

Intriguing Two-Dimensional Assembly of Cobaloxime with a  $[\text{Zn}_2(\text{OOCR})_4]$  CenterSarvendra Kumar<sup>\*,†,‡</sup> and B. D. Gupta<sup>‡,§</sup><sup>†</sup>DQIAQF/INQUIMAE, Universidad de Buenos Aires, Ciudad Universitaria, Pab. II, p. 3, EHA1428 Buenos Aires, Argentina<sup>‡</sup>Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

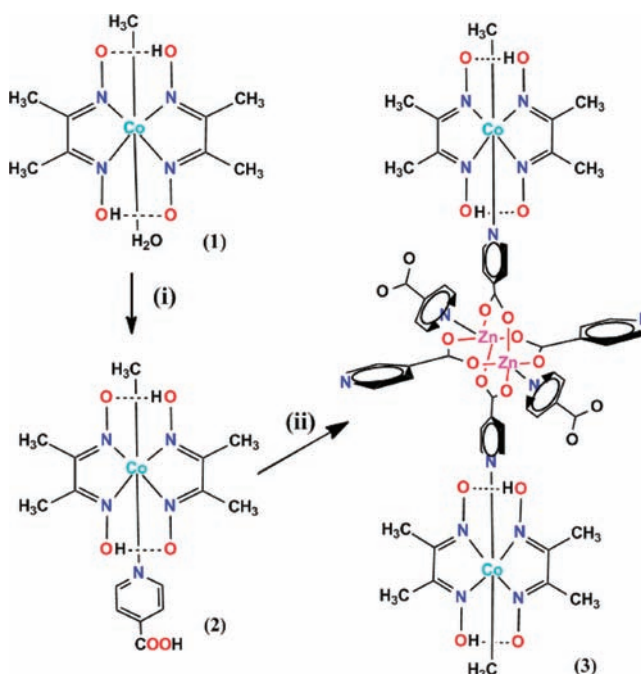
Supporting Information

**ABSTRACT:** We report the synthesis and crystallographic studies of paddlewheel-based methyl cobaloxime assembly formed from methyl cobaloxime, isonicotinic acid, and  $\text{Zn}(\text{NO}_3)_2$ . The cobaloxime units are assembled over two-dimensional metal–organic polyhedra constructed from isonicotinate and Zn metal ions.

The design and synthesis of supramolecular architectures based on the coordination-driven self-assembly of relatively simple structural units has attracted considerable attention.<sup>1</sup> In supramolecular coordination architectures, metal–organic frameworks<sup>2</sup> have attracted particular interest because of their well-defined and confined cavities, high symmetry and stability, and rich chemical properties.<sup>1a–d</sup> Some of these materials also show interesting physical properties such as magnetism, luminescence, and optoelectronic effects.<sup>3</sup> The incorporation of a paddlewheel  $[\text{M}_2(\text{RCOO})_4\text{L}_2]$  ( $\text{M}$  = metal ion;  $\text{L}$  = axial ligand) has resulted in the formation of highly porous paddlewheel frameworks.<sup>4</sup> Zinc is considered to have a flexible coordination sphere; it easily adopts the coordination geometry and forms different clusters to fit the minimum energy according to the requirements of the ligands.<sup>5</sup> Although organocobaloximes have been studied for a long time as vitamin B<sub>12</sub> models, their description, spectroscopic data, structure–property relationships, and correlation to Co–C bond lengths have been emphasized in recent years.<sup>6</sup> However, the molecular assemblage of organocobaloximes is a relatively unexplored area of research, and much has not been reported because of the weak Co–C bond.<sup>7</sup>

