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A New Dinuclear Complex Derived from Cobaloxime Units Held Together by 3-Pyridylboronic Acid Residues

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Introduction

There is currently an increasing interest toward the self-assembly of multinuclear species driven by noncovalent interactions owing to the efficiency of these synthetic methods. Since these processes occur under equilibrium conditions, the end products may be in equilibrium not only with their components but with other undesirable compounds as well.[1] Using a template is a valid method to improve the self-assembly and to direct it toward the desired product.[2] The template effect was systematically studied by Busch at the beginning of the 1960s,[3] but only recently has it been used to generate efficiently supramolecular species,[4] the geometry of the final product being dependent on the coordination properties of both the assembled metal complexes and the template itself.

We have recently shown that either one or both of the hydrogen bonds of bis(dimethylglyoximato) complexes may be replaced by diphenylboron bridges through relatively fast equilibrium reactions[5] (Chart 1). These results suggested that boronic acids containing donor groups may act as templates in directing the syntheses of multinuclear complexes, by exploiting the interactions of boron with the oxime oxygens and those of the donor group with the metal center. We report here the synthesis, characterization, and X-ray structure of the new dinuclear species $[CH_3Co(DH)(DB(OCH_3)(3\text{-}Py))]_2$ (**1**) in which two methylcobaloxime units are assembled by two $B(OCH_3)$-(3-Py) residuals (Chart 1).

Experimental Section

Synthesis of $[CH_3Co(DH)(DB(OCH_3)(3\text{-}Py))]_2$ (1). To a solution of 0.13 g of methylaquocobaloxime[6] (0.4 mmol) in 100 mL of 50% CH_2Cl_2/CH_3OH were added a 4-fold excess of 3-pyridylboronic acid[7] (0.4 g, 3.2 mmol) and then some drops of 1 M NaOH, until the color turned from red to yellow. The solution was heated at 40 °C for 2 days; evaporation of the solvent afforded yellow crystals of **1**, suitable for X-ray studies. The NMR spectra recorded at this stage show that the crude material is almost pure **1**, with some traces of solvents. Spectroscopic data for **1** are as follows: ^{1}H NMR: ($CDCl_3$) 1.15 (3H, s, C*H*$_3$ ax,), 2.05 (6H, s, C*H*$_3$C=NOH), 2.17 (6H, s, C*H*$_3$C=NOB), 3.31 (3H, s, OC*H*$_3$), 7.23 (1H, t, *H*5 of Py),7.96 (1H, d, *H*6 of Py), 8.22 (1H, d, *H*4 of Py), 9.47 (1H, s, *H*2 of Py). ^{13}C NMR ($CDCl_3$): 12.14, 12.60 (equatorial CH_3), 50.09 (O*C*H$_3$), 123.94, 140.74, 146.27, 147.93 (Py), 155.70, 156.53 (*C*=N).

Table 1. Crystallographic Data for **1**

formula	$C_{15}H_{23}CoBN_5O_5\cdot 2.5CH_3OH$
a, Å	10.290(6)
b, Å	18.681(12)
c, Å	13.047(8)
β, deg	99.59(5)
V, Å^3	2473(2)
D_{calcd}, g cm^{-3}	1.35
D_{obds}, g cm^{-3}	1.33
Z	4
fw	503.2
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
λ, Å	0.710 73
μ, cm^{-1}	9.6
F(000)	1325
$R(F_o)$	0.071[a]
$R_w(F_o)$	0.086[b]

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. $w = 1/[\sigma^2(F_o) + (0.20F_o)^2 + 1.0]$.

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

Co−N(1)	1.872(7)	Co−C(14)	1.99(1)
Co−N(2)	1.862(8)	O(1)...O(2)	2.485(10)
Co−N(3)	1.868(8)	O(3)...O(4)	2.524(8)
Co−N(4)	1.872(7)	O(3)...O(3)’	4.97(1)
Co−N(5)	2.068(8)	C(9)...C(9)’	3.85(1)
N(1)−Co−N(2)	98.7(4)	N(3)−Co−N(4)	96.7(3)
N(1)−Co−N(3)	82.2(3)	N(3)−Co−N(5)	91.9(3)
N(1)−Co−N(4)	177.8(4)	N(3)−Co−C(14)	91.6(4)
N(1)−Co−N(5)	91.0(3)	N(4)−Co−N(5)	90.9(3)
N(2)−Co−N(4)	82.3(3)	N(4)−Co−C(14)	91.8(4)
N(2)−Co−N(5)	90.8(3)	N(5)−Co−C(14)	175.4(4)
N(2)−Co−C(14)	85.8(4)		

Crystal Structure Determination of 1. Yellow prisms of **1** were obtained as described above, and a crystal of approximate dimensions 0.40 × 0.20 × 0.20 mm^3 was used for the diffraction study. Crystallographic data are summarized in Table 1.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation to a maximum 2θ value of 54°. A total of 5800 reflections were measured, 2297 independent reflections having $I > 3\sigma(I)$.

The structure was solved by conventional Patterson and Fourier methods and refined by the full-matrix least-squares (on F) with all non-hydrogen atoms treated anisotropically. Only the atoms of the crystallization methanol molecules were treated isotropically, and all hydrogen atoms were included at calculated positions. The structure was refined using 2297 reflections and 268 variables, to give a final $R(F_o) = 0.071$, with a goodness of fit of 0.43 and a highest peak in the ΔF map of 0.80 eÅ^{-3}.

The programs used are given in refs 8 and 9. Atomic scattering factors were taken from ref 10.

Selected bond lengths and angles are reported in Table 2.

