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A Double Helix Is the Repeating Unit in a Luminescent Calcium 5-Amino-isophthalate Supramolecular Edifice with Water-Filled Hexagonal Channels

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Calcium 5-aminoisophthalate $\{[Ca(AIP)(OH_2)_4](H_2O)\}_\infty$ (**1**), synthesized from $Ca(OH)_2$ and H_2AIP, exists as a double helix. Hydrogen-bonding interactions between metal-bound water molecules, carboxylate oxygen, and the $-NH_2$ group result in the formation of a supramolecular assembly, where the double helices are connected to each other to form hexagonal channels filled with water molecules.

The coordination chemistry of poly(carboxylic acid)s has been a dominating theme in supramolecular chemistry in recent times because of the realization that porous solids with interesting framework structures can be obtained from them, especially when the $-COOH$ groups are appropriately oriented on the ligand to embrace more than one metal ion. Benzenedicarboxylic acids, 1,3,5-benzenetricarboxylic acid (H_3BTC), 1,2,4,5-benzenetetracarboxylic acid, and their variants have been studied as building blocks for synthesizing a variety of interesting coordination polymers, some of them with open-framework structures (MOFs).[1] 5-Aminoisophthalic acid (H_2AIP) is closely related to H_3BTC and differs from the latter by substitution of one of the three $-COOH$ groups by a $-NH_2$ group. Despite the fact that the coordination chemistry of H_3BTC has been exhaustively investigated in the past decade,[2] only a few reports have appeared in the literature on the use of H_2AIP for building supramolecular structures.[3] Unlike H_3BTC, H_2AIP is expected to form zigzag or helical 1-D chains because of the absence of the third carboxylate group, at least when metal ions that are reluctant to bind to N donors are used. On the other hand, the $-NH_2$ group can enhance the number of noncovalent interactions and form supramolecular assemblies. Hence, because of the reduced proclivity of s-block elements to bind to N donors, we have investigated in the present study the reaction of a calcium ion with H_2AIP.[4,5]

The calcium 5-aminoisophthalate complex $\{[Ca(AIP)(OH_2)_4](H_2O)\}_\infty$ (**1**) is synthesized from an equimolar reaction between $Ca(OH)_2$ and H_2AIP in water.[6] The IR spectrum shows a strong absorption in the region 3200−3500 cm^{-1}, indicating the presence of a large number of water molecules in the final product. The N−H absorption of AIP is masked by the much broader O−H absorption of water molecules. Two sharp peaks that appear at 1639 and 1608 cm^{-1} are due to the asymmetric stretching of the carboxylate anion.

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(6) Preparation of **1**. The reaction was carried out by adding $Ca(OH)_2$ (0.41 g, 5 mmol) to a hot solution of H_2AIP (1 g, 5 mmol) in water (15 mL) in a 1:1 molar ratio. The resulting colorless solution was heated for 48 h to obtain a light-brown solution. The mixture was filtered, and the filtrate was kept at 25 °C to obtain crystals of **1** in 60% yield (920 mg). See the Supporting Information for characterization data. Crystal data for **1**: $C_8H_{15}CaNO_9$, trigonal, $R\bar{3}$, $a = 23.692(2)$ Å, $c = 13.374(2)$ Å, $V = 6501.2(9)$ Å^3, $Z = 18$, $D_c = 1.422$ Mg·m^{-3}, $\mu = 0.472$ mm^{-1}, $T = 298$ K, crystal size = 0.4 × 0.3 × 0.2 mm^3, θ range = 1.82−24.98°, unique reflections = 2542, parameters = 172, GOF = 1.060, R1 $[I > 2\sigma(I)] = 0.0558$, wR2 $[I >\_2\sigma(I)] = 0.1752$. Crystal data for **1′**: $C_8H_{15.67}CaNO_{9.33}$, trigonal, $R\bar{3}$, $a = 23.7031(5)$ Å, $c = 13.2750(3)$ Å, $V = 6459.1(2)$ Å^3, $Z = 18$, $D_c = 1.459$ Mg·m^{-3}, $\mu = 0.478$ mm^{-1}, $T = 151$ K, crystal size = 0.1 × 0.09 × 0.08 mm^3, θ range = 2.98−30.12°, unique reflections = 4223, parameters = 179, GOF = 1.157, R1 $[I > 2\sigma(I)] = 0.0842$, wR2 $[I > 2\sigma(I)] = 0.2605$. The structure was solved by direct methods (*SHELXS-96*[11a]) and refined using *SHELXL-96*.[11b] See the Supporting Information (CIF) for other details.

