Steric Effect of a Capping Ligand on the Formation of Supramolecular Coordination Networks of Ni(II): Solid-State Entrapment of Cyclic Water Dimer

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ABSTRACT: Supramolecular dimer of water is the simplest of the small water clusters [(H2O)n, n = 2–10]. During the course of our work on supramolecular coordination networks of three-component systems (divalent metal ion, tridentate capping ligand, and ditopic carboxylate linker), a cyclic water dimer is found to be entrapped in the network of [Ni2(6-Mebpta)(adc)2](H2O) (1) (6-Mebpta = 2-methyl-N-(6-methylpyridin-2-yl)methyl)-N-(pyridin-2-ylmethyl)propan-2-amine and adc = acetylenedicarboxylate). Based on the single-crystal structure of 1, the water dimer plays an important role in connecting the bis(adc) bridged dinickel synthons to form a one-dimensional (1D) supramolecular network. To emphasize the role of 6-Mebpta in the judicious choice of components for 1, one simple modification to it by having another methyl group in the second pendant pyridyl group to make 6,6′-Me2bpta (2-methyl-N,N-bis(6-methylpyridin-2-yl)methyl)propan-2-amine did not allow the formation of any water cluster in [Ni(6,6′-Me2bpta)(adc)(H2O)]H2O (2), where a different coordination environment around Ni(II) is also observed. Further quantification of the difference in supramolecular interactions observed in 1 and 2 has been assessed by Hirshfeld surface analysis. Both 1 and 2 are obtained in good yields at room temperature (methanol as solvent) and are further characterized by elemental analysis, Fourier transform infrared (FTIR) and Raman spectroscopy, powder X-ray diffraction, and thermogravimetric analysis.

INTRODUCTION

For the importance in both chemical and biological processes, the water–water interaction in water aggregates of varying degree has been the subject of both experimental and theoretical research in the past few decades.1–15 These efforts have been primarily targeted to elucidate the structure–property correlations in such systems. In the biological systems, water maintains the stability and proper functioning of enzymes and proteins.16–19 With the help of theoretical calculations, in some of these water clusters, the most stable conformations in the gas phase with distinct nuclearity as well as properties of bulk water have been obtained.20 Inspired by the biological systems, mechanistic details of chemical processes such as catalysis,17,21 sensing,22 ion exchange,23 etc. are understood via several intermolecular interactions among the species involved.

In the past few decades, a large number of supramolecular coordination networks (SCNs) have been designed and developed using various metal centers and nitrogen- and oxygen-containing ligands/linkers. Some of these SCNs are two-dimensional (2D) or three-dimensional (3D) coordination architectures formed by the association of one-dimensional (1D) or 2D SCNs through strong and/or weak hydrogen bonds, π-π stacking of aromatic moieties, C–H···O interactions, etc. These SCNs provide suitable environments for encapsulation/entrapment of water clusters of different sizes (discrete and polymeric)24,25 through moderate to strong hydrogen-bonding interactions. In the literature, different types of water clusters like cyclic, fused cyclic, branched, and chain are reported.11,26–29 Among the small water clusters [(H2O)n, n = 2–10], supramolecular dimer of water is the simplest. Interestingly, three possible structures for dimer of water have been reported in the literature (Scheme S1).30–33 A Cambridge Structural Database (CSD) search can result in several thousands of examples where the cyclic dimer structure is a part of larger clusters, such as the one reported recently;34 however, the difficulty in performing an autosearch to find the cyclic dimer structure, which only connects the hosts, is to be considered. Both open-chain19 and cyclic structures33 were observed in SCNs, while the bifurcated structure was identified.
in the gas phase.\textsuperscript{30,31} Therefore, the encapsulation/entrainment of cyclic water dimer is of great interest at any time.

For our interests in unmasking unusual water clusters and their further role in stabilizing SCN\textsubscript{s}, we have explored various three-component systems (divalent metal ions, di- and tricarboxylates, and multidentate polypyridyl ligands).\textsuperscript{28,35} In particular, our work indicated that a proper combination of these components was needed to yield such water clusters, one of the fascinating water clusters being the cyclic quasi-planar hexamer of water.\textsuperscript{39} Our success with the tridentate capping ligand bpta (where bpta = N\textsubscript{2}N'-bis(2-pyridylmethyl)-1-tert-butylamine) has encouraged us to go beyond the induction of reaction parameters on the products based on the demonstration of a para-substituent effect in the successful trapping of octameric water cluster in the solid state by the 26-membered unclosed pentamide cryptands.\textsuperscript{36} Thus, we have made a hexamer of water in the gas phase.\textsuperscript{30,31} Therefore, the encapsulation/entrainment of cyclic water dimer is of great interest at any time.

