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Identification of Hexameric Water and Hybrid Water–Chloride Clusters Intercalated in the Crystal Hosts of (Imidoylamidine)nickel(II) Complexes

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Two structurally related bis(imidoylamidine or 1,3,5-triazapentadiene)nickel(II) compounds {Ni[HN=C(3-py)NC(3-py)=NH]$_2$}·H_2O·MeOH (**1**) and [Ni{HN=C(3-py)N(H)C(3-py)=NH}$_2$]Cl_2 (**2**) with symmetrical 3-pyridyl (3-py) substituents have been prepared by direct 2-butanone oxime mediated transformation of 3-cyanopyridine in the presence of $Ni(MeCO_2)_2·4H_2O$ or $NiCl_2·2H_2O$, respectively. Compounds **1** and **2** have been characterized by elemental analyses, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and FAB$^+$ mass spectrometry, while their slow recrystallization in air from organic solvents revealed a high affinity for water and resulted in the formation of the derived compounds [Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·6H_2O (**1′**) and [Ni{HN=C(3-py)N(H)$_{0.5}$C(3-py)=NH}$_2$]Cl·2H_2O (**2′**). Single-crystal X-ray diffraction analyses allowed the identification of discrete hexameric water or hybrid water–chloride clusters hosted by the crystal matrixes of **1′** and **2′**, respectively. Both the $(H_2O)_6$ and $[(H_2O)_4(Cl)_2]^{2-}$ clusters possess similar geometries and consist of cyclic planar tetranuclear $(H_2O)_4$ or $[(H_2O)_2(Cl)_2]^{2-}$ cores with two dangling water molecules. These water associates occupy voids in the crystal cells and display extensive H-bonding interactions with monomeric nickel–organic units, thus playing a key role in the formation of 3D hydrogen-bonded supramolecular assemblies.
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Introduction

The identification, characterization, and classification of various water assemblies in different crystalline materials has recently become a popular research field, namely towards understanding the properties of bulk water in its liquid and solid phases as well as interpretation of water–water interactions in various environments including, for example, inorganic materials, supramolecular systems, and biomolecules.[1–3] In contrast, the investigation of hybrid H_2O clusters composed of hydrogen-bonded water associates with other solvents, counterions, or small molecules has received less attention.[1b,4] In particular, there are only a few reports focused on the experimental identification and analysis of discrete water–chloride clusters[5a,5g] or H-bonded networks between water of crystallization and chloride counterions[1b,5b–5f,5h] in crystalline materials, in spite of the substantial theoretical studies[6] on such objects, and the importance of the latter in, for example, natural environments, biochemistry, materials chemistry, drug design, catalysis, and atmospheric research.[5,6]

Within our ongoing studies on the self-assembly synthesis of various transition-metal complexes,[7] we have recently reported the new Cu/Na[3a] and Ni[3b] coordination compounds and shown that their metal–organic matrixes host different types of decameric water clusters with unusual geometries. Thus, in pursuit of these and other studies, namely focusing on the new synthetic methods for phthalocyanines[8a] and analogous imidoylamidine (imam) compounds,[8b,8c] we report herein the preparation and full characterization of two structurally related bis(imidoylamidine)nickel(II) complexes **1** and **2**, which upon recrystallization lead to the derived compounds **1′** and **2′** that act in the solid state as crystal hosts for water-containing clusters. We also show how a slight modification of the synthetic and crystallization procedures may result in the incorporation of geometrically related, but in their composition distinctly different, hexameric $(H_2O)_6$ or $[(H_2O)_4(Cl)_2]^{2-}$ clusters.

Results and Discussion

Synthesis and Spectroscopic Characterization

The bis(imidoylamidine or 1,3,5-triazapentadiene) compounds [Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·H_2O·MeOH (**1**)