Results and Discussion

The crystal of **1** is built up by dimeric units and crystallization methanol molecules. The dimer is arranged around a crystallographic symmetry center so that the pendant pyridine residue of one moiety coordinates to the Co atom of the other in one axial position, as shown in Figure 1. The dimer forms a large rectangular cage limited by the two pyridine residues and by

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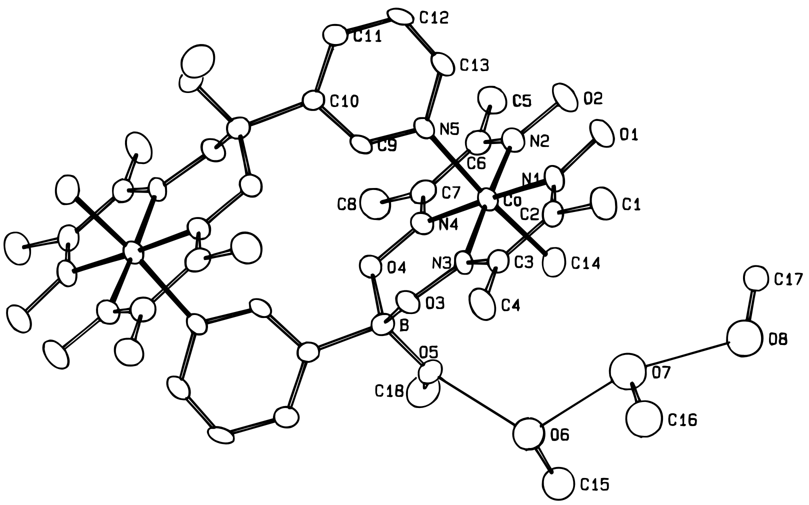
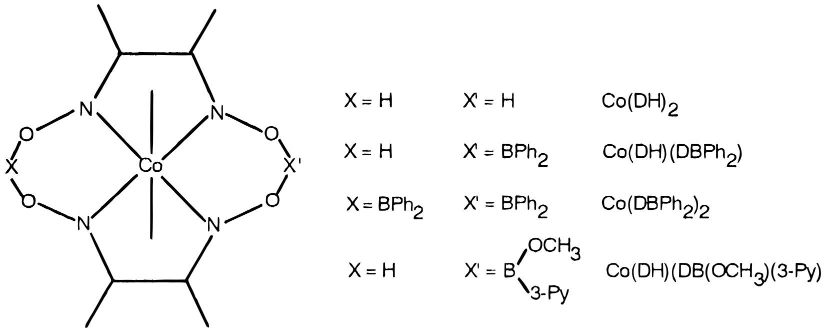


Figure 1. ORTEP drawing (thermal ellipsoids, 20% probability) and labeling scheme for the independent atoms in [$CH_3Co(DH)(DB(OCH_3)$(3-Py))]$_2$·2.5CH_3OH (**1**). H-bonds are represented by thin lines.

Chart 1



the complex moieties. The two pyridine rings are nearly coplanar within ±0.5 Å with a shortest approach C(9)···C(9)′ of 3.85 Å (Figure 1). The cobalt has a distorted octahedral coordination, the equatorial positions being occupied by the four N donors of one ligand and the axial positions by the methyl group and the pyridine residue of the other ligand. The axial fragment is characterized by the Co−C and Co−N distances of 1.99(1) and 2.068(8) Å, respectively, very close to those found in the cobaloxime $CH_3Co(DH)_2Py$.[11] The Co−N equatorial distances vary in the range 1.862(8)−1.872(7) Å, comparable with those already reported in the monomeric $CH_3Co(DH)(DBPh_2)$(*N*-MeIm) (*N*-MeIm = *N*-methylimidazole).[5a] The cobalt atom is slightly displaced by 0.034 Å out of the equatorial plane toward the axial pyridine residue. In the equatorial six-membered cycle the tetrahedral B atom is displaced out of the mean plane toward the axial C(14) atom as observed in monomeric $CH_3Co(DH)(DBPh_2)$(*N*-MeIm).[5a] The pyridine orientation with respect to the equatorial plane is such that the Py plane nearly bisects the oxime bridge, as usually found in pyridine cobaloxime derivatives. This orientation is the most favorable to the formation of the dimeric species.

The O(6) atom of one crystallization methanol molecule is at a distance of 2.72(1) Å from the O(5) atom of the $B(OCH_3)$-(3-Py) grouping and of 2.70(1) Å from the O(7) of the other methanol molecule. A contact between O(7) and O(8) of 2.80(1) Å is also detected. O(8) is the oxygen atom of the crystallization CH_3OH molecule with half-occupancy.

Compound **1** is very stable in solution: the NMR spectra do not show any trace of dissociation or of any other rearrangement, such as the formation of polymeric species, even after some days. The UV−visible spectra show that the addition of a 100:1 excess of *N*-methylimidazole to the complex does not displace the axial pyridine; in $CH_3Co(DH)_2$ Py the replacement is almost complete under the same experimental conditions,[12] with a 10-fold excess of *N*-MeIm. Consequently, the dimerization strongly stabilizes the Co−Py bond. The esterification of the OH group bound to the boronic acid and the formation of a OCH_3 group is likely due to the prolonged heating in methanol; this suggests that the OH group is an additional reactive site to which a pendant arm could be attached.

While this work was in progress, a paper was published concerning the assembling into dimers of a Zn dicatechol porphyrin using 3-pyridylboronic acid as template.[13] It is interesting to note that in this compound the boron atom remains tricoordinated, whereas in **1** it assumes a tetrahedral coordination.

Further explorations of the possibility of multinuclear assembling using different starting complexes and other boronic acids are now in progress.

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Supporting Information Available: Listings of crystallographic data and refinement details, anisotropic thermal parameters for non-hydrogen atoms, positional parameters for all atoms, and complete bond lengths and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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