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First Study of Metal Hybrids of Boronic Acids: Second-Sphere Coordination Networks in the Structures of 4-Carboxyphenylboronic Acid with Some Transition Metals

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Metal–organic hybrids of a boronic acid (4-carboxylphenylboronic acid) with Co(II), Mn(II), and Ni(II) salts have been reported for the first time. In all of the complexes, there is no interaction between the metal and boronic acid through dative bonds. Furthermore, second-sphere coordination, along with water clusters in the form of octamers, was observed in the absence of any other additional ligands. However, in the presence of aza-donor molecules such as 1,2-bis(4-pyridyl)ethane, metal ions formed coordination polymers with those ligands, replacing the second-sphere coordination.

The design and synthesis of metal−organic hybrid structures in the form of well-defined architectures, often referred to as metal−organic frameworks (MOFs), are of current research interests in different avenues of materials chemistry.[1,2] Often, the targeted assembly is dependent on the judicious choice of the secondary building units (SBUs), which, in turn, are controlled by the functionalities present on the ligands and also by the coordination features of the metal ions.[3,4] Thus, the thrust for the novel coordination ligands is always a continuum exercise, and indeed it is quite challenging.

Boronic acids, generally represented as $R-B(OH)_2$ ($R =$ alkyl or aryl), are quite versatile for their unusual properties of bioactivity and fire retardance and as reagents for several chemical and biological transformations but have not been well explored for their solid-state structural features, except that a few examples toward the development of organic supramolecular assemblies have recently appeared.[5] Furthermore, no metal hybrids of boronic acids are known in the literature. Hence, we have considered exploring possibility of boronic acids as new potential ligands that could play a vital role in the further development of MOFs, especially taking into account the physical and chemical properties of boronic acids. However, molecules possessing only boronic acid functionality, like phenylboronic acids, failed to yield complexes with metal ions. As a result, we employed polyfunctional compounds while keeping $-B(OH)_2$ a con-

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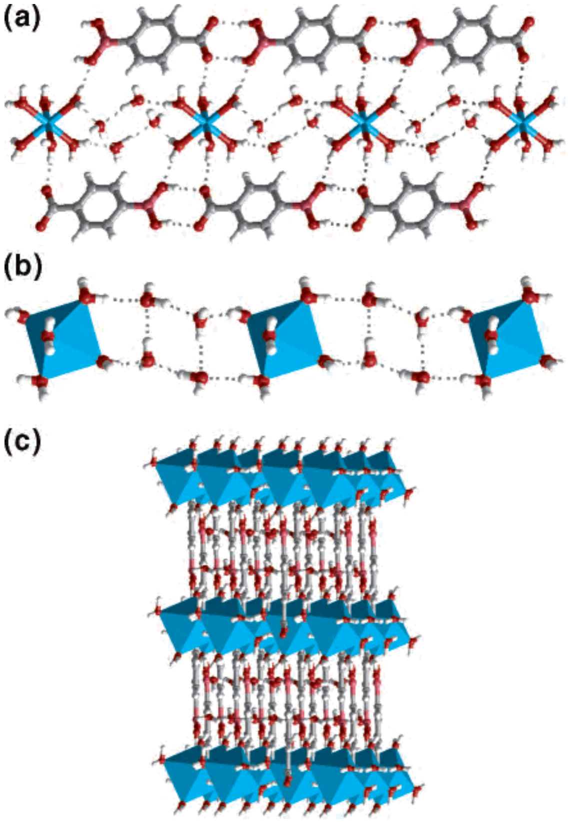

Figure 1. (a) Arrangement of the molecules in a molecular sheet in the structure of **1a**, with the $Co(H_2O)_6^{2+}$ being inserted between the tapes of **1**. (b) Interaction between the adjacent $Co(H_2O)_6^{2+}$ species through hydrogen bonds formed by uncoordinated water molecules, forming a octamer network. (c) Three-dimensional arrangement of **1** and hexahydrate Co(II) species in the crystal lattice of **1a**.

stant moiety. Thus, herein, we report, for the first time, metal hybrids of a (4-carboxyphenyl)boronic acid (**1**) with Mn(II), Co(II), and Ni(II).

The hybrids were prepared by slow evaporation of an aqueous methanol solution of the monosodium salt of **1** and corresponding metal salts, as the case may be, at ambient conditions. The single crystals, **1a**−**c**, thus obtained, corresponding to Co(II), Mn(II), and Ni(II), respectively,[6] were characterized by X-ray diffraction methods, and it was found that **1a**−**c** are indeed isomorphic as well as isostructural.