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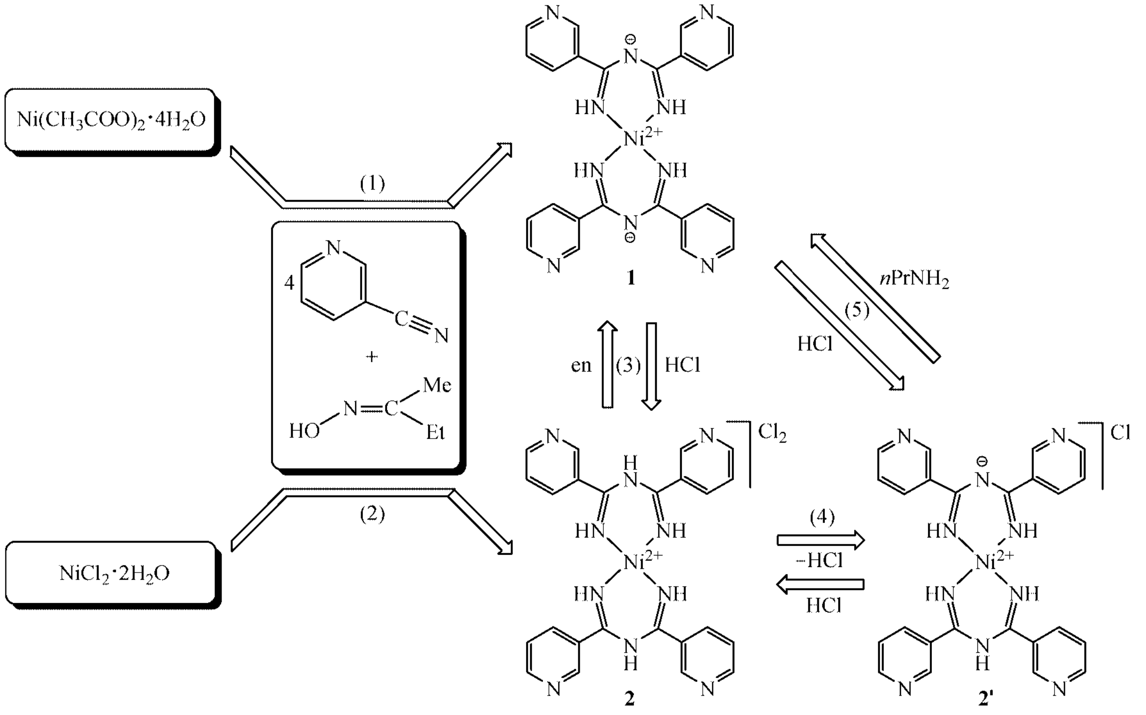

Scheme 1. Synthesis of bis(imidoylamidine)nickel(II) complexes (solvent molecules of crystallization are omitted for the sake of clarity); en = $H_2NCH_2CH_2NH_2$.

and [Ni{HN=C(3-py)N(H)C(3-py)=NH}$_2$]Cl$_2$ (**2**) with symmetrical 3-pyridyl (3-py) substituents were easily synthesized by modifying our previously reported[8c] (ketoxime)nickel(II)-mediated procedure for a variety of related bis(imidoylamidine) complexes. Hence, treatment of nickel(II) acetate tetrahydrate with 4 equiv. of 3-cyanopyridine in solution of 2-butanone oxime at 70 °C resulted in a single-pot formation of the neutral Ni(imam)$_2$ complex **1** [Scheme 1, reaction (1)]. It was isolated as a bright yellow crystalline solid in the form of a methanol/water solvate upon recrystallization from hot methanol in the presence of ethylenediamine.

However, the repetition of this synthetic procedure using nickel(II) chloride dihydrate as the nickel salt led to the formation of the cationic (+2) complex **2** isolated as a yellow powder from the reaction mixture [Scheme 1, reaction (2)]. The interconversion of compounds **1** and **2** can be achieved by treatment with HCl (**1**→**2**) or ethylenediamine (**2**→**1**) [Scheme 1, reactions (3)]. It should be mentioned that related bis(imidoylamidine)nickel(II) and -copper(II) complexes with various aromatic substituents have been previously reported,[9] but their synthetic procedures are different and more complicated than those now reported for compounds **1** and **2**, usually involving several reaction steps or rather harsh reaction conditions (e.g. solvothermal synthesis).

The presence of 2-butanone oxime (another oxime can also be applied) is essential for the synthesis of **1** and **2**, since the respective reactions between the nickel(II) salts and 3-cyanopyridine do not proceed in the absence of the oxime. In fact, this reagent, namely upon nucleophilic addition to the nitrile (NCR), can promote its hydrolytic conversion into ammonia and amidine RC(=NH)NH$_2$ (the latter upon coupling of NH_3 to NCR) which, on further nucleophilic addition to a ligated nitrile, leads to the imidoylamidine products. The reaction can proceed via an intermediate complex derived from double addition of the oxime to the nitrile ligand, as proposed for the oxime-mediated conversion of phthalonitriles into phthalocyanines and for related (ketoxime)nickel(II)-promoted processes.[8] The compounds **1** and **2** have been characterized by IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, FAB$^+$ mass spectrometry, elemental and single-crystal X-ray diffraction (for products **1′** and **2′** derived upon recrystallization) analysis.