RESULTS AND DISCUSSION

Synthesis and General Characterization. For this work, the new ligands 6-Mebpta and 6,6′-Me\textsubscript{2}bpta are the key to obtaining diverse supramolecular networks (Scheme 1). 6-Mebpta has been synthesized by a condensation reaction between an aldehyde and an amine, followed by reduction of the resultant imine using NaBH\textsubscript{4}. Furthermore, a substitution reaction was carried out with the reduced Schiff base and picolylchloride hydrochloride salt in the presence of a base. On the other hand, 6,6′-Me\textsubscript{2}bpta has been synthesized in one step using an aldehyde and an amine in the presence of sodium triacetoxyborohydride in dry dichloroethane (DCE) (Figures S1–S3). Both 1 and 2 were synthesized under ambient conditions using the respective ligand, H\textsubscript{2}adc, and Ni(OAc)\textsubscript{2}·4H\textsubscript{2}O in methanol having a 1:1:1 ratio (Scheme 2). However, the formulas of 1 and 2 differ due to the change in the tridentate ligand. This shows the influence of an additional methyl group in 6,6′-Me\textsubscript{2}bpta.

Description of Structures. Crystals of 1 and 2 suitable for single-crystal X-ray diffraction were grown from the direct evaporation of an acetonitrile–water solution of the respective compounds.

Compound 1 crystallizes in the monoclinic P\textsubscript{2\textsubscript{1}}/n space group (Table 1). The dinuclear unit consisting of two Ni(II) centers bridged by two adc groups, each of which binds in both monodentate and bidentate manner, sits on an inversion center. The geometry around each Ni(II) center is distorted octahedral and is surrounded by three nitrogens of the 6-Mebpta ligand with Ni–N\textsubscript{py} (2.048 and 2.080 Å) and Ni–N\textsubscript{akyl} (2.132 Å) bonds, two oxygens of one adc (unsymmetrical chelated having bond distances of 2.106 and 2.212 Å), and one oxygen of the other adc (monodentate having a bond distance of 2.052 Å) molecule. These parameters are in the range of those found in mono- and bis(adc) bridged dinuclear and polynuclear compounds.\textsuperscript{28,29,33,37,38} The selected bond distances and angles are listed in Tables S1 and S2. A 14-membered ring with dimensions 7.952 Å × 3.277 Å (Figure 2) is formed by two Ni(II) centers, four oxygen atoms, and eight carbon atoms (from both adc). To the best of our knowledge, it is the first example with a bis(adc)Ni\textsubscript{2}(II) core. There are two lattice water molecules in 1, which are involved in the formation of a linear supramolecular assembly of the dinuclear synthons. These two lattice water molecules form a doubly hydrogen-bonded cyclic water dimer, which as a bridge between two bis(adc)Ni\textsubscript{2}(II) units, as shown in Figure 2. These two water molecules OS and OS′ in 1 show doubly

![Scheme 1. Synthesis of 6-Mebpta and 6,6′-Me\textsubscript{2}bpta](image-url)
hydrogen bonding with each other to form a cyclic water dimer with an O···O distance of 3.248 Å and O···H···O of 139°. On the other hand, the distance between O4 (uncoordinated oxygen) and O5 is 2.746 Å with a O···H···O angle of 146°. A relevant example with an O···O distance of 2.93 Å was reported, but the water dimer plays no further role in connecting other entities in the supramolecular network. Thus, the water dimer with a double hydrogen bond that is entrapped between the dinuclear units of 1 is noteworthy. All hydrogen-bond parameters are listed in Table 2. The overall packing of 1 in different directions is shown in Figure S4.