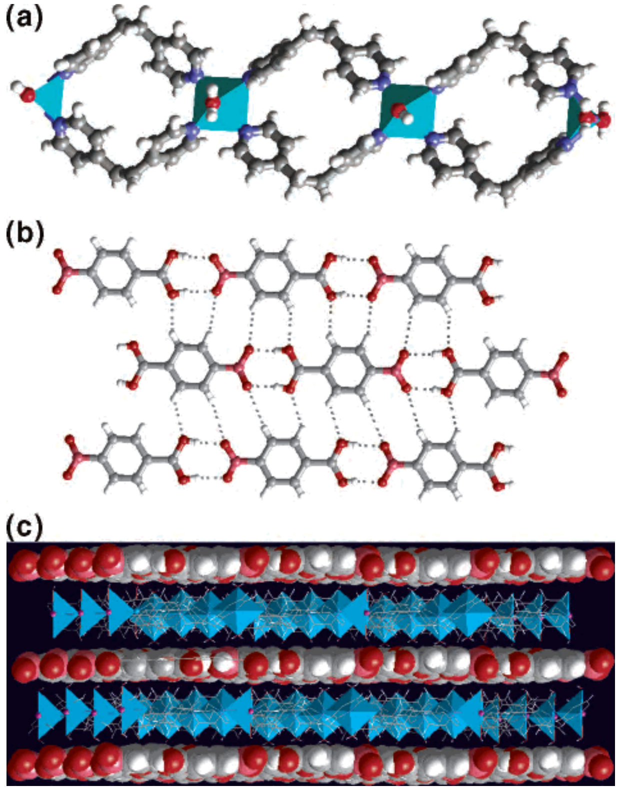

Figure 2. (a) Coordination sphere formed by Co(II) in the crystal structure of **1d** through two water molecules and four molecules of 1,2-bis(4-pyridyl)-ethane. We omitted disorder of the aza compound for the purpose of clarity. (b) Two-dimensional molecular sheet formed by the molecules of **1**. (c) Stacking of sheets formed by **1** and Co(II) coordination spheres.

Herein, we focus our discussion on the analysis of the structure of **1a**, which can be extrapolated to **1b** and **1c**. The three-dimensional structure and intermolecular interactions between the molecules within a two-dimensional arrangement are shown in Figure 1. The corresponding figures for **1b** and **1c** are given in the Supporting Information to appreciate the similarity among the structures **1a**−**c**.

Analysis of the molecular arrangement in **1a** reveals that there is no coordination bond between the acid **1** and Co(II) ions. Instead, the Co(II) ions form a hexahydrate, by coordinating to six water molecules, which were further held to the boronic acid tapes through hydrogen bonds, forming second-sphere coordination networks (see Figure 1a).[7] These units are further sandwiched between the molecular tapes of boronic acid that are formed because of the interaction between $-COO^-$ and $-B(OH)_2$ groups through $O-H\cdots O$/$O-H\cdots O^-$ hydrogen bonds ($H\cdots O$, 1.67 Å). The interaction between the boronic acid and Co(II) species is established through $O-H\cdots O$/$O-H\cdots O^-$ hydrogen bonds ($H\cdots O$, 1.91 and 1.68 Å) formed by the coordinated water molecules with $-COO^-$ and $B(OH)_2$ functionalities. Furthermore, the ad-

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[6] Crystal data for complex **1a**: $[Co(H_2O)_6]\cdot 4H_2O\cdot 2C_7H_6BO_4$, triclinic, $P\bar{1}$, $M_r = 568.95$, $a = 6.776(3)$ Å, $b = 9.592(4)$ Å, $c = 9.786(5)$ Å, $\alpha = 98.19(7)°$, $\beta = 91.66(8)°$, $\gamma = 108.35(7)°$, $V = 595.7(5)$ Å^3, $Z = 1$, $D_c = 1.586$ g cm^{-3}, $T = 133(2)$ K, $\mu = 0.804$ mm^{-1}, $2\theta_{max} = 56.56$, 6817 total reflections, R1 = 0.041 for 2699 reflections [$I > 2\sigma(I)$], wR2 = 0.099, CCDC 284916. Crystal data for complex **1b**: $[Mn(H_2O)_6]\cdot 4H_2O\cdot 2C_7H_6BO_4$, triclinic, $P\bar{1}$, $M_r = 564.96$, $a = 6.862(2)$ Å, $b = 9.705(3)$ Å, $c = 9.806(3)$ Å, $\alpha = 98.33(5)°$, $\beta = 92.21(5)°$, $\gamma = 108.22(5)°$, $V = 611.3(3)$ Å^3, $Z = 1$, $D_c = 1.535$ g cm^{-3}, $T = 133(2)$ K, $\mu = 0.621$ mm^{-1}, $2\theta_{max} = 56.70$, 7016 total reflections, R1 = 0.034 for 2776 reflections [$I > 2\sigma(I)$], wR2 = 0.088, CCDC 284917. Crystal data for complex **1c**: $[Ni(H_2O)_6]\cdot 4H_2O\cdot 2C_7H_6BO_4$, triclinic, $P\bar{1}$, $M_r = 568.73$, $a = 6.781(2)$ Å, $b = 9.572(3)$ Å, $c = 9.824(3)$ Å, $\alpha = 97.89(4)°$, $\beta = 92.05(5)°$, $\gamma = 108.55(4)°$, $V = 596.7(3)$ Å^3, $Z = 1$, $D_c = 1.583$ g cm^{-3}, $T = 133(2)$ K, $\mu = 0.897$ mm^{-1}, $2\theta_{max} = 56.38$, 3532 total reflections, R1 = 0.041 for 2557 reflections [$I > 2\sigma(I)$], wR2 = 0.098, CCDC 284918. Crystal data for complex **1d**: $[Co(H_2O)_2(C_{12}H_{12}N_2)_2]\cdot 2C_7H_6BO_4$, monoclinic, $C2/c$, $M_r = 786.23$, $a = 19.478(5)$ Å, $b = 16.672(4)$ Å, $c = 22.781(6)$ Å, $\beta = 93.23(5)°$, $V = 7386(3)$ Å^3, $Z = 8$, $D_c = 1.414$ g cm^{-3}, $T = 133(2)$ K, $\mu = 0.529$ mm^{-1}, $2\theta_{max} = 56.50$, 21 571 total reflections, R1 = 0.091 for 8363 reflections [$I > 2\sigma(I)$], wR2 = 0.238, CCDC 284919.