The IR spectra of **1** and **2** show typical bands for bis(imidoylamidine)nickel(II) complexes[8b,8c] due to ν(NH), ν(C=N), and δ(NH) vibrations with absorbance maxima in the ranges of 3292–3169, 1655–1642, and 1548–1547 cm^{-1}, respectively. The overall identical [M + H]$^+$ (for **1**) and [M – H]$^+$ (for **2**) ions are observed at m/z = 507, with the expected isotopic distribution patterns, in the FAB$^+$ mass spectra. The ^{1}H and ^{13}C{^{1}H} NMR spectra reveal the expected resonances at typical chemical shifts for the corresponding imam ligands[8b,8c,9b–9d,10] (and solvents of crystallization in the case of **1**), while the elemental analyses are consistent with the proposed formulations. Complexes **1** and **2** are insoluble in water, but during the crystal growth experiments in organic medium, they appear to show a high affinity for water, absorbing its traces from organic solvents and/or air, and resulting in the formation of the derived compounds [Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·6H$_2$O (**1′**) and [Ni{HN=C(3-py)N(H)$_{0.5}$C(3-py)=NH}$_2$]Cl·2H$_2$O (**2′**), whose crystal cells according to the X-ray analyses contain 6 or 2 strongly associated water molecules of crystallization, respectively, as discussed below. Compound **2′** resulted from deprotonation of **2** upon recrystallization in air from a methanol/chloroform solution, and regenerated **2** on reaction with HCl [Scheme 1, reactions (4)]. It is also obtained by single protonation (by HCl) of **1** and conversely yielded the latter upon reaction with *n*PrNH$_2$ [Scheme 1, reactions (5)].

X-ray Crystal Structure of [Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·6H$_2$O (1′)

Compound **1′** crystallizes in the triclinic space group $P\bar{1}$, and consists of the neutral bis(imidoylamidine) [Ni{H*N*=C(3-py)NC(3-py)=*N*H}$_2$] unit (Figure 1a) and six water molecules of crystallization. The nearly square-planar coordination environment around the centrosymmetric tetracoordinate Ni(1) center is filled by two imam ligands. They act as *N*,*N*-chelators through equivalent Ni(1)–N(1) [1.847(1) Å] and Ni(1)–N(3) [1.848(1) Å] bonds, forming the six-membered Ni(1)–N(1)–C(1)–N(2)–C(14)–N(3) rings with N(1)–Ni(1)–N(3) bite angles of 89.48(6)° (Figure 1a). Within the Ni(imam)$_2$ core the N(1)–C(1) [1.310(2) Å] and N(3)–C(14) [1.315(2) Å] bonds are only slightly shorter (by ca. 0.03 Å) than N(2)–C(1) [1.357(2) Å] and N(2)–C(14) [1.353(2) Å], thus potentially indicating a delocalized character of Ni–imam rings, as reported previously for related compounds.[9b] Although the Ni(imam)$_2$ core is almost planar, the 3-pyridyl substituents are significantly bent out of its plane. Most of the bonding parameters in **1′** are comparable to those reported previously for related bis(imidoylamidine)nickel complexes.[8b,8c,9b–9d,10]

The most interesting feature of the solid-state structure of **1′** is the hydrogen-bonding interactions of all six water molecules of crystallization (Table 1), providing the formation of finite hexameric water clusters intercalated in the crystal host of the (imidoylamidine)nickel complex (Figure 2a). Hence, two symmetry-generated water trimers [O(1)···O(2)···O(3)] are doubly interconnected through the O(2)–H(2OA)···O(3)^{ii} [2.901(2) Å] hydrogen bonds generating the (H$_2$O)$_6$ clusters composed of a cyclic tetrameric core [O(2)···O(3)···O(2)···O(3)] and two pendent water molecules O(1). According to the systematization introduced by Infantes et al.,[1a,1b] such (H$_2$O)$_6$ clusters can be classified within the *R*4 type. The (H$_2$O)$_4$ core possesses a planar geometry with the O(2)···O(3)···O(2) and O(3)···O(2)···O(3) angles of ca. 76.89 and 103.11°, respectively (Figure 2a). Within the hexameric water associate the average O···O contact of ca. 2.82 Å (Table 1) is comparable to one found in liquid water (i.e. 2.85 Å)[1d] and in other discrete (H$_2$O)$_6$ clusters,[1a–1c,2] which are trapped by various metal–organic matrixes and composed of (i) a cyclic hexameric core of diverse conformations,[2a,2b,2d] (ii) a hexameric chain,[3b] or (iii) a cyclic tetrameric core with two pendent water molecules.[2c]

The (H$_2$O)$_6$ clusters occupy voids in the crystal cell of **1′** (Figure 3a) and extensively interact through multiple O–H···O or N–H···O hydrogen bonds [avg. 2.902(2) Å] with the host metal–organic matrix (Table 1). Hence, each dangling O(1) water molecule interacts with three imam nitrogen atoms [N(1), N(2), and N(5)] and each O(3) water contacts with one N(4) nitrogen atom (Figure 2a, Table 1), leading to the simultaneous multidimensional binding of every (H$_2$O)$_6$ cluster to eight different Ni(imam)$_2$ units in total. These multiple interactions play a key role in the