Randaccio et al.<sup>8a</sup> have reported that derivatives of organocobaloximes are good building blocks for the construction of supramolecular systems by the reaction with functionalized aromatic (pyridyl or aminophenyl) boric acid.<sup>9</sup> In another approach, the reaction of methyl aquacobaloxime and 1,4-phenyldiboric acid in the presence of pyrazine leads to the formation of a “molecular box” containing pyrazine as a guest molecule.<sup>10</sup> It is worth noting that the assembly does not occur in the absence of pyrazine, and among the other tested ditopic ligands, only ethylenediamine allows partial assembly. Therefore, in this case, the guest induces organization of the host.<sup>11</sup> The synthesis is highly convergent, and after some days, the dinuclear “molecular box” is the only supramolecular species in solution. The assembly of cobaloximes through organobridges and ligand

Scheme 1. Path of the Synthesis of Compounds 2 and 3



Reaction conditions: (i) acetone +  $\text{CH}_3\text{OH}$ , isonicotinic acid; (ii)  $\text{Zn}(\text{NO}_3)_2$ , pyridine,  $\text{CH}_3\text{OH}$  + DMF (8:2).

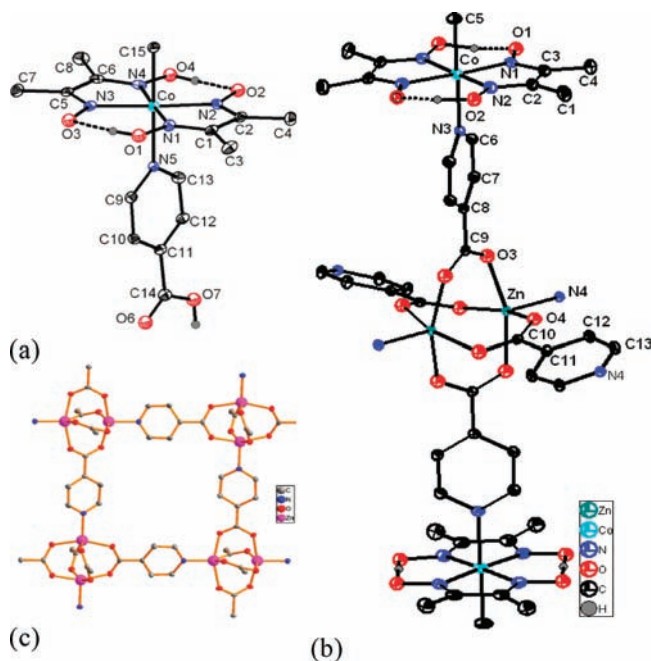
bridges has also been reported.<sup>8</sup> Moss et al.<sup>12</sup> have reported the cobaloxime dendrimer precursor by the reactions of di- and trihydroxy alcohol with cobaloxime.

Herein, we report the synthesis<sup>13</sup> and structure of the first example of the zinc-directed assembly of organocobaloximes.

The addition of isonicotinic acid to the aqua complex  $\text{CH}_3\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$  (**1**; dmgh = dimethylglyoxime) in acetone/methanol afforded isonicotinic acid  $\text{CH}_3\text{Co}(\text{dmgH})_2$  (**2**; Scheme 1). The molecular structure of **2** is shown in Figure 1a. The geometry around the Co atom is distorted octahedral with four N atoms of dimethylglyoxime (dmgH) in the equatorial plane, and methyl and isonicotinic acid are axially coordinated. The Co–C and Co–N mean bond lengths are 1.999(4) and 2.055(3) Å, respectively, which are close to those found in  $\text{MeCo}(\text{dmgH})_2\text{Py}$ .<sup>7</sup> There are two

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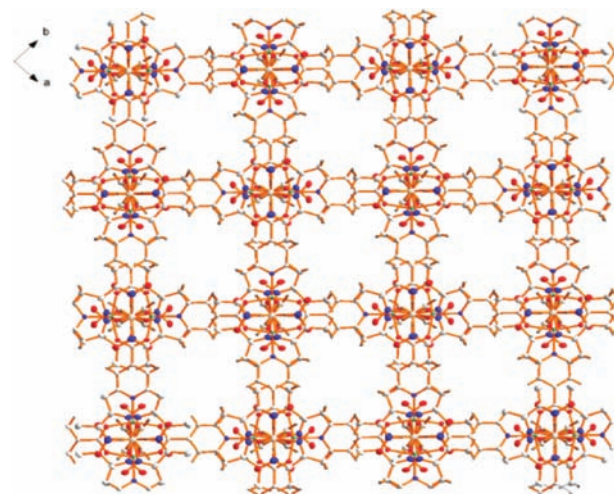