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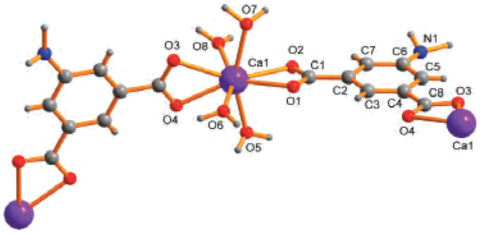

Figure 1. Section of polymeric chain of **1**. Selected bond distances (Å): Ca1−O1 2.473(3), Ca1−O2 2.510(3), Ca1−O3 2.530(3), Ca1−O4 2.459(3), Ca1−O5 2.371(3), Ca1−O6 2.391(4), Ca1−O7 2.459(4), Ca1−O8 2.426(3). Bond angles (deg): O1−Ca1−O2 52.3(1), O4−Ca1−O3 52.1(1), O5−Ca1−O6 89.1(1), O5−Ca1−O8 101.1(1), O5−Ca1−O4 74.2(1), O6−Ca1−O4 80.4(1), O8−Ca1−O4 81.4(1), O5−Ca1−O7 157.2(1), O6−Ca1−O8 155.9(1), O2−Ca1−O3 150.6(1).

The symmetric stretching vibration appears at 1446 cm^{-1}. An aqueous solution of **1** shows a single absorption in the UV−visible spectrum at 315 nm ($\epsilon = 2329$ L·mol^{-1}·cm^{-1}). For comparison, pure H_2AIP also absorbs at the same wavelength but with a low intensity ($\epsilon = 334$ L·mol^{-1}·cm^{-1}).

Compound **1** crystallizes in the $R\bar{3}$ space group.[6] The calcium ion is octacoordinated, as found in several calcium complexes synthesized in water.[5,7] Two chelating carboxylate units and four terminal water molecules surround the metal ion in a severely distorted square-antiprism geometry (Figure 1). Because of the hardness of the Ca^{2+} ion, the $-NH_2$ group does not coordinate to the metal ion. The observed Ca−O distances vary over a range [2.371(3)−2.530(3) Å] but are comparable to similar distances in other calcium carboxylate polymeric complexes.[5,7,8] The O−Ca−O bond angles fall in a very wide range [52.1(1)−157.2(1)°].

Each carboxylate moiety of AIP functions as a chelating ligand. Because the two COO units of each AIP chelate to two different metal ions, a polymeric chain is formed. As a result of the angular relationship (120°) of the two carboxylate groups on AIP and the irregular coordination geometry around calcium, the polymeric chain is helical. Interestingly, two such helical chains form a double helix, as shown in Figure 2. Resembling DNA, the double helix is held together by extensive interstrand hydrogen bonding, where two of the coordinated water molecules on each calcium form hydrogen bonds with the carboxylate oxygen atoms of the other strand (O5−H5A···O1 and O6−H6B···O4). Thus, every metal and every AIP ligand along the helical chain contribute to two strong hydrogen bonds, resulting in a very high hydrogen-bond density along the double helix (Figure 2).

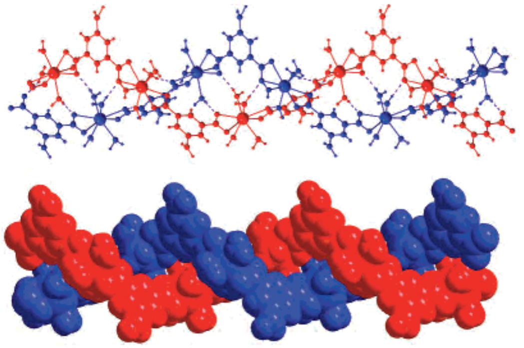

Figure 2. Double helix held together by O−H···O hydrogen bonds (top). Space-filling model (bottom).

