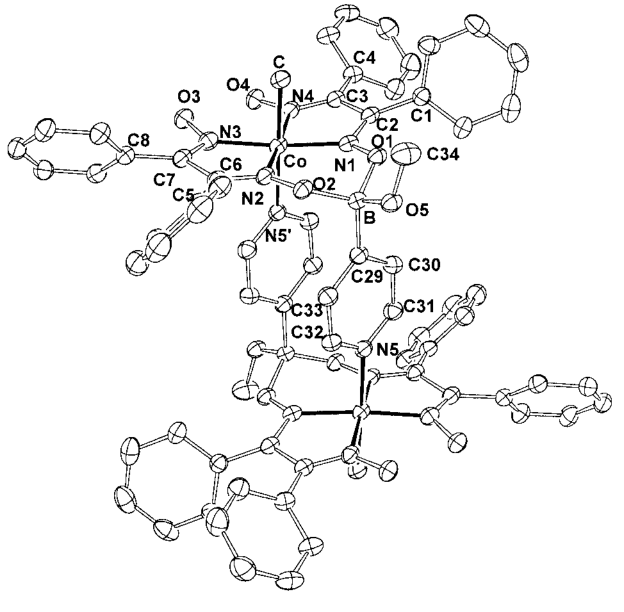
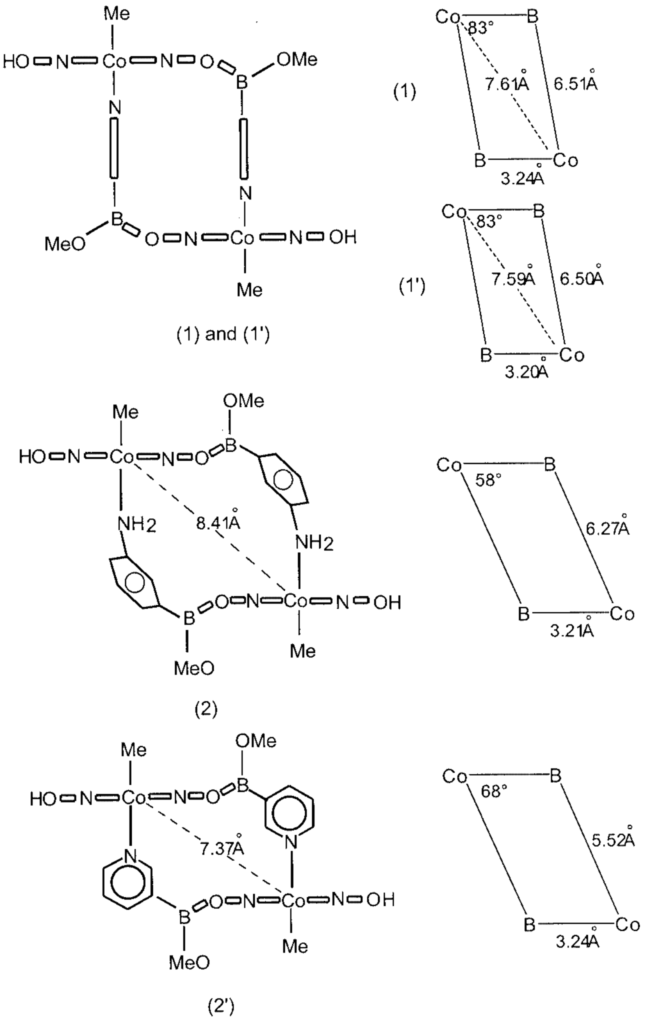


Figure 1. ORTEP drawing (thermal ellipsoids at 30% probability) and labeling scheme for the independent atoms in the dimer **1**; the crystallization solvent molecules have been removed



