Interlayered Host Created by Assemblies of Monomeric Nickel Complex with Imidazole-4-acetate Chelate Ligands

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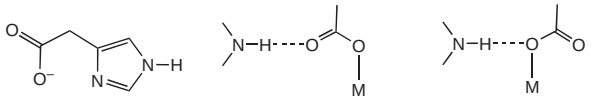
A new nickel(II) complex with two imidazole-4-acetate (ima) and a 1,10-phenanthroline (phen) was synthesized and characterized. The monomeric units are assembled by two NH···O–C intermolecular hydrogen bonds and π–π interactions, yielding two-dimensional layers. This complex includes six-water molecules per a nickel atom between the layers. The assembled interlayered host framework reversibly releases and reincludes water molecules.

Hydrogen bonds and π–π interactions have often been utilized for rational assemblies of metal complexes.[1,2] We have shown that imidazole-carboxylate type ligands are useful for creation of new hydrogen-bonded network structures.[3] For example, we have reported metal complexes with imidazole-4-carboxylate (imc) and imidazole-4-acetate (ima), which are constructed by NH···O=C intermolecular hydrogen bonds between imidazole-NH and uncoordinating carboxylate oxygen atoms (Scheme 1).

One of the target structures of the assembled complexes is a porous framework that can include various guest molecules. However, hydrogen-bonded porous frameworks are, in many cases, unstable and do not retain the initial porous structures after removal of guest molecules from their channels; that is, they generally afford amorphous materials upon guest removal. Nevertheless, the resulting dried complexes often show porous functions that adsorb guest molecules, accompanying reconstructions of the initial frameworks.[2]

Interlayered host framework is a unique porous structure that can include guest molecules. They are generally observed in many inorganic materials such as graphite and inorganic solids. We have succeeded in constructions of a new monomeric nickel complex with two ima and a 1,10-phenanthroline (phen), $[Ni(ima)_2(phen)]\cdot 6H_2O$ (**1**), which shows a 2-D framework constructed by intermolecular hydrogen bonds and π–π interactions. This paper describes its interlayered host structure and reversible structural changes caused by release and reinclusion of guest molecules.

Complex **1** was prepared by reaction of $Ni(ClO_4)_2\cdot 6H_2O$ with two equiv of Na(ima) and one equiv of phen$\cdot H_2O$ in an $EtOH/H_2O$ (2/1) mixed solution (15% yield as single crystals.



Scheme 1.

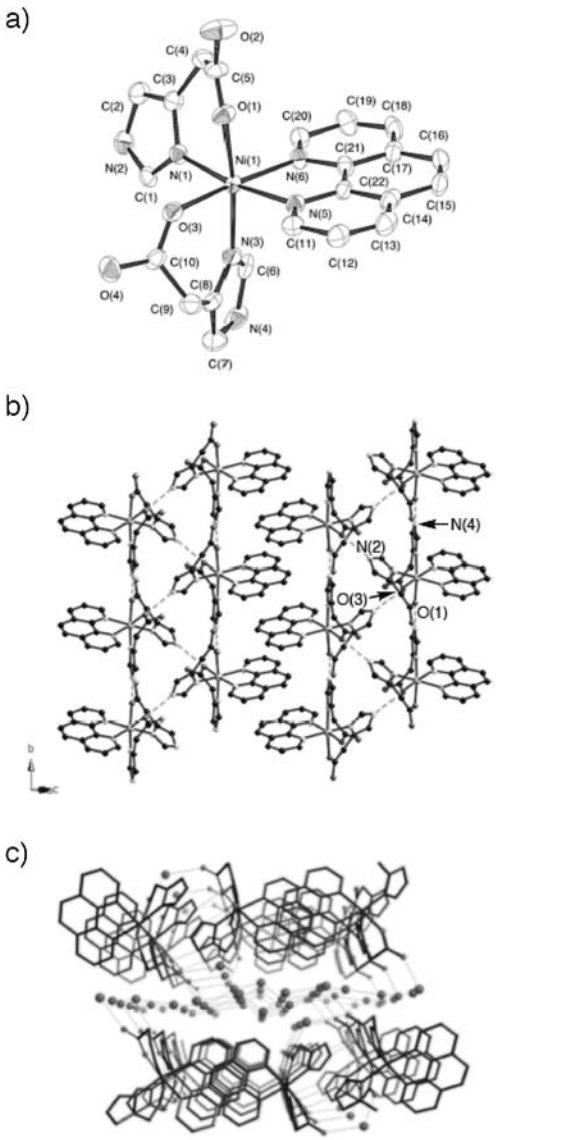


Figure 1. Views of the coordination conditions of the Ni(1) center (a), 2-D framework (b), and the layer structure (c).