**Figure 1.** (a) Molecular structure of **2**: thermal ellipsoids drawn at the 50% probability level; H atoms omitted for clarity. (b) Molecular structure of **3**: thermal ellipsoids drawn at the 50% probability level; H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1–C5 1.989(4); Co1–N3 2.047(3); Zn1–Zn1' 2.9265(9); Zn1–N3 2.007(2); Zn1–O3 2.047(2); Zn1–O4 2.040(2); N3–Co1–C5 180.00. (c) Unit of the square-planar base of a 2D sheet, separated by a spacer, isonicotinate with a paddlewheel via Zn<sup>II</sup> ions.

independent molecules of complex **2** in the crystal lattice, and average bond lengths and angles are used in the text.

Complex **3** has been synthesized by the reaction of **2** with Zn(NO<sub>3</sub>)<sub>2</sub> in the presence of a few drops of pyridine in CH<sub>3</sub>OH/DMF (8:2 ratio) at room temperature. The solution was kept for crystallization at room temperature, and after 3 weeks, orange-colored crystals, suitable for X-ray studies, were obtained. Refinement of collected data suggested that complex **3** crystallized in the tetragonal system with space group *I4<sub>1</sub>/acd*. The formation of complex **3** has led us to the conclusion that complex **2** exists as an equilibrium mixture<sup>14</sup> of the solvated penta- and hexacoordinated species. Such a situation would be obtained if electron-donating substituted alkylcobaloximes were largely unliganded (pentacoordinate) and electron-withdrawing substituted alkylcobaloximes were largely liganded (hexacoordinate) by a solvent in aqueous solution, in which case the greatest net change in axial ligation in forming the pyridine complex would occur with the electron-donating substituted alkylcobaloximes. The important bond lengths and angles and some structural parameters of complexes **2** and **3** are given in Table S1 in the Supporting Information.

A crystallographic study on complex **3** (Figure 1b) shows that two methylcobaloximes and two isonicotinic acids are connected to two Zn atoms in a paddlewheel fashion. The Zn–Zn distance is 2.9265(5) Å in a paddlewheel (Figure 1c), and each Zn<sup>2+</sup> ion has square-pyramidal coordination geometry in which the apical position is occupied by the pyridine N atom of isonicotinic acid. The Co–C and Co–N<sub>ax</sub> bond distances in **3** are 1.989(4) and 2.047(3) Å, respectively, and do not significantly differ from those found in **2**. The two cobaloxime units are present in a



**Figure 2.** Tetragonal channels constructed of four zinc paddlewheel clusters, when viewed along the *c* axis.

staggered conformation (the angle between planes of pyridine bound to cobalt is 70.38°). Interestingly, it has been observed<sup>15</sup> in organo-bridged as well as in ligand-bridged dicobaloximes that both cobaloxime units attained an eclipsed conformation.

The crystal structure of complex **3** revealed that the two-dimensional (2D) planar polyhedral sheet constructed by coordination of carboxylate O atoms and the pyridine N atom of isonicotinate with Zn<sup>2+</sup> ions on *b* and *c* axis extensions. Methylcobaloximes are regularly arranged on the upper and lower sides of the 2D polyhedral sheets, i.e., trans position (Figure 1S in the Supporting Information) on each paddlewheel cluster. The crystal lattice, when viewed along the *b* axis, reveals the formation of infinite one-dimensional (1D) coordination polymeric chains through the isonicotinate bridges, leading to 2D tetragonal channels constructed of four zinc paddlewheel clusters (Figure 2). Methylcobaloximes are arranged like pillars: the height of the pillar is 10.876(6) Å, and the distance between the pillars is 10.281(1) Å (Figure 2S in the Supporting Information). In the 2D sheet, the voids between pillars of four cobaloximes are occupied by the cobaloxime unit of adjacent 2D sheets. The crystal lattice is further stabilized by C–H... $\pi$  interactions (C11–H11C... $\pi_{py}$  = 3.094 Å) between dmGH methyl protons of one 2D sheet and the pyridine rings of cobalt-bound isonicotinate of adjacent 2D sheets. These sheets are switched to form a polymeric switched supramolecular assembly (Figure 3S in the Supporting Information). The distance of the two sheets is 12.479 Å.