Similar to 1, compound 2 also crystallizes in the monoclinic P2₁/n space group (Table 1). As shown in Figure 3, it consists of a mononuclear unit, in which the Ni(II) center has an octahedral geometry and is surrounded by three nitrogens of the 6,6'-Me2bpta ligand (bond distances: Ni−Npy (2.0834 Å) and Ni−Nalkyl (2.1109 Å)), two oxygens of the adc (unsymmetrical chelated having bond distances of 2.1675 and 2.1216 Å), and one coordinated water molecule (bond distance: 2.0834 Å). The selected bond distances and angles are listed in Tables S3 and S4. Unlike 1, one end of the adc binds to the Ni(II) center in a chelated manner, while the other end is free, though it is deprotonated (Figure 3). Two units are connected via hydrogen bonding between the coordinated water molecule: one lattice water molecule and two oxygen atoms of the uncoordinated adc to form a tetragonal motif (R₁²(8)), resulting in the formation of a zigzag-shaped supramolecular assembly, as shown in Figure 3. All hydrogen-bond parameters are listed in Table 2. The overall packing of 2 in different directions is shown in Figure S5.

In view of the structural differences in 1 and 2, it is clear that a simple structural modification in the tridentate capping ligand (from 6-Mepta to 6,6'-Me₂bpta) has affected the binding mode of the rigid adc to the metal center and thereby the overall supramolecular assembly. Such a small structural modification, however, has a decisive impact on the formation of the transient cyclic dimer of water cluster. Our observation is in accordance with many other reports where a subtle change in the reaction conditions or a structural variation in one of the components of the hosts, particularly the classical example of the formation (or absence) of water octamer where it was demonstrated that the presence of a para-substituent in the lariat arm of 26-membered unclosed pentamidine cryptands, was crucial. This further demonstrates that even a small structural perturbation of a component in a host on the trapping of water clusters requires a systematic study for our understanding.

**Phase Purity and Thermal Behavior.** For confirming whether the single crystals and the bulk material are the same, powder X-ray diffraction (PXRD) patterns were recorded for 1 and 2 at room temperature. As shown in Figure S6, the experimental and simulated (from the single-crystal data) patterns are similar. It also confirms the phase purity of the bulk sample.

For understanding their thermal stability, thermogravimetric analysis of the single-phase polycrystalline samples of 1 and 2 was conducted between 25 and 500 °C under a dinitrogen atmosphere (Figure S7). From the multistep weight loss process of 1, it is clearly evident that the lattice water molecules are lost first, followed by the loss of coordinated water molecules, H₂adc, and then 6-Mepta. A loss of 7.56% (calcd: 6.61%) in the range of 25–100 °C corresponds to four lattice water molecules. The continuous weight loss of 1 between 180 and 350 °C corresponds to the removal of one 6-Mepta and one acetylene dicarboxylic acid molecule (found: 43.3%; calcd: 45.44%). Compound 2 exhibits the first weight loss of 4.55%, corresponding to two water molecules (calcd: 5.01%). The second weight loss of 62.33% between 170 and 350 °C corresponds to the removal of the 6,6'-Me₂bpta molecule (calcd: 62.90%). The third weight loss of 12.84% between 350 and 430 °C corresponds to one carbon dioxide molecule from the carboxylate group of adc (calcd: 13.3%).

**Table 1. Crystallographic Data and Structure Refinement Parameters for 1 and 2**

| Compound | 1 | 2 |
|----------|---|---|
| CCDC no. | 1873839 | 1873840 |
| Chemical formula | C₂₄H₃₆N₄Ni₂O₁₀ | C₂₂H₂₉N₃NiO₆ |
| Formula weight (g/mol) | 827.01 | 550.26 |
| Temperature (K) | 100(2) | 100(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic |
| Space group | P2₁/n | P2₁/n |
| a (Å) | 10.1941(14) | 10.2641(8) |
| b (Å) | 15.966(2) | 16.8498(13) |
| c (Å) | 12.4434(18) | 13.0024(10) |
| α (deg) | 90 | 90 |
| β (deg) | 103.751(6) | 98.545(3) |
| γ (deg) | 90 | 90 |
| V (Å³) | 2030.6(5) | 2223.8(3) |
| D (g/cm³) | 1.499 | 1.464 |
| M (mm⁻¹) | 0.994 | 0.916 |
| Fl(000) | 960 | 1032 |
| Fl(deg) range for data coll. | 2.072–24.849 | 1.992–25.106 |
| Independent reflections | 13001 | 18501 |
| Reflections with Fl(001) > 2σ(Fl) | 3475 | 3952 |
| R₁ and R₃ (all data) | 0.112 | 0.0242 |
| No. of parameters refined | 291 | 306 |
| GoF on F² | 0.982 | 1.047 |
| Fl(001) | 0.0609/0.1024 | 0.0249/0.0618 |
| Fl(Fl(001)) | 0.1359/0.1655 | 0.0292/0.0406 |
| Largest diff. peak and hole (e/Å³) | 0.445 and -0.463 | 0.33 and -0.26 |