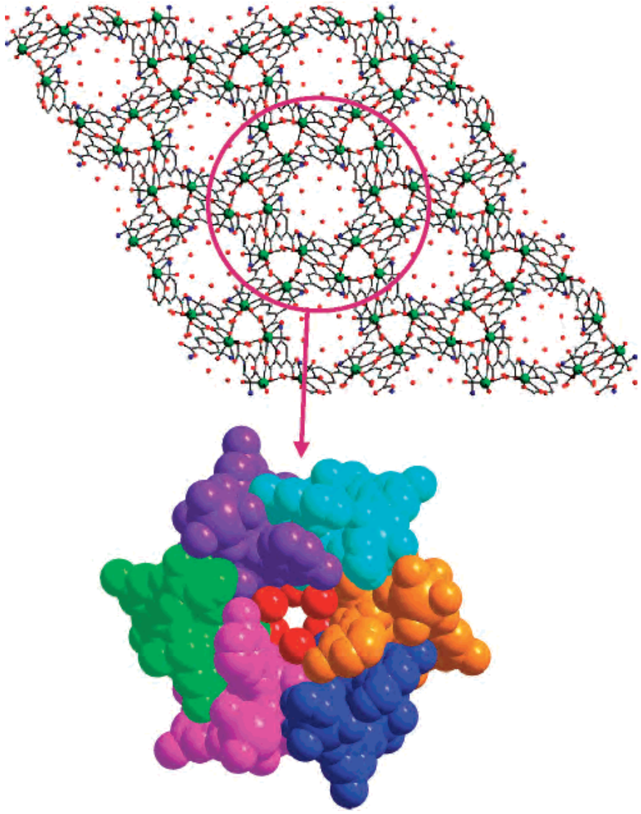

Figure 3. Supramolecular assembly in **1** (down the *c* axis). The double helices are arranged about the −3 axis to result in a hexagonal pore filled with water molecules. In the space-filling model, each color represents a double helix.

A closer look at the structure of **1** reveals more interesting supramolecular organization beyond the formation of a double helix. For example, the double helix shown in Figure 2 does not exist as an individual entity but finds three more double helices of the same kind as its neighbors (Figure 3). Because each double helix is surrounded by three more double helices, with a 120° relationship with respect to each other, a hexagonal organization of numerous double helices results in the crystal (Figure 3). The formation of this supramolecular assembly is amply aided by the presence of the $-NH_2$ group of the AIP on the surface of each double helix and the water molecules (O7 and O8), which are not involved in stabilizing the double helix. Thus, the hydrogen of O6, bound to the calcium ion, from one double helix forms an inter-double helix hydrogen bond with the N1 of an adjacent double helix (O6−H6A···N1). Similar inter-double helix hydrogen bonds are also formed between the coordinated water molecules (O7−H7A···O5) and between the coordinated water molecule and carboxylate oxygens (O5−H5B···O3 and O8−H8A···O2) (see the Supporting Information).

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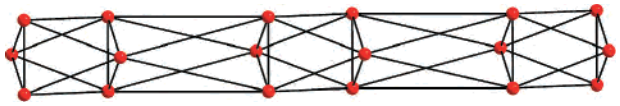

Figure 4. Water O9 present inside the hexagonal channel in **1** (the lines do not denote true hydrogen bonds) viewed perpendicular to the *c* axis. In **1′**, O10 lies on the center of each of the triangular units O9.

Another significant aspect of the supramolecular aggregation in **1** is the entrapment of water molecules in the hexagonal channel (Figure 4). These water molecules form a tubular structure.[9] Quite surprisingly, there are no hydrogen-bonding interactions between the water molecules in the channel. The closest O···O separation in **1** within the water pipe (3.996 Å) corresponds to the distance between the oxygen atoms that are related by a 3-fold axis.