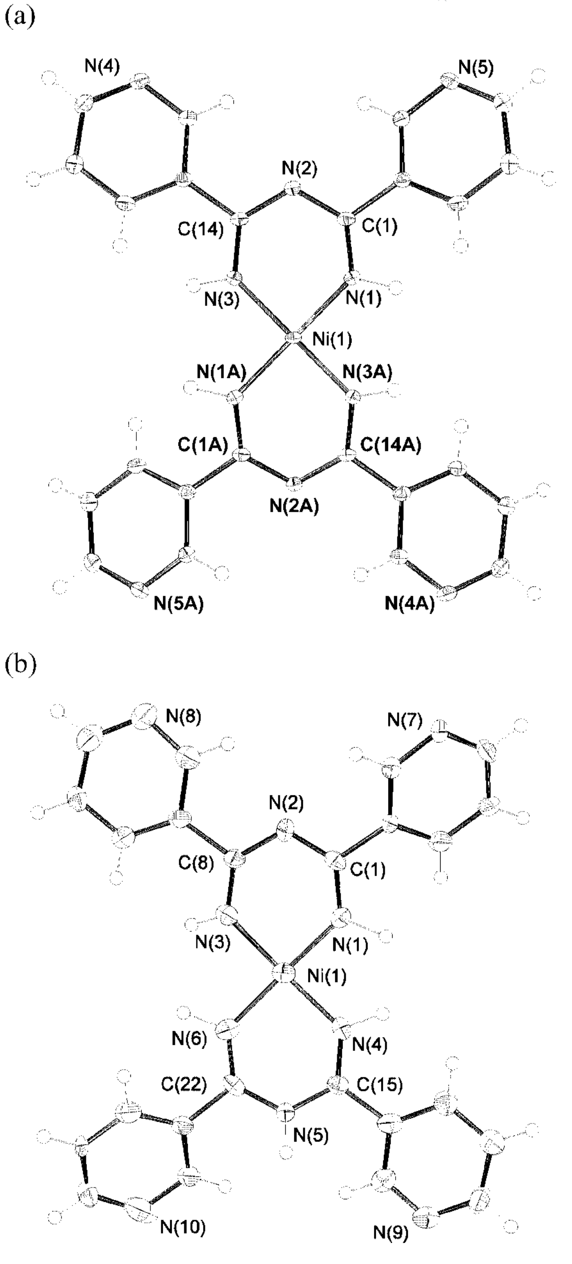

Figure 1. Thermal ellipsoid views of **1′** (a) and **2′** (b) with partial atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Water molecules of crystallization and counterions are omitted for clarity. Symmetry transformations used to generate the equivalent atoms in **1′**: (A) $-x + 1, -y, -z + 1$. Selected bond lengths [Å] and angles [°] in **1′**: Ni(1)–N(1) 1.847(1), Ni(1)–N(3) 1.848(1), N(1)–C(1) 1.310(2), N(3)–C(14) 1.315(2), N(2)–C(1) 1.357(2), N(2)–C(14) 1.353(2); N(1)–Ni(1)–N(1A) 180.0, N(1)–Ni(1)–N(3) 89.48(6), N(3)–Ni(1)–N(3A) 179.999(2).

Table 1. Hydrogen bonds [Å] in **1′**.[a]

D–H···A	*d*(D···A)
Within hexameric water cluster	
O(2)–H(2OB)···O(1)^{i}	2.757(2)
O(2)–H(2OA)···O(3)^{ii}	2.901(2)
O(3)–H(3OA)···O(2)^{iii}	2.788(2)
Between water cluster and metal–organic matrix	
O(1)–H(1OA)···N(5)^{iii}	2.8030(19)
O(1)–H(1OB)···N(2)^{iv}	2.8320(18)
O(3)–H(3OB)···N(4)	2.9149(19)
N(1)–H(1N)···O(1)	3.0584(18)

[a] Symmetry transformations used to generate equivalent atoms: (i) –*x* + 1, –*y*, –*z* + 1; (ii) *x*, *y* – 1, *z* + 1; (iii) –*x* + 2, –*y* + 1, –*z* + 1; (iv) *x*, *y* – 1, *z* + 1.