**Scheme 2. Synthesis of 1 and 2**

[Diagram showing the synthesis of 1 and 2 with chemical formulas and reaction conditions]
Spectroscopic Characterization. Various functional groups and their modes of binding to the divalent metal ions in the coordination architectures can be well deduced from the Fourier transform infrared (FTIR) stretching frequencies. In these coordination architectures, the binding mode of carboxylates plays a very important role in deciding the overall structure of the framework. The carboxylate binding to the metal centers in the architectures can be well predicted from the difference between their asymmetric ($\nu_1$) and symmetric ($\nu_2$) stretching frequencies (the $\Delta\nu$ value). When the $\Delta\nu$ value is greater than 210 cm$^{-1}$, a monodentate binding mode is observed, whereas a value below 200 cm$^{-1}$ suggests a bidentate binding mode.\(^\text{39}\) The solid-state FTIR spectrum of 1 (Figure S8) shows one broad peak centered at 3408 cm$^{-1}$ corresponding to the presence of a lattice water molecules. It also shows a series of peaks between 1621 and 1310 cm$^{-1}$. While some of these features are due to the 6-Mebpta ligand, there are two sets of peaks at 1621 and 1351 cm$^{-1}$, and at 1596 and 1439 cm$^{-1}$ due to the symmetric and symmetric stretching modes of the carboxylate groups of adc respectively, for both

| D–H···A | r(D–H) (Å) | r(H–A) (Å) | r(D–A) (Å) | D–H–A (deg) | symmetry |
|---------|------------|------------|------------|-------------|----------|
| (1)     |            |            |            |             |          |
| O(5)–H(5A)···O(4) | 0.86       | 1.89       | 2.7462     | 175         | $-x, -y, 1 - z$ |
| O(5)–H(5B)···O(5) | 0.85       | 2.56       | 3.2487     | 139         | $-x, -y, 1 - z$ |
| C(2)–H(2C)···O(1) | 0.98       | 2.44       | 3.2923     | 146         |          |
| C(3)–H(3)···O(3)  | 0.95       | 2.55       | 3.2926     | 136         | $x, y, 1 - z$ |
| C(7)–H(7A)···O(5) | 0.99       | 2.34       | 3.3156     | 167         | $1/2 + x, 1/2 - y, -1/2 + z$ |
| C(9)–H(9B)···O(2) | 0.99       | 2.44       | 3.3068     | 148         |          |
| C(11)–H(11C)···O(2) | 0.98      | 2.53       | 3.3933     | 146         |          |
| C(16)–H(16)···O(4) | 0.95       | 2.41       | 3.2165     | 142         | $-x, -y, 1 - z$ |
| (2)     |            |            |            |             |          |
| O(5)–H(5A)···O(2) | 0.84       | 1.84       | 2.6788     | 173         | $3/2 - x, 1/2 + y, 1/2 - z$ |
| O(5)–H(5B)···O(6) | 0.84       | 2.05       | 2.863      | 164         | $3/2 - x, 1/2 + y, 1/2 - z$ |
| O(6)–H(6A)···O(1) | 0.85       | 1.86       | 2.6908     | 168         | $x, 1 + y, z$ |
| C(6)–H(6)···O(2) | 0.93       | 2.57       | 3.1666     | 122         | $-1 + x, y, z$ |
| C(10)–H(10C)···O(4) | 0.96       | 2.3       | 3.1276     | 145         |          |
| C(13)–H(13A)···O(5) | 0.96       | 2.4       | 3.2268     | 144         |          |
| C(14)–H(14A)···O(5) | 0.96       | 2.47       | 3.2851     | 143         |          |
| C(16)–H(16A)···O(1) | 0.97       | 2.58       | 3.1505     | 118         | $1/2 - x, 1/2 + y, 1/2 - z$ |

*Numbers in parenthesis are the estimated standard deviations in the last significant digits, D = donor, and A = acceptor.

Figure 2. (Top) ORTEP diagram of 1 with the ellipsoids represented at 30% probability level (hydrogens are excluded for clarity). (Bottom) Formation of 1D ladder-type supramolecular assembly in 1 and the structure of a cyclic dimer of water cluster.