[7] Cambridge Structural Database (CSD, version 5.26, May 2005) analysis reveals that there are only 766 hits possessing second-sphere coordination in the metal complexes. Some of the pertinent references are as follows: (a) Loeb, S. J. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Elsevier Science: New York, 1996; Vol. 1, p 733F. (b) Dalrymple, S. A.; Parvez, M.; Shimizu, G. K. H. *Chem. Commun.* **2001**, 2672−2673. (c) Beauchamp, D. A.; Loeb, S. L. *Chem.−Eur. J.* **2002**, *8*, 5084−5088.

jacent Co(II) coordination spheres are held together by uncoordinated water molecules, which exist as tetramers forming a square network, through O−H···O hydrogen bonds (H···O, 1.75, 1.82, 1.88, and 189 Å), as shown in Figure 1b. As a result, the interaction between coordinated and uncoordinated water molecules appears as an octameric water cluster. In a three-dimensional arrangement, these sheets are stacked in such a manner that the $Co(H_2O)_6^{2+}$ clusters and boronic acid molecules are arranged alternately, as shown in Figure 1c. Thus, the structures of **1a**−**c** could be summarized as representative examples with a blend of unusual features such as second-sphere coordination, water clusters, etc., in the metal−organic assemblies. Further novelty of the metal hybrids of boronic acid molecules is well reflected in the structure of Co(II) and acid **1** along with 1,2-bis(4-pyridyl)ethane **1d**, which was synthesized to study the influence of the spacer molecules such as aza-donor compounds on the unusual features noted in **1a**−**c**.

Analysis of **1d** reveals that there is no dative bond between acid **1** and Co(II). However, unlike in **1a**−**c**, now each Co(II) forms a coordination sphere through two water molecules and four disordered molecules of 1,2-bis(4-pyridyl)ethane, yielding a coordination polymer, as shown in Figure 2a, which constitutes sheets in two dimensions. However, molecules of **1** are held together by $O-H\cdots O^-$ hydrogen bonds (H···O, 1.66 Å), forming molecular tapes as observed in **1a**−**c**, but these tapes further interact with each other through C−H···O and $C-H\cdots O^-$ hydrogen bonds (H···O, 2.51, 2.57, 2.39, and 2.76 Å), yielding molecular sheets unlike those in the earlier structures (see Figure 2b). Thus, in a three-dimensional arrangement, the two sheets formed by boronic acid molecules and metal−pyridyl moieties arrange alternately, mimicking inorganic−clay-type structures. It is interesting to note that from all of these structures of **1a**−**d**, the absence of metal−boronic acid bonding is something intriguing and requires further exploration to elucidate whether it is unique for the acid **1** or could be generalized for the wide spectrum of boronic acids.

In conclusion, metal hybrids of boronic acids have been reported for the first time, and their structure elucidation has been carried out by X-ray diffraction methods. The preliminary results show the ability of boronic acids to form metal complexes through second-sphere coordination and demonstrate their utilization as novel ligands for the creation of exotic architectures with a purpose.

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Supporting Information Available: CIF files for the structures **1a**−**d** and corresponding tables and diagrams of the complexes **1b** and **1c** are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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