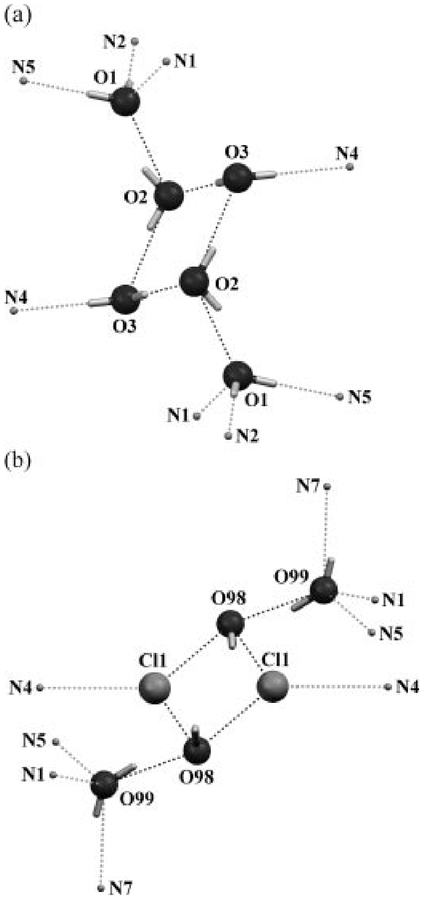

Figure 2. Perspective representations along the *a* crystallographic axis of discrete hexameric water (a) and water–chloride (b) clusters found in the crystal cells of **1′** (a) and **2′** (b). H-bonds are shown as dotted lines; water oxygen atoms and chloride atoms forming clusters are represented as spheres. Hydrogen-bond geometry parameters are those of Tables 1 and 2. Selected angles [°] within water-containing clusters: **1′**: O(1)···O(2)···O(3) 124.24 and 82.76, O(2)···O(3)···O(2) 76.89, O(3)···O(2)···O(3) 103.11; **2′**: O(99)···O(98)···Cl(1) 137.73 and 85.80, O(98)···Cl(1)···O(98) 70.20, Cl(1)···O(98)···Cl(1) 109.80.

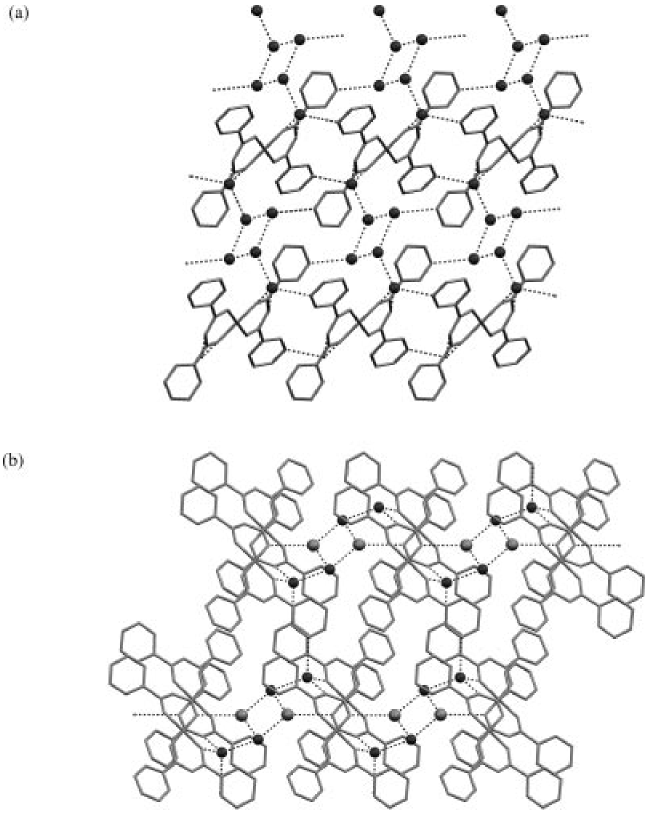

Figure 3. Fragments of the crystal packing diagrams along the *a* crystallographic axis of **1′** (a) and **2′** (b) with extensive hydrogen-bonded networks showing the interactions within the $(H_2O)_6$ and $[(H_2O)_4(Cl)_2]^{2-}$ clusters and between these clusters and the metal–organic matrixes; hydrogen atoms are omitted for clarity. Water oxygen atoms and chloride atoms forming clusters are shown as spheres.

structure stabilization and formation of an extended 3D hydrogen-bonded supramolecular assembly (Figure 3a). The separations between neighboring horizontal and vertical $(H_2O)_6$ clusters depicted in Figure 3a are within 8.7894(3) and 12.1448(6) Å, respectively, being equivalent to the *b* and *c* unit-cell dimensions.

X-ray Crystal Structure of [Ni{HN=C(3-py)N(H)$_{0.5}$C(3-py)=NH}$_2$]Cl·2H$_2$O (2′)

The molecular structure of **2′** is composed of the cationic bis(imidoylamidine) [Ni{H*N*=C(3-py)NC(3-py)=*N*H}{H*N*=C(3-py)N(H)C(3-py)=*N*H}]$^+$ unit (Figure 1b), represented by [Ni{H*N*=C(3-py)N(H)$_{0.5}$C(3-py)=*N*H}$_2$]$^+$, with two water molecules of crystallization and one chloride counterion equalizing the positive charge. The latter is caused by protonation of the middle nitrogen atom in one of the two imidoylamidine ligands which, nevertheless, possess almost identical geometry and bonding parameters, both being also similar to those found in **1′** (Figure 1a). Thus, the basic structure of **2′** is not discussed in detail.