Table 2. Hydrogen Bonding Parameters for 1 and 2 with Symmetry Codes$^a$

is greater than 210 cm$^{-1}$, a monodentate binding mode is observed, whereas a value below 200 cm$^{-1}$ suggests a bidentate binding mode.\(^\text{39}\) The solid-state FTIR spectrum of 1 (Figure S8) shows one broad peak centered at 3408 cm$^{-1}$ corresponding to the presence of a lattice water molecules. It also shows a series of peaks between 1621 and 1310 cm$^{-1}$. While some of these features are due to the 6-Mebpta ligand, there are two sets of peaks at 1621 and 1351 cm$^{-1}$, and at 1596 and 1439 cm$^{-1}$ due to the symmetric and symmetric stretching modes of the carboxylate groups of adc respectively, for both
chelated and monodentate binding modes of adc, as found in its crystal structure. For 2, the two broad peaks at 3428 and 3221 cm$^{-1}$ show two types of water molecules, i.e., lattice and coordinated, and the peak at 1704 cm$^{-1}$ corresponds to the free carboxylate group of adc$^{2-}$ (Figure S8). On the other hand, one set of peaks at 1604 and 1339 cm$^{-1}$ was observed due to the asymmetric and symmetric stretching modes of the chelated carboxylate groups of adc, respectively.

The Raman spectrum of 1 (Figure S9) shows a peak at 2203 cm$^{-1}$ for the C–C triple bond, two peaks (1575 and 1399 cm$^{-1}$) for the carboxylate groups of adc, and the other features for the bpta ligand, corroborating with its FTIR spectrum. In 2, the peak for the C–C triple bond appears at 2233 cm$^{-1}$. The
observed values for the C−C triple bond in 1 and 2 are very close to those (2239 and 2220 cm⁻¹) found in other Ni(II)—adcb complexes. Results from FTIR and Raman spectroscopy analyses show a good agreement with the X-ray structures of 1 and 2.

Hirshfeld Surface Analysis. The intermolecular interaction between two molecules cannot be readily apparent through the examination of a single-crystal structure. The pattern of intermolecular interactions in the solid-state structures of 1 and 2 prompted us to explore and quantify the contribution of noncovalent interactions in the crystal packing. Visualization and exploration of intermolecular close contacts of a structure is invaluable. This can be achieved using Hirshfeld surface analysis. Using CrystalExplorer 3.1 software, we have generated these surfaces based on their crystal structures; bond lengths to hydrogen atoms were set to standard values. Various Hirshfeld surfaces have been mapped with respect to \( d_{\text{norm}} \) shape index, curvedness, and the 2D fingerprint plots. The value of \( d_{\text{norm}} \) can be negative or positive depending on the intermolecular contacts. The negative value is obtained when the sum of \( d_i \) and \( d_e \) is less than the sum of the relevant van der Waals radii. This represents the closest contact and is shown in red color, while blue color is due to the positive value of \( d_{\text{norm}} \), which reflects longer contacts than the sum of van der Waals radii. Along with this, the white color represents intermolecular contacts which are close to van der Waals radii. The \( d_{\text{norm}} \) surface of 1 is shown in Figure 4 for both water and metal complex separately. The \( d_{\text{norm}} \) surface is calculated in the range of \(-1.0 \) to \( 1.0 \) Å, in which red color represents the atoms of the \( \pi \)-stacked molecule above them, while blue color indicates the ring atom of the molecule inside the surface. Furthermore, the shape of the surface area of the molecule has been studied by calculating the curvedness of the molecule in which the sharp curvature shows a high value and the flat area shows a low value of curvedness (Figure 5). This curvedness has been calculated to be in the range of \(-4.0 \) to \( 0.4 \) Å. These graphs show how one molecule interacts with another molecule through various weak interactions like \( \pi \cdots \pi \) stacking, hydrogen bonding, etc. The intermolecular interactions present in the structure are also visible on the two-dimensional fingerprint plot, which can be segregated to quantify the individual contributions of each intermolecular interaction involved in the molecular structure. Complementary regions are visible in the fingerprint plots, where one molecule acts as a donor (\( d_e > d_i \)) and the other acts as an acceptor (\( d_e < d_i \)). In 1, the maximum contribution is due to the H−H contacts, which is 50.5%, while due to C−H, O−H, and N−H contacts, the contributions are 24.7, 22.1, and 1%, respectively. The remaining 1.7% contribution in 1 is due to other contacts.