Scheme 4

An ORTEP view of **2** is shown in Figure 2. The structure consists of dimeric units arranged around a crystallographic symmetry center so that the pendant 3-aminophenyl residue of one moiety coordinates the Co atom of the other unit in one axial position, as shown in Figure 2. The dimeric unit may be considered a molecular box, similar to that of **1**, but more distorted. In fact, the Co_2B_2 group, which forms a nearly regular rectangle in **1**, forms a distorted parallelogram in **2** (Scheme 4). This parallelogram is similar to that observed in $[Co(CH_3)(dmgH)\{dmgB(OMe)(3\text{-}Py)\}]_2$ (**2′**).[3] However, owing to the greater conformational freedom of the aminophenyl group with respect to that of the 3-pyridinyl one, a molecular box with the two phenyl groups oriented face to face is formed in **2**, whereas a "molecular parallelogram" is formed in **2′**.[3] In fact, in the latter the two pyridinyl residues are not faced but nearly coplanar. In **2**, the Co···Co distance of 8.410(2) Å is significantly longer than that observed in **2′** [7.365(4) Å]. The orientation of the axial aminophenyl residue with respect to the equatorial plane in **2** (dihedral angle Co′N5−C33C34 = 86.2°, interplanar angle 33.2°) is similar to that observed in the trimeric species $[Co(CH_3)(dmgH)\{dmgB(OH)(3\text{-}NH_2Ph)\}]_3$ (**3**; mean value 102.1°; interplanar mean angle 31.4°).[5] However, in the latter a trinuclear molecular triangle of cobalt atoms of about 9.47 Å side, was found. The difference between **2** and **3** can be ascribed to the replacement of the Me groups on the equatorial moiety by Ph groups. In fact, in **3** the closure of the Co triangle imposes the orientation of three methyl groups towards the centre of the Co tri-

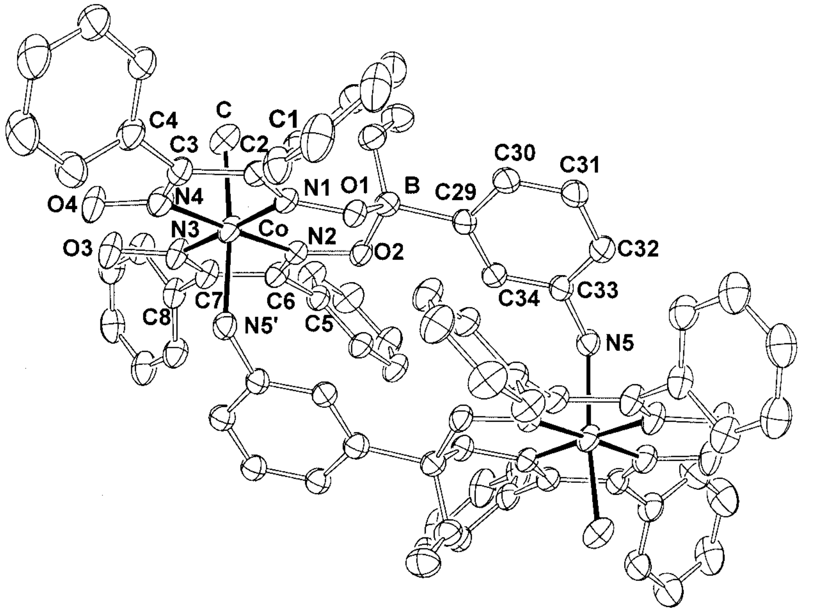
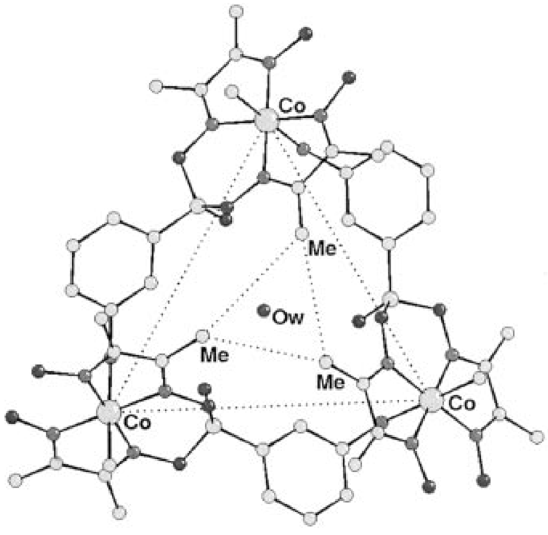


Figure 2. ORTEP drawing (thermal ellipsoids at 30% probability) and labeling scheme for the independent atoms in the dimer **2**; the crystallization solvent molecules have been removed

angle. Therefore the arrangement requires that the three C(Me) atoms are at about 3.89 Å (Scheme 5). When a phenyl group replaces the methyl group, the trimeric arrangement of **2** is prevented because of the steric hindrance between the phenyl groups.