As in the case of **1′**, the analysis of hydrogen-bonding interactions in **2′** (Table 2) reveals the formation of hexameric water-containing clusters. Besides, they possess a geometry that is similar to that of **1′** and consists of a cyclic planar tetranuclear core and two dangling water molecules (Figure 2). The main difference arises from the substitution of two water molecules in the $(H_2O)_4$ core of **1′** for two chloride atoms, thus leading to the formation of the $[(H_2O)_2(Cl)_2]^{2-}$ core and resulting in a hexanuclear hybrid $[(H_2O)_4(Cl)_2]^{2-}$ cluster in **2′** (Figure 2b). Hence, two symmetry-equivalent water molecules of crystallization O(98) and chloride ions Cl(1) from neighboring units are doubly hydrogen-bonded [O(98)–H(98B)···Cl(1)^{i} 3.172(7) Å] generating the tetranuclear core, which is further connected through the O(99)–H(99A)···O(98) [2.706(9) Å] interactions to give the hexanuclear associate. Within this cluster the O···O and O···Cl separations as well as the corresponding angles (Figure 2b) lie in the range found in other previously identified water–chloride assemblies, which include, for example, discrete cyclic $[(H_2O)_4(Cl)]^{-}$[5g] and $[(H_2O)_6(Cl)_2]^{2-}$[5a] clusters, as well as various 1D or 2D hydrogen-bonded networks with $\{[(H_2O)_4(Cl_2)]^{2-}\}_n$,[5h] $\{[(H_2O)_6(Cl)_2]^{2-}\}_n$,[5h] $[(H_2O)_7(HCl)_2]_n$,[5f] $\{[(H_2O)_{11}(Cl)_7]^{7-}\}_n$,[5b] $\{[(H_2O)_{14}(Cl)_2]^{2-}\}_n$,[5d] $\{[(H_2O)_{14}(Cl)_4]^{4-}\}_n$,[5e] and $\{[(H_2O)_{14}(Cl)_5]^{5-}\}_n$[5c] compositions.

Table 2. Hydrogen bonds [Å] in **2′**.[a]

D–H···A	*d*(D···A)
Within hexameric water–chloride cluster	
O(99)–H(99A)···O(98)	2.706(9)
O(98)–H(98B)···Cl(1)^{i}	3.172(7)
Between water–chloride cluster and metal–organic matrix	
O(99)–H(99B)···N(7)^{ii}	2.808(8)
N(5)–H(05)···O(99)	2.765(8)
N(1)–H(01)···O(99)^{i}	3.115(8)
N(4)–H(04)···Cl(1)	3.277(7)

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y, -z$; (ii) $x, y - 1, z - 1$.

The $[(H_2O)_4(Cl)_2]^{2-}$ clusters are held in cavities between the monomeric metal–organic units in the crystal cell of **2′** (Figure 3b) by means of extensive H-bonding contacts. Three types have been identified and include the O–H···N, N–H···O, and N–H···Cl interactions ranging from 2.808(8) to 3.277(7) Å (Table 2). As in the case of the $(H_2O)_6$ cluster in **1′**, the pendent water molecules O(99) in **2′** act as both hydrogen-bond donors or acceptors, bridging concurrently between three imidoylamidine nitrogen atoms (Figure 2b), thus leading, along with the N(4)–H(04)···Cl(1) interactions, to the multidimensional linkage of eight different Ni(imam)$_2$ units and resulting in the 3D hydrogen-bonded supramolecular pattern (Figure 3b). The separations between neighboring horizontal and vertical $[(H_2O)_4(Cl)_2]^{2-}$ clusters shown in Figure 3b are also equivalent to the *b* and *c* unit-cell dimensions, respectively (Table 3).

Conclusion

In the present work we have shown that the previously reported (ketoxime)nickel(II)-mediated transformations of various organonitriles[8] can be applied to 3-cyanopyridine, resulting in the direct synthesis of Ni(imam)$_2$ complexes **1** and **2** with symmetrical 3-pyridyl substituents. We have also demonstrated that the modification of a starting nickel salt [i.e. $Ni(MeCO_2)_2\cdot 4H_2O$ vs. $NiCl_2\cdot 2H_2O$] leads to either neutral (**1**) or cationic (**2**) (imidoylamidine)nickel(II) compounds. In spite of being insoluble in water, upon recrystallization **1** and **2** exhibit a high affinity for water, absorbing its traces from organic solvents and/or air, and giving the derivatives **1′** and **2′** with a higher content of water of crystallization.