For comparison, a similar analysis was performed with 2 (Figure S10). From the fingerprint plots (Figures S11 and S12) of 2 without a water molecule, it was found that the
maximum contribution is due to the H···H contacts (45.1%), while C···H, H···O, and H···N contributions are 24.9, 28.3, and 0.1% respectively. The remaining 1.5% is due to other contacts in 2 (Figure 6). Furthermore, the fingerprint analysis for 2 without a water molecule and 2 shows that the maximum contribution is due to the H···H contacts, which is around 47%, while C···H, O···H, and N···H contributions are 23.7, 27.6, and 0.1%, respectively. The remaining 1.5% is due to other contacts in 2.

From the surface analysis of 1, $d_{\text{norm}}$ and surface studies indicate that two bis(adc)Ni$_2$(II) units form a cavity between them. This cavity can easily accommodate two water molecules. As shown in Figure 4a, the red surface in $d_{\text{norm}}$ is toward the hydrogen atom of the lattice water molecule, indicating the closest distance of interaction. Furthermore, the same surface in the water molecules also shows a red region toward the carboxylate of the metal complex. Based on the above two results, we observe a good correlation in the combined surface of the complex and water molecule. Furthermore, the same analysis has also been confirmed by shape index as well as curvedness.

In case of 2, there is no formation of a closed cavity because of the arrangement of supramolecular assembly of the mononuclear Ni(II) synthon, although a half cavity is formed which is open from one side and does not have any molecule to interact in that side. The red surface in the $d_{\text{norm}}$ of metal complex is toward the hydrogen of water molecule (Figure S10), while there is nothing with respect to the other hydrogen atom of the water molecule. On the other hand, the oxygen atom of the lattice water shows a strong interaction with the hydrogen atom of the coordinated water molecule. Furthermore, the same analysis has also been confirmed by shape index as well as curvedness, which show a good correlation for stronger interactions.

## CONCLUSIONS

In summary, we explored a chemical modification in the pyridyl moiety of the bpta ligand to make two new ligands, 6-Mebpta and 6,6'-Me$_2$bpta, to demonstrate the steric effect on the self-assembled supramolecular networks for the Ni(II)–adc system (adc = acetylene dicarboxylate), namely, [Ni$_2$(6-Mebpta)$_2$(adc)$_2$]·2H$_2$O (1) and [Ni(6,6'-Me$_2$bpta)(adc)]·(H$_2$O)·H$_2$O (2). For an extra methyl group in the ligand (from 6-Mebpta to 6,6'-Me$_2$bpta), a tremendous change in the crystal structure was observed in 2. The difference in supramolecular interactions in 1 and 2 was examined through the Hirshfeld surface analysis. This structural difference was critical for the entrapment of a cyclic doubly hydrogen-bonded water dimer only in 1. The water dimer played an important role as a double hydrogen-bond donor in connecting the bis(adc) bridged dinickel synthon to form the 1D supramolecular network. This work provides a way to undertake further work utilizing chemical modifications in the linker/ligand systems used for the formation of supramolecular coordination networks with a focus on entrapment of unusual water clusters.

## EXPERIMENTAL SECTION

**Materials and Methods.** All chemicals and solvents used for synthesis were obtained from commercial sources and were used as received. All reactions were carried out under aerobic conditions.

**Physical Measurements.** The $^1$H NMR spectra of all ligands were obtained in CDCl$_3$ solution at 25 °C on a Bruker ARX-400 spectrometer; chemical shifts are reported relative to the residual solvent signals. Elemental analysis (C, H, N) was carried out using a Mettler CHNS analyzer, thermogravimetric analysis was carried out from 25 to 500 °C (at a heating rate of 10 °C/min) under a dinitrogen atmosphere on a Mettler 851 E, and electrospray ionization (ESI) mass spectrometry was performed using a Thermo Scientific LTQ XL LC-MS instrument for the 50–2000 amu range. IR spectra were measured in the 4000–400 cm$^{-1}$ range on a PerkinElmer Spectrum I spectrometer with samples prepared as KBr pellets. Raman spectra were recorded on a Renishaw Invia Raman microscope equipped with a 785 nm high-power near-infrared laser working at 300 mW power and a Renishaw CCD detector. Analysis of the Raman spectra was performed in reflection mode on powder samples placed on the sample stage and aligned in optical path using a camera, with 10–50% laser power and using 20–50× optics in the range of 500–4000 cm$^{-1}$. Powder data were recorded on a Rigaku Ultima IV diffractometer equipped with a 3 kW sealed-tube Cu Kα X-ray radiation (generator power settings: 40 kV and 40 mA) and a DTex Ultra detector using BB geometry (2.5° primary and secondary solar slits, 0.5° divergence slit with 10 mm height limit slit). Each sample was ground into a fine powder using a mortar and a pestle and was placed on a glass sample holder that was placed on the sample rotation stage (120 rpm) attachment. The data were collected over an angle range of 5–50° with a scanning speed of 1°/min with 0.01° steps.