Scheme 5. A view of the molecular triangle **3**; the dotted lines indicate the Co···Co (mean value 9.47 Å) and the C(Me)···C(Me) (mean value 3.9 Å) distances

The coordination bond lengths in **1** and **2** are given in Table 1 and compared with those in **1′**, **2′** and **3**. As expected, the Co−N5′ (sp^2) distances in **1**, **1′**, and **2′** are essentially identical and shorter than the corresponding Co−N5′ (sp^3) distances in **2** and **3**.

Table 1. Selected bond lengths (Å) and angles (°) in **1**, **2**, and other similar models

	1	**1′**	**2**	**2′**	**3**
Co−N1	1.872(3)	1.85(1)	1.855(4)	1.868(8)	1.864(7)
Co−N2	1.884(3)	1.88(1)	1.881(4)	1.872(7)	1.869(6)
Co−N3	1.867(3)	1.86(1)	1.871(4)	1.872(7)	1.865(7)
Co−N4	1.894(3)	1.87(1)	1.877(4)	1.862(8)	1.873(7)
Co−C	2.013(4)	2.00(1)	1.997(6)	1.99(1)	1.987(8)
Co−N5′	2.068(3)	2.08(1)	2.085(4)	2.068(8)	2.102(6)
C−Co−N5′	178.6(1)	175.4(4)	174.2(2)	175.4(4)	178.2(4)
B···Co···B′	83.3(1)	82.9(9)	58.3(2)	68.2(3)	73.1(3)
Co···Co	7.605(1)	7.592(6)	8.410(2)	7.365(4)	9.474(4)
Co···B	3.240(4)	3.20(1)	3.207(6)	3.244(7)	3.221(7)
Co···B′	6.510(4)	6.51(1)	6.269(6)	5.515(7)	6.451(7)

^{1}H NMR Spectra

The ^{1}H NMR spectrum of **1** in $CDCl_3$ shows a single set of signals because of the presence of a symmetry center in the molecule. The axial methyl resonates at $\delta = 1.59$ ppm, deshielded with respect to $[Co(CH_3)(dpgH)_2py]$ ($\delta = 1.44$ ppm),[7] probably due to the electron-withdrawing effect of the boryl bridge. The singlet at $\delta = 3.27$ ppm is due to the $BOCH_3$ protons. The *ortho* protons of the pyridinyl residue, assigned from a ^{1}H-^{1}H COSY experiment, resonate at $\delta = 7.35$ ppm and the *meta* protons at $\delta = 6.75$ ppm, considerably upfield shifted relative to those of $[Co(CH_3)(dpgH)_2py]$ ($\delta = 8.92$ and 7.44 ppm, respectively), due to the shielding effect of the two faced pyridinyl rings.[7] The phenyl protons give rise to a multiplet in the range $\delta = 7.18-7.43$ ppm.

The ^1H NMR spectrum of **2** was recorded in C_6D_6 because the compound is almost insoluble in the most common deuterated solvents. The magnetic anisotropy of this solvent spreads the signals of the aromatic protons over a larger range, allowing an almost complete assignment. The axial methyl resonates at $\delta = 2.30$ ppm and the $BOCH_3$ group at $\delta = 3.20$ ppm. The NH_2 protons, which are diastereotopic as a consequence of the coordination, give rise to a doublet of doublets at $\delta = 3.32$ and 3.80 ppm. The protons of the four non-equivalent phenyls and the aminic protons resonate in the range $\delta = 6.20-8.01$ ppm.

These results are entirely consistent with the solid-state structures, suggesting that **1** and **2** are stable in solution in aprotic solvents: they do not dissociate and are not in equilibrium with species having different nuclearity.

Conclusion

The most interesting consequence of the increase of the steric hindrance in the equatorial ligand of the metal complex on going from bis(dimethylglyoximato) to bis(diphenylglyoximato), is the change in the nuclearity of the supramolecular species assembled from L^3. The molecular triangle **3** was obtained starting from bis(dimethylglyoximato) whereas the dimeric species **2** was obtained from bis(diphenylglyoximato). Assembly is still possible because of the conformational freedom of the boron bridge, which is directed toward the methyl group in **2**, whereas it is directed towards the opposite side in the triangle **3**; however, the trimeric arrangement is prevented because of the steric hindrance of the phenyl groups.