The thermal stability of compound **3** has been studied by thermogravimetric analysis (TGA). The TGA curve (Figure 4S in the Supporting Information) shows that **3** exhibits a first weight loss of 48.60% in the temperature range 95–160 °C corresponding to the loss of a cobaloxime molecule (calculated weight loss 48.55%). A second weight loss, corresponding to decarboxylation and breakdown of the framework, is found in the temperature range 410–585 °C. This analysis shows that the thermal stability of cobaloxime is weak.

In conclusion, we have successfully synthesized and investigated the structural features of supramolecular assemblies of organocobaloxime units, which are regularly arranged in the upper and lower sides of 2D metal–organic polyhedra constructed from isonicotinic acids and Zn metal ions. Extension to



Cu<sup>2+</sup>, Co<sup>2+</sup>, Mo<sup>2+</sup>, and Cd<sup>2+</sup> paddlewheels is also under investigation. TGA shows that cobaloxime is thermally weak.

## ASSOCIATED CONTENT

**S Supporting Information.** Synthetic procedure, crystallographic data in CIF format, a table, and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

<sup>S</sup>Sadly, Prof. B. D. Gupta passed away during manuscript preparation.

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- (13) Elem anal. calcd for C<sub>15</sub>H<sub>22</sub>CoN<sub>5</sub>O<sub>6</sub> (2): C, 42.16; H, 5.19; N, 16.39. Found: C, 42.24; H, 5.12; N, 16.45. <sup>1</sup>H NMR: δ 8.7219 (d, CH, pyridine ring, 2H), 7.8848 (d, CH, pyridine ring, 2H), 2.069 (s, methyl of dmgh, 12H), 0.8318 (s, methyl, 3H). Compound 2 (C<sub>15</sub>H<sub>22</sub>CoN<sub>5</sub>O<sub>6</sub>) crystallizes in the monoclinic system, space group P2<sub>1</sub>/n with a = 8.042(3) Å, b = 33.383(10) Å, c = 13.643(3) Å, α = 90.00°, β = 92.741(5)°, γ = 90.00°, V = 3658.3 (19) Å<sup>3</sup>, M = 427.31, Z = 8, D<sub>c</sub> = 4.552 g cm<sup>-3</sup>. A Bruker X-ray diffraction CCD system with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) was used to collect 19 390 reflections (6753 unique) in the range 2.36 < θ < 25.56 at 100 K, giving a final residual value of R1 = 0.060 (all data) and wR2 = 0.1390 [I > 2σ(I)]. Elem anal. Calcd for C<sub>21</sub>H<sub>25</sub>CoN<sub>6</sub>O<sub>8</sub>Zn (3): C, 41.09; H, 4.11; N, 13.70. Found: C, 40.14; H, 4.11; N, 13.85. Compound 3 (C<sub>21</sub>H<sub>25</sub>CoN<sub>6</sub>O<sub>8</sub>Zn) crystallizes in the tetragonal system, space group I4<sub>1</sub>/acd with a = 14.540(2) Å, b = 14.540(2) Å, c = 49.916(12) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 10553 (3) Å<sup>3</sup>, M = 613.77, Z = 16, D<sub>c</sub> = 1.545 g cm<sup>-3</sup>. A Bruker X-ray diffraction CCD system with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) was used to collect 25 747 reflections (2463 unique) in the range 2.91 < θ < 28.08 at 100 K, giving a final residual value of R1 = 0.043 (all data) and wR2 = 0.1089 [I > 2σ(I)].
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