The single-crystal X-ray diffraction analysis of **1′** and **2′** reveals the formation of hexameric water or hybrid water–chloride clusters, respectively, which are geometrically related, but distinctly different, in composition. They are shown to play the principal role in the formation of 3D supramolecular networks in the solid state through multiple hydrogen-bonding interactions. Hence, the current work provides well-identified examples of such cases and expands the constantly growing family of water[1–3] and, to a lesser extent, water–chloride[5] clusters trapped by various crystalline materials, as well as showing that imidoylamidine compounds can act as suitable matrixes to host different types of water-containing assemblies.

Further developments of this study towards widening of the family of imidoylamidine complexes and the search for their potential applications in various areas (e.g. as coloring materials and/or analogues of phthalocyanines), as well as the identification of new types of hybrid water clusters in diverse crystalline environments, are currently in progress.

Experimental Section

General Materials and Procedures: All synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, i.e. without further purification or drying. $NiCl_2\cdot 2H_2O$ was prepared according to an earlier described procedure.[8c] C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined with a Leica Gallen III instrument. Positive-ion FAB mass spectra were obtained with a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (*m*NBA) matrices of the samples with 8 keV (ca. 1.18 10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on KBr pellets with a BIO-RAD FTS 3000MX or Jasco FT/IR-430 instrument. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured with a Varian UNITY 300 or Bruker 300 UltraShield™ spectrometer at ambient temperature.

[Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·H$_2$O·MeOH (1): $Ni(MeCO_2)_2\cdot 4H_2O$ (248 mg, 1.00 mmol; Aldrich) was stirred in 2-butanone oxime (5 mL; Aldrich) at 70 °C for 30 min, giving a homogeneous light green solution (solution **a**). 3-Cyanopyridine (416 mg, 4.00 mmol; Aldrich) was stirred separately in 2-butanone oxime (5 mL; Aldrich) at 70 °C for 30 min and then added to the abovementioned solution **a**. The resulting reaction mixture was heated at 70 °C for 12 h, which resulted in the transformation of the clear green solution to a brownish-orange suspension. This was left to cool to room temperature yielding a dark orange product that was separated by filtration, washed with ethanol (15 mL), diethyl ether (10 mL), and then dried in air at room temperature. Recrystallization of the product from hot methanol with addition of

Table 3. Crystal data and structure refinement details for complexes **1′** and **2′**.

	1′	**2′**
Empirical formula	$C_{24}H_{32}N_{10}NiO_6$	$C_{24}H_{25}ClN_{10}NiO_2$
Formula mass	615.31	579.70
Temperature [K]	120(2)	100(2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	7.2503(4)	9.4184(14)
b [Å]	8.7894(3)	10.972(3)
c [Å]	12.1448(6)	13.017(3)
α [°]	92.115(3)	110.330(10)
β [°]	105.803(2)	97.629(13)
γ [°]	112.183(3)	102.445(13)
V [Å^3]	681.03(6)	1199.7(4)
Z	1	2
$\rho_{\text{calcd.}}$ [Mg m^{-3}]	1.500	1.605
μ(Mo-K_α) [mm^{-1}]	0.772	0.967
No. of collected reflections	8289	10611
No. of unique reflections	3115	4178
$R_{\text{int.}}$	0.0448	0.1071
Final R_1,[a] wR_2[b] ($I \geq 2\sigma$)	0.0344, 0.0739	0.0769, 0.1601
R_1, wR_2 (all data)	0.0447, 0.0781	0.1609, 0.1987
GOF on F^2	1.106	1.064
Largest difference in peak/hole [e Å^{-3}]	0.282/–0.464	0.564/–0.443

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

1.00 mmol of ethylenediamine gave a bright yellow crystalline precipitate of [Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·H_2O·MeOH (**1**). Yield: 58%, based on nickel acetate. The compound does not have a characteristic melting point and upon heating decomposes at >300 °C. $C_{25}H_{26}N_{10}NiO_2$ (557.2): calcd. C 53.89, H 4.70, N 25.14; found C 53.67, H 5.06, N 24.55. FAB-MS(+) (*m*NBA): *m*/*z* = 507 [M + H]$^+$ (M = molecular ion of the complex part of the compound). IR (KBr): $\tilde{\nu}$ = 3397 [(s br.) ν(H_2O+OH)], 3292 (s br.) [ν(NH)], 1655 [(m-w) ν(C=N)], 1548 [(s) δ(NH)] cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]acetone, Me_4Si): δ = 9.22 [s, 4 H, 2-C*H*(3-py)], 8.67 [d, *J* = 6.3 Hz, 4 H, 4-C*H*(3-py)], 8.37 [d, *J* = 7.8 Hz, 4 H, 6-C*H*-(3-py)], 7.46 [dd, *J* = 7.8 and 7.5 Hz, 4 H, 5-C*H*(3-py)], 6.93 (br. s, 4 H, N*H*), 4.11 (s, 1 H, MeO*H*), 3.49 (s, 3 H, C*H*$_3$OH), 3.31 (s, 2 H, *H*$_2$O) ppm. No reliable ^{13}C{^{1}H} NMR spectrum could be accumulated due to the poor solubility of **1** in common deuterated solvents. The X-ray quality crystals of {Ni[HN=C(3-py)NC-(3-py)=NH]$_2$}·6H_2O (**1′**) were grown by slow concentration in air at ca. 25 °C of an acetone/toluene (1:10, v/v) solution of **1**.