A further structural difference is the esterification of the B(OH) residual groups by methanol in **2**, which does not occur in **3**. In this case the esterification is probably hampered by the network of H-bonds between a water molecule lying approximately in the center of the triangle (Ow, Scheme 5) and the three boron OH groups.

Finally, both electronic and steric effects may be responsible for the longer time required for the assembly reaction in comparison with cobaloximes.

Experimental Section

General Remarks: NMR spectra were recorded on a Jeol EX-400 spectrometer 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. $[Co(CH_3)(dpgH)_2py]$ was prepared according to a literature procedure.[6,7] All other reagents were reagent grade and used without further purification.

Synthesis of $[Co(CH_3)(dpgH)_2(H_2O)]$: $[Co(CH_3)(dpgH)_2py]$ (0.10 g, 0.16 mmol) was dissolved in 10 mL of CH_2Cl_2 and 40 mL of CH_3OH. The solution was filtered to remove the undissolved residue and 0.30 g of the acidic cation exchange resin Dowex 50 W was added. The solution was heated at 50 °C for 2 h and then filtered and concentrated to half volume on a rotary evaporator. Red crystals of $[Co(CH_3)(dpgH)_2(H_2O)]$ were recovered from the solution after allowing it to stand. Yield: 63.7 mg (69%). $C_{29}H_{27}CoN_4O_5$ (570.48): calcd. C 61.06, H 4.77, N 9.82; found C 60.7, H 4.91, N

Table 2. Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{36}H_{36}BCoN_5O_{6.5}$	$C_{38.5}H_{43}BCoN_5O_{7.5}$
Molecular mass	712.44	765.52
T (K)	150(2)	150(2)
λ (Å)	0.71069	0.71069
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	10.543(4)	10.858(3)
b (Å)	12.445(4)	12.688(13)
c (Å)	13.937(6)	16.497(4)
α (°)	94.23(2)	106.75(2)
β (°)	103.53(2)	110.02(2)
γ (°)	94.95(2)	82.16(2)
V (Å^3)	1762.9(12)	1995.7(8)
Z	2	2
$\rho_{calcd.}$ (g cm^{-3})	1.342	1.274
$F(000)$	742	802
μ (mm^{-1})	0.540	0.484
Θ (°)	3−26	4−26
Reflections collected	10258	12001
Reflections observed	6319	7045
Criterion for obs.	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Variables	450	466
Final R_{int} [$I > 2\sigma(I)$]	R_1 [a] = 0.070, wR_2 [b] = 0.191	R_1 = 0.078, wR_2 = 0.212
R_{int} (all data)	R_1 = 0.083, wR_2 = 0.206	R_1 = 0.109, wR_2 = 0.239
GOF	1.05	1.02
Max. resid. dens. (e/Å^3)	0.91	0.65

[a] $R_1 = ||F_o| - |F_c||/|F_o|$. [b] $wR_2 = [w(|F_o^2| - |F_c^2|)^2/w|F_o^2|^2]^{1/2}$.

9.60. ESI-MS (60 V, CH_3OH; m/z^+): calcd. for $CH_3Co(dpgH)_2H_2O$ 570.482; found 553.1 (100%) $[CH_3Co(dpgH)_2H_2O - H_2O]$. ^1H NMR ($CDCl_3$, 400 MHz, TMS): $\delta = 1.23$ (s, 3 H, CH_3 ax.), 7.26 (m, 20 H, equatorial phenyls) ppm.

Synthesis of $[Co(CH_3)(dpgH)\{dpgB(OMe)(4\text{-}Py)\}]_2$ (1): 4-Pyridinylboronic acid (0.012 g, 0.1 mmol) was added whilst stirring to a solution of $[Co(CH_3)(dpgH)_2py]$ (0.03 g, 0.05 mmol) in a mixture of methanol (10 mL) and CH_2Cl_2 (2 mL). The resulting mixture was filtered and the pH was adjusted to 5 by addition of $HClO_4$ (70% w/w). X-ray quality crystals formed from the solution in 1 week. Yield: 0.014 g (40%). $C_{70}H_{62}B_2Co_2N_{10}O_{10}$ (1342.8): calcd. C 62.00, H 4.65, N 10.43; found C 61.8, H 4.69, N 10.18. ESI-MS (60 V, CH_2Cl_2/HCOOH 1%; m/z^+): calcd. for **1** 1342.8; found 1343.2. (43%) [**1** + H^+]. ^1H NMR ($CDCl_3$, 400 MHz, TMS): $\delta =$ 1.59 (s, 6 H, CH_3 ax.), 3.27 (s, 6 H, OCH_3), 6.72 (d, $^3J_{H,H} = 6.4$ Hz, 4 H, *meta* of py), 7.18−7.43 (m, 40 H, equatorial phenyls), 7.35 (d, $^3J_{H,H} = 6.4$ Hz, 4 H, *ortho* of py), 18.24 (s, 2 H, O···H···O) ppm.