**Single-Crystal X-ray Data Collection and Refinement.** Following the general procedures published earlier, from a batch of crystals of each compound, a single crystal was placed inside a nylon loop on a goniometer head, which was then attached to the instrument. Initial crystal evaluation and data collection were performed on a Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealed-tube monochromated Mo Kα radiation and interfaced to a PC that controlled the crystal centering, unit cell determination, refinement of the cell parameters, and data collection through the program APEX2. Using the program SAINT, for the integration of the data, reflection profiles were fitted and values of $R^2$ and $\sigma(F^2)$ for each reflection were obtained. Data were also corrected for Lorentz and polarization effects. The subroutine XPREP was used for the processing of data that included determination of space group, application of an absorption correction (SAINT), merging of data, and generation of files necessary for solution and refinement. The crystal structures were solved and refined using SHELX 97. In each case, the space group was chosen based on systematic absences and confirmed by the successful refinement of the structure. Positions of most of the nonhydrogen atoms were obtained from a direct methods solution. Several full-matrix least-squares/difference Fourier cycles were performed, locating the remainder of the nonhydrogen atoms. In the final difference Fourier map in each case there was no other significant peak >1 e/Å$^3$. All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, except those for the lattice water molecule, were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. For the hydrgens in lattice water molecules, the OLEX2 hydrogen placement command was used to get the corresponding restraints. All figures were drawn electronically.
using MERCURY v 3.056 and DIAMOND v 4.5.0.50. Hydrogen bonding parameters were generated using PLATON.51 The final positional and thermal parameters of the nonhydrogen atoms for 1 and 2 are listed in the CIF files (Supporting Information).

**Synthesis of 2-Methyl-N-((6-methylpyridin-2-yl)methyl)-N-(pyridin-2-ylmethyl)propan-2-amine (6-Mebpta).** Step 1: To a methanolic solution of 6-methylpyridine-2-carboxaldehyde (242 mg, 2 mmol), tertiary butyl amine (146 mg, 2 mmol) was added and stirred for 12 h at 27 °C. An excess of sodium borohydride (1.5 equiv) was added slowly to the above reaction mixture at 0–4 °C and stirred for another 12 h. The resulting reduced Schiff base was isolated from the reaction mixture by extracting with chloroform followed by drying with anhydrous sodium sulfate. The solvent was evaporated to reduce pressure, affording a yellow oily substance. Yield: 155 mg (60%). 1H NMR (CDCl3): δ 7.49 (t, 1H), 7.12 (d, 1H), 6.99 (d, 1H), 3.83 (s, 2H), 2.52 (s, 3H), 1.18 (s, 9H). Step 2: To an aqueous solution of the reduced Schiff base (150 mg, 0.84 mmol) obtained in Step 1, picolylchloride hydroxide salt (138 mg, 0.84 mmol) was added. A sodium hydroxide solution (80 mg, 2 mmol in 2 mL water) was added dropwise to the above reaction mixture and stirred for another 24 h. The product was extracted with chloroform followed by drying the organic layer over anhydrous sodium sulfate. The solvent was evaporated to dryness using reduced pressure, affording a light-yellow semisolid. Yield: 178 mg (79%). 1H NMR (CDCl3): δ 8.41 (d, 1H), 7.45 (d, 2H), 7.41 (d, 1H), 7.35 (d, 1H), 7.02 (t, 1H), 6.87 (d, J = 7.6 Hz, 1H), 3.97 (s, 4H), 2.46 (s, 3H), 1.18 (s, 9H). HRMS (ESI-TOF): m/z calcd for [(6-Mebpta)H]+, 270.1926; found, 270.1913.