Anal. Calcd for $C_{22}H_{30}N_6NiO_{10}$: C, 44.25; H, 5.06; N, 14.07%. Found: C, 44.16; H, 4.69; N, 13.72%). Single crystal X-ray diffraction study clarified the structure of **1**. Figure 1 shows the monomeric unit of **1** and its overall structure.[4] Two ima and a phen bind to the nickel center, yielding a distorted

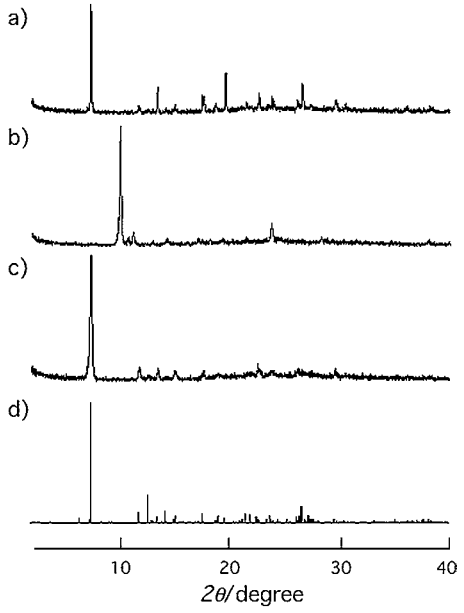


Figure 2. XRPD patterns of **1** (a), **2** (b), and powder sample obtained by exposure of water vapor to **2** (c). Simulated XRPD pattern for **1** (d).

octahedral geometry (Figure 1a). The monomeric units are connected by two sets of NH···O–C intermolecular hydrogen bonds (Scheme 1), yielding 1-D framework along the *b* axis. One is formed between N(4) and O(1) [N···O = 2.912(9) Å], while the other is observed between N(2) and O(3) [N···O = 2.883(7) Å] as shown in Figure 1b. The former hydrogen bond connects monomeric units linearly along the *b* axis, whereas the latter connects these chains in a zig-zag manner.

These chains are further associated by intermolecular π–π interactions formed between phen ligands in the adjacent chains. Their plane–plane distance is about 3.4 Å, in which their chains are mutually connected as two gears are engaged. As a result, the two-dimensional layer is created in the $(1\,0\,-1)$ plane.

Six water molecules per a nickel atom are included between the layers. These water molecules mutually form hydrogen bonds, in which two of them, O(5) and O(6), form hydrogen bonds to noncoordinating carbonyl oxygen atoms. Water molecule O(5) binds to O(2) and O(4), while O(6) is associated with O(4) atom [O(5)···O(2) = 2.657, O(5)···O(4) = 2.825, O(6)···O(4) = 2.86 Å]. Based on thermogravimetric (TG) analysis (see Supporting Information),[5] which shows that these water molecules are removed by heating to 70 °C, we prepared the dried complex [Ni(ima)$_2$(phen)] (**2**) by treatment of **1** at 100 °C (Anal. Calcd for $C_{22}H_{18}N_6NiO_4$: C, 54.02; H, 3.71; N, 17.18%. Found: C, 54.02; H, 3.76; N, 17.06%).

The structural changes caused by guest removal and reinclusion were monitored by measurement of XRPD pattern. Figures 2a and 2b reveal the observed XRPD patterns for **1** and **2** respectively, while Figure 2c indicates the XRPD pattern of the powder sample obtained by exposure of **2** to water vapor for 3 days. Figure 2d illustrates the calculated pattern for **1** based on the X-ray data. For **1**, the repetitions of the layers are observed at 7.4° as an intense peak (Figure 2a).

For **2**, the intense peak shifts to 10.0°, implying that the initial layer–layer distance was shortened by about 2.7 Å. This value is consistent with that of effective space in **1** estimated from the X-ray structure. These results suggest that the dried complex **2** retains the 2-D framework, which would be just stacked.

In summary, we have successfully synthesized a new nickel complex [Ni(ima)$_2$(phen)]·6H$_2$O, which has a 2-D structure constructed by intermolecular hydrogen bonds and intermolecular π–π interactions. The complex includes six water molecules per nickel atom, which are easily removed by heating to yield the dried complex. The dried complex acts as an interlayered host that reincludes the water molecules to reconstruct the initial structure of the complex. This is a unique example of a new interlayered host framework built up by monomeric complex units through weak chemical interactions.

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References and Notes

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4 Crystallographic data for the complex: $C_{22}H_{30}N_6NiO_{10}$, M_r = 597.2, monoclinic, space group $C2/c$ (No. 15), a = 25.93(7), b = 7.853(2), c = 29.8(1) Å, β = 115.29(2)°, V = 5476(31), Å^3, Z = 8, D_{calcd} 1.449 g cm^{-3}, μ(Mo Kα) = 0.772 mm^{-1}, T = 293 K, λ = 0.7107 Å, ω scan, R = 0.090, wR = 0.1674 for 4398 unique reflections (R_{int} = 0.046) with $I > 2\sigma(I)$ and 344 parameters. The data collection was performed on a Rigaku CCD Mercury system. The structure was solved by direct methods using SHELXS97. Hydrogen atoms were located on their calculated positions. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included but not refined. Crystallographic data reported in this paper has been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-694565.

5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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