Synthesis of $[Co(CH_3)(dpgH)\{dpgB(OMe)(3\text{-}NH_2Ph)\}]_2$ (2): 3-Aminophenylboronic acid monohydrate(0.03 g, 0.18 mmol) was added whilst stirring to a solution of $[Co(CH_3)(dpgH)_2(H_2O)]$ (0.10 g, 0.18 mmol) in methanol (100 mL). The resulting solution was filtered and the pH was adjusted to 8 by addition of $HClO_4$ (70% w/w). X-ray quality crystals formed from the solution within 4 days. Yield: 0.037 g (30%). $C_{72}H_{66}B_2Co_2N_{10}O_{10}$ (1370.8): calcd. C 63.08, H 4.85, N 10.22; found C 62.7, H 5.02, N 10.2. ^1H NMR (C_6D_6, 400 MHz, TMS): $\delta = 2.3$ (s, 6 H, CH_3 ax.), 3.20 (s, 6 H, OCH_3), 3.32 (d, 2 H, NH_2), 3.80 (d, 2 H, NH_2), 6.21 (d, $^3J_{H,H} = 8.3$ Hz, 1 H, *ortho*-C_6H_4-NH_2), 6.29 (t, 4 H, *meta*-Ph^I), 6.37 (d, $^3J_{H,H} =$ 7.8 Hz, 4 H, *ortho*-Ph^I), 6.67 (m, 2 H, *para*-Ph^I); 6.75 (t, 4 H, *meta*-Ph^{II}), 6.82 (m, 2 H, *para*-Ph^{II}), 7.10 (d, $^3J_{H,H} = 7.8$ Hz, 4 H, *ortho*-Ph^{II}), 6.92 (m, 2 H, *para*-Ph^{IV}), 7.10 (t, 4 H, *meta*-Ph^{IV}), 7.91 (d, $^3J_{H,H} = 7.3$ Hz, 4 H, *ortho*-Ph^{IV}), 6.95−7.05 (m, 6 H, *meta*- and *para*-Ph^{III}), 7.56 (d, $^3J_{H,H} = 7.3$ Hz, 4 H, *ortho*-Ph^{III}), 7.25 (m, 2 H, *meta* -C_6H_4-NH_2), 7.43 (s, 2 H, *ortho*-C_6H_4-NH_2), 8.01 (d, $^3J_{H,H} = 7.3$ Hz, 2 H, *para*-C_6H_4-NH_2), 19.50 (s, 2 H, O···H···O) ppm.

X-ray Crystallographic Study: Single crystals suitable for X-ray data collection,were obtained as reported above. X-ray diffraction data were collected at 150 K, with a Nonius DIP 1030 H System, using graphite-monochromated Mo-K_α radiation. For all compounds a total of 30 frames were collected, using the Xpress program,[12] over a half 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 reflection intensities and data scaling were performed using MOSFLM and SCALA from the CCP4 program suite.[13] Reflections, which were measured on previous and following frames, were used to scale the frames with each other, a procedure that partially eliminated absorption effects, taking into account also any crystal decay. The structures were solved by direct methods,[14] followed by Fourier syntheses and refined by full-matrix least-squares (on F^2) cycles.[15] Compound **1** crystallized with one water and two independent methanol molecules (all with occupancy factor 0.5), while **2** co-crystallized with three methanol molecules (one with o.f. 0.5). The solvent molecules were refined isotropically. The H-atoms were included at calculated positions in the final refinements. A suite of programs[5] was also used in the geometrical and final calculation. Crystal and refinement data of interest are given in Table 2.

CCDC-236499 (for **1**) and -236500 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by MIUR (PRIN 2003 no. 2003037058) and Cofinlab CE00338925. We thank Dr. Fabio Hollan for recording mass spectra.

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Received April 20, 2004
Early View Article
Published Online September 2, 2004