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Cesium(I)-Mediated 3-D Superstructures by One-Pot Self-Organization of Hydrogen-Bonded Nickel Complexes

Makoto Tadokoro,[*,†] Takumasa Shiomi,[†] Kiyoshi Isobe,[†] and Kazuhiro Nakasuji[‡]

Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan, and Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

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Developments in crystal engineering have shown that molecule-based building blocks can spontaneously assemble into multidimensional structures using such intermolecular interactions as hydrogen bonding and coordination.[1] A major goal of this field is to control rationally the assembly of three-dimensional (3-D) arrays using intermolecular interactions and specific molecular topologies. We have found that the Cs^+ ion can be used as a new tool to manipulate an H-bonded superstructure built with building block **1**, tris(biimidazolato)nickelate(II) anion, $[Ni(Hbim)_3]^-$. Two of the three 2,2′-biimidazolate ligands in building block **1** can be bound to a Cs^+ ion in the crystal by an electrostatic π-bonding interaction, which is not possible for other stable alkali metal ions. Furthermore, a more complicated 3-D superstructure of the double-helical racemate was formed in the crystal by cooperative application of an organic cation and the Cs^+ interaction.

Superstructures with many 3-D frameworks have been created in different crystals by a self-assembly process. Most of the 3-D frameworks were developed by employing various topological building blocks as coordination polymers[3] and as H-bonding polymers.[4] However, the cooperative construction of 3-D arrays using both the weak H-bonding and coordination interactions has rarely been achieved to date.[5] We reported previously that the $Hbim^-$ (2,2′-biimidazolate anion) system could form controlled superstructures by simultaneously using a didentate chelate coordination and complementary intermolecular dual H-bonds of the type NH···N.[6] Thus, depending upon the kind of organic countercations,[7] the tris(biimidazolato)nickelate(II) anion, $[Ni(Hbim)_3]^-$ (**1**), with D_3 symmetry, formed a variety of H-bonded networks in a crystal with multidimensionalities by a one-pot preparation in MeOH.

This paper explores the effects of alkali metal ions, as well as organic cations, on superstructures formed by **1**. Generally, alkali metal ions with a large polarizability can coordinate to aromatic rings in a multihaptic mode.[8] Of all the stable alkali metal cations (i.e., Li^+, Na^+, K^+, Rb^+, and Cs^+), only the Cs^+ ion was found to have a rational electrostatic interaction with **1**. A few examples of organocesium complexes, such as cesiocarbazole−pmdta complexes,[9a] triple-decker[9b] and calix[4]arene[9c] and Cs^+−crown ether compounds[9d] have been reported as crystal structures with such an electrostatic interaction. In this study, we have prepared not only a 3-D double interlocking polycatenate superstructure of interpenetrated two-dimensional (2-D) honeycomb sheets by using such a Cs^+ interaction but also a double-helical 3-D racemate with (10,3)-a nets by using the cooperative interactions between organic cations and Cs^+.[10]

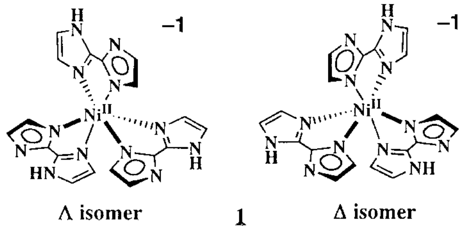

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Figure 1a shows a fragment of the structure of ($\{Cs[Ni(Hbim)_3]\}_n$) in crystal **A** formed from the interaction of the Δ and Λ optical isomers of **1** with Cs^+ as countercations. The three $Hbim^-$ ligands in **1** are involved in H-bonding interactions forming a 2-D honeycomb sheet with (6,3) nets. Four Cs^+ ions are located in each hexagonal cavity of the sheet constructed by six **1**s, and fix the two interpenetrating rods of the other two sheets at an inclination of ∼70° to create a 3-D polycatenate superstructure with a double interlocking interpenetration (Figure S 2-3, Supporting Information). Electrostatic interaction between Cs^+ and the two different optical isomers of **1** forms a one-dimensional (1-D) alternative coordination polymer with the general formula $\{(\Delta)\text{-}Cs[Ni(Hbim)_3]\text{-}(\Lambda)\text{-}Cs[Ni(Hbim)_3]\}_n$ (**2**) as

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[*] Author to whom correspondence should be addressed.

[†] Osaka City University.

[‡] Osaka University.