[Ni{HN=C(3-py)N(H)C(3-py)=NH}$_2$]Cl_2 (2): $NiCl_2$·2H_2O (166 mg, 1.00 mmol) was stirred in 2-butanone oxime (5 mL; Aldrich) for 5 min, whereupon 3-cyanopyridine (416 mg, 4.00 mmol; Aldrich) was added and the reaction mixture heated at 70 °C for 1 d. Upon addition of 3-cyanopyridine, the homogenization of the reaction mixture was observed for 10 min, giving a greenish-brown solution. The color of the reaction mixture changed with time (ca. 1 h) from greenish-brown to dark brown, and a yellow powder began to form after ca. 3 h, which after 24 h was separated by filtration, washed with three 15-mL portions of acetone and dried in vacuo at room temperature to give **2**. Yield: 55% based on nickel chloride. Compound **2** does not have a characteristic melting point and upon heating decomposes at >300 °C. $C_{24}H_{22}Cl_2N_{10}Ni$ (580.1): calcd. C 49.69, H 3.82, N 24.15; found C 49.30, H 4.02, N 24.19. FAB-MS (+) (*m*NBA): *m*/*z* = 507 [M – H]$^+$. IR (KBr): $\tilde{\nu}$ = 3169 [(s br.) ν(NH)], 1642 [(s) ν(C=N)], 1547 [(s) δ(NH)] cm^{-1}. ^{1}H NMR [300 MHz, $CDCl_3$ (90%) + CD_3OD (10%), Me_4Si]: δ = 8.98 [s, 4 H, 2-C*H*(3-py)], 8.53 [d, *J* = 4.4 Hz, 4 H, 4-C*H*(3-py)], 8.26 [d, *J* = 7.9 Hz, 4 H, 6-C*H*(3-py)], 7.34 [dd, *J* = 7.9 and 7.8 Hz, 4 H, 5-C*H*(3-py)] ppm; NH signals were not observed due to proton exchange with the solvent. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$ (90%) + CD_3OD (10%), Me_4Si): δ = 123.5 [*5*-*C*H(3-py)], 134.4 [*1*-*C*H-(3-py)], 135.6 [*6*-*C*H(3-py)], 147.7 [*2*-*C*H(3-py)], 149.9 [*4*-*C*H(3-py)], 162.7 [*C*=N(–N)] ppm. Slow concentration in air at ca. 25 °C of a methanol/chloroform (1:1, v/v) solution of **2** resulted in its dehydrochlorination, giving X-ray quality crystals of [Ni{HN=C(3-py)-N(H)$_{0.5}$C(3-py)=NH}$_2$]Cl·2H_2O (**2′**).

X-ray Crystal Structure Determinations: X-ray quality single crystals of **1′** and **2′** were mounted in inert oil within the cold gas stream of the diffractometer. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer at 120 (**1′**) or 100 (**2′**) K. Since the crystals of **2′** were poorly diffracting leading to a lower data quality, the data were collected at lower temperature in order to obtain a satisfactory structure. The Denzo-Scalepack[11] program package was used for cell refinements and data reduction. Structures were solved by direct methods using the SIR-2004 (**1′**) or SHELXS-97 (**2′**) programs.[12,13] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL)[14] was applied to all data. The structures were refined with SHELXL-97[15] and the WinGX graphical user interface.[16] Only NH (in **1′** and **2′**) and H_2O (in **1′**) hydrogen atoms were located from the difference Fourier map, but not refined. Other hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. The hydrogen-bond geometry parameters as well as the crystallographic data for **1′** and **2′** are summarized in Tables 1–3. The molecular structures of **1′** and **2′** are depicted in Figure 1, the perspective representations of hexameric water-containing clusters found in these compounds are drawn in Figure 2, while the crystal packing diagrams exhibiting the formation of extended hydrogen-bonded polymeric patterns are shown in Figure 3. All symmetry codes in the discussion are those of Tables 1 and 2. CCDC-644970 (**1′**) and -644971 (**2′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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