**Synthesis of 2-Methyl-N,N-bis((6-methylpyridin-2-yl)methyl)propan-2-amine (6,6′-Mebpta).** To a stirred mixture of 6-methylpyridine-2-carboxaldehyde (605 mg, 5 mmol) in 8 mL of dry dichloroethane, tertiary butyl amine (146 mg, 2 mmol) was added and stirred for 3 h under inert conditions at room temperature. To the above stirred reaction mixture, sodium triacetoxy borohydride (1.2 g, 6 mmol) was added very carefully at 0–4 °C in an inert atmosphere, followed by the addition of 5 mL of DCE and was further stirred for another 24 h. A saturated solution of sodium bicarbonate (19 mL) was added to make it slightly alkaline. The product was extracted with chloroform, dried over anhydrous sodium sulfate to remove the moisture, and the solvent was evaporated to dryness under reduced pressure, affording a yellow liquid substance, which was further recrystallized using ethyl acetate and hexane mixture, affording white crystals. Yield: 435 mg (66%). 1H NMR (CDCl3): δ 7.46 (t, 2H), 7.42 (d, 2H), 6.89 (d, 2H), 3.94 (s, 4H), 2.46 (s, 3H), 1.17 (s, 9H). HRMS (ESI-TOF): m/z calcd for [(6-Mebpta)H]+, 284.2082; found, 284.2079.

**Synthesis of [Ni2(6-Mebpta)2(adc)2·H2O (1).** To a stirred solution of Ni(OAc)2·4H2O (49.6 mg, 0.2 mmol) and 6-Mebpta (53.8 mg, 0.2 mmol) in 4 mL of methanol, acetylene dicarboxylic acid (22.8 mg, 0.2 mmol) was added. The reaction mixture was stirred for 4 h at 27 °C. The resulting slurry was evaporated to dryness under reduced pressure and treated with 4 mL of an acetonitrile–toluene mixture (50:50 v/v) to remove the acetic acid byproduct, affording a green solid. Yield: 65 mg (72%). Single crystals were obtained by slow evaporation of its water–acetonitrile aqueous solution. Anal. calcd for C28H32N6O12Ni2 (MW 952.29): C, 52.97; H, 5.72; N, 7.95. Found: C, 52.88; H, 5.35; N, 7.95. It should be noted that the formula of 1 used for the calculation of CHN analysis is with 1.5 lattice water molecules, while one water molecule can be found in its crystal structure. Selected FTIR peaks (KBr, cm−1): 3408 (br), 1621 (m), 1607 (s), 1596 (s), 1552 (m), 1440 (m), 1377 (s), 1351 (s), 1195 (m), 792 (m), 779 (m), 772 (m), 690 (m). Selected Raman peaks (cm−1): 2204, 1575, 1399, 1027, 772.

**Synthesis of [Ni(6,6′-Me2bpta)(adc)(H2O)]·H2O (2).** To a solution of Ni(OAc)2·4H2O (24 mg, 0.1 mmol) and 6,6′- Me2bpta (28 mg, 0.1 mmol) in 4 mL of methanol, acetylene dicarboxylic acid (11 mg, 0.1 mmol) were added. The reaction mixture was stirred for 4 h at room temperature. The resulting slurry was evaporated to dryness under reduced pressure, treated with an acetonitrile–toluene mixture (50:50 v/v) to remove the acetic acid byproduct, affording a green solid. Yield: 30 mg (66%). Single crystals were obtained by slow evaporation of its water–acetonitrile aqueous solution. Anal. calc. for C22H28N4O6Ni (MW 499.18): C, 52.91; H, 5.96; N, 8.57. Found: C, 52.70; H, 5.79; N, 8.41. It should be noted that the formula of 2 used for the calculation of CHN analysis is with 1.5 lattice water molecules, while one water molecule can be found in its crystal structure. Selected FTIR peaks (KBr, cm−1): 3435 (br), 3221 (br), 1704 (m), 1604 (s), 1580 (s), 1406 (m), 1339 (s), 1226 (m), 1192 (m), 1022 (m) 789 (m), 690 (m). Selected Raman peaks (cm−1): 2233, 1401, 1003, 775.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03065.

* 1H NMR spectra of ligands; additional figures related to single-crystal structure analysis; FTIR spectra; PXRD scans; thermogravimetric analysis (TGA) scans; and Hirshfeld analysis (PDF)

Final positional and thermal parameters of the non-hydrogen atoms for 1 (CIF)

Final positional and thermal parameters of the non-hydrogen atoms for 2 (CIF)

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### Notes

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