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(10) Crystal data for **A**: $C_{18}H_{15}N_{12}NiCs$, fw = 591.00, monoclinic, space group $P2_1/n$ (No. 14) with $a = 12.601(3)$ Å, $b = 13.274(3)$ Å, $c = 13.363(3)$, $\beta = 97.02(2)°$, $V = 2218.3(9)$ Å^3, $Z = 4$, $T = 23$ °C, $\lambda = 1.54178$ Å, $\rho_{calcd} = 1.769$ g cm^{-3}, $F(000) = 1160.00$. 289 parameters, and $R_1(F_o) = 0.063$ and $R_w(F_o) = 0.084$ and GOF = 1.17 for all 1620 data ($I > 3\sigma(I)$), values of minimum and maximum residual electron density 1.80 and −0.85 e Å^3. Elemental anal. Calcd for $[Ni(Hbim)_3]Cs{\cdot}H_2O$ ($C_{18}H_{15}N_{12}NiCs$): C, 35.50; H, 2.81; N, 27.60. Found: C, 35.77; H, 2.81; N, 27.98. IR (KBr): 2920 cm^{-1} (br, ν(NH)); 1900 cm^{-1} (br, 2γ(NH)). Crystal data for **B**: $C_{49}H_{62}ON_{25}NiCs$, fw = 1267.50, orthorhombic, space group *Ccca* (No. 68) with $a = 25.422(6)$ Å, $b = 28.228(5)$ Å, $c = 16.741(8)$ Å, $V = 12013(5)$ Å^3, $Z = 8$, $T = 23$ °C, $\lambda = 0.71069$ Å, $\rho_{calcd} = 1.401$ g cm^{-3}, $F(000) = 5200.00$. 349 parameters, and $R_1(F_o) = 0.041$ and $R_w(F_o) = 0.052$ and GOF = 1.24 for all 2796 data ($I > 3\sigma(I)$), values of minimum and maximum residual electron density 0.59 and −0.35 e Å^3. Elemental anal. Calcd for $\{[Ni(Hbim)_3]_2Cs\}(N^nPr_4){\cdot}0.5MeOH$ ($C_{48.5}H_{60}O_{0.5}N_{25}NiCs$): C, 46.55; H, 4.83; N, 27.98. Found: C, 46.35; H, 4.80; N, 28.10 (the sample was dried under vacuum for 6 h at 100 °C). IR (KBr): 2788 cm^{-1} (br, ν(NH)); 1919 cm^{-1} (br, 2γ(NH)).

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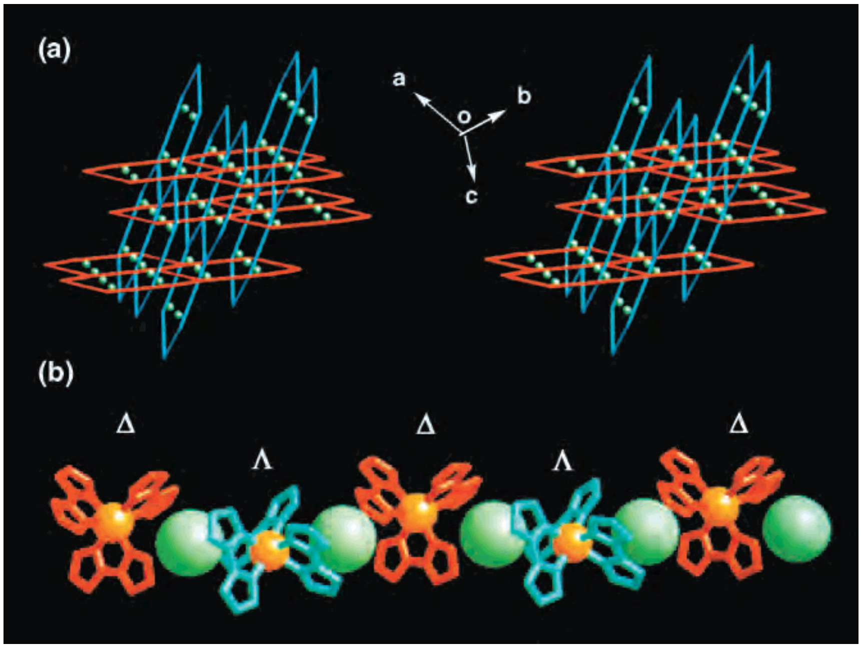

Figure 1. **(**a) A stereoview showing the whole structure of crystal **A** by the red and light blue lines with the shortest Ni−Ni atoms and the green spots of Cs^+. The main frameworks form a two-hold interpenetration with (6,3) nets. **(**b) A view of the 1-D coordination polymer in crystal **A** is shown. Cesium(I) ion and nickel(II) ion are indicated by green and orange, respectively. The structure was built up by an alternate interaction between the blue (Λ)-$[Ni(Hbim)_3]$−Cs and the red (Δ)-$[Ni(Hbim)_3]$−Cs building units.

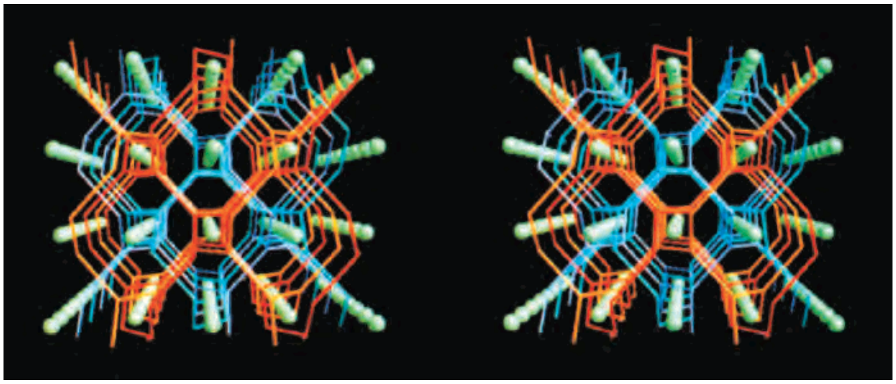

Figure 2. A perspective stereoview along the *c* axis showing the whole network with (10,3)-a nets of crystal **B**. It is drawn by the color lines between the shortest Ni−Ni distances of Δ isomers (red and yellow) and Λ isomers (blue and light blue) of **1**, and the green spots of Cs^+ ions.

shown in a different view (Figure 1b). Each Δ or Λ optical isomer fixed by two Cs^+ ions participates in the formation of a different interpenetrating sheet, respectively. Such a 3-D double interlocking interpenetration based on **1** has already been prepared by using an organic NEt_4^+ (tetraethylammonium) cation as described in a previous report.[7]

Moreover, an organic cation can work cooperatively with Cs^+ to manipulate the new superstructure formed in the crystal. The addition of tetra-*n*-propylammonium ion ($^nPr_4N^+$) led crystal **B** ($\{Cs[Ni(Hbim)_3]_2(^nPr_4N)\cdot MeOH\}_n$) to form a 3-D double-helical structure of racemate (10,3)-a nets having a 1-D column of Cs^+ in the center (Figure 2). The columns of Cs^+ in the 4_1 double helices lie along the *c* axis with Cs−Cs distances of 8.60 and 8.14 Å. Figure 3a shows a view of the dimers, Δ−Δ and Λ−Λ, which are composed of the same optical isomer of building block **1** linked by one Cs^+ ion. In other words, each 4_1 strand in the helix is formed by using only one optical isomer of **1**. Furthermore, each helix is H-bonded to four other identical optical isomers by using the $Hbim^-$ moiety. The 3-D H-bonded network forms an 8_7 chiral double helix with large cavities (Figure 3b). The entire racemate structure is created by combining the 4_1 helices into an opposite-handed 8_7 helical structure.

There have been several reports concerning coordination polymers, for example, $\{[Fe_2(ox)_3][Fe(bpy)_3]\}_n$[11a] and $[Ag(hmt)](PF_6)\cdot H_2O$,[11b] $\{[Ag(hat)ClO_4]\cdot 2MeNO_2\}_n$,[11c] $[Zn(tpt)_{2/3}(SiF_6)(H_2O)_2\cdot(MeOH)]$,[11d] $[Ag(hmt)](PF_6)\cdot H_2O$,[11e] and $[Ni_3(btc)_2(py)_6\cdot x eg\cdot y H_2O]$,[11f] Ag−phenazine derivative complex[11g] and of an H-bonded polymer of a cyanamide crystal,[12] creating 3-D crystal arrays with a (10,3)-a net. However, crystal **B** is the first racemate with a (10,3)-a net formed by simultaneous control of H-bonding and coordination chemistry. Also, the 4_1 double helices with a column of Cs^+ ions in the center found in crystal **B** have a pitch of 33.4 Å, which is similar to that of B-DNA, whose pitch is

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