Intrigued by the large isotropic thermal parameter for O9 as well as the lack of hydrogen bonds between the channel and coordinated water molecules, we redetermined the molecular structure of **1** at lower temperature with a fresh crystal using faster scan rates.[6] The results obtained are significant not only in terms of an improved thermal parameter for O9 but also by the appearance of an additional water molecule (O10) on the -3 axis with a site occupancy of 0.33, thus yielding an empirical formula of $\{[Ca(AIP)(OH_2)_4](H_2O)_{1.33}\}_\infty$ (**1′**) for the redetermined structure. While O9 is arranged in the form of triangles, O10 lies on the -3 axis in the center of each O9 triangle. The fact that both O9 and O10 still have fairly large U_{33} values and that there are fewer hydrogen bonds between channel water and the helical chains indicates free movement of the water molecules along the channel.

The loose binding of the water has further been investigated with the aid of thermogravimetric and elemental analyses. The first water molecule is lost even before the vacuum-dried sample of **1** is loaded into an elemental analyzer or thermogravimetric balance. At this point, the as-synthesized and vacuum-dried samples have the same powder X-ray diffraction (PXRD) pattern. However, when the sample is heated up to 200 °C, the coordinated water molecules are lost and the sample at this point has a different PXRD pattern, showing the amorphous nature of the sample. The onset of loss of water from the structure of **1** starts just above room temperature (40 °C) and continues until about 200 °C, where all of the five water molecules per formula unit have been lost.

It has been reported that the Ca(bdc) complex (bdc = 1,3-benzenedicarboxylate) forms a 1-D polymer resembling a right-handed triple helix.[8] However, the postulated triple helix essentially arises out of a single coordination polymer, while the double helix in **1** is made up of two separate coordination polymers that are hydrogen-bonded to each other. Likewise, compound **1** differs considerably from the $Ca_3(btc)_2$ complex, which forms a 2-D sheet structure as a result of the binding of three separate calcium ions by the three different carboxylate groups of the btc ligand.[2b] Thus, it can be concluded that the observed unique supramolecular architecture in **1** is driven by the presence of the $-NH_2$ group on AIP compared to the calcium complexes formed by bdc and btc ligands.[2b,8]

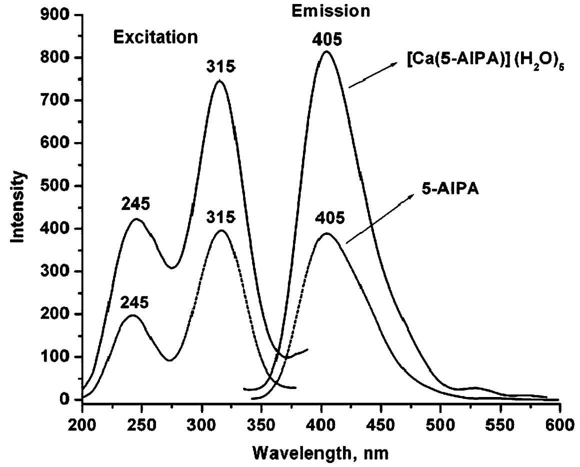

Figure 5. Excitation and emission spectra of H_2AIP and **1** showing a significant fluorescence enhancement in **1**.

When **1** is excited at 312 nm at room temperature in solution, a strong blue fluorescence is observed at 405 nm. A similar emission is also observed for the free ligand albeit with lower intensity (Figure 5). The increase in the fluorescence intensity in **1**, both in solution and in the solid state, is attributable to the metal ion binding to AIP, resulting in a more rigid structure (of the ligand as well as the polymer formation after complexation). Similar fluorescence enhancement has been observed for calcium carboxylate coordination polymers incorporating 4-cyanobenzoic acid and 1,3-benzenedicarboxylic acid.[8]

In summary, the synthesis of **1** assumes importance in view of the current interest in the formation of helical supramolecular assemblies with unusual architectures by coordinating simple organic molecules with metal ions.[10] We are currently exploring the possibility of synthesizing Ca(AIP) complexes with other structure-directing ligands such as *N*,*N′*-dimethylformamide, dimethyl sulfoxide, piperazine, etc., in place of water.

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Supporting Information Available: Details of X-ray diffraction studies (CIF) and the complete spectroscopic characterization (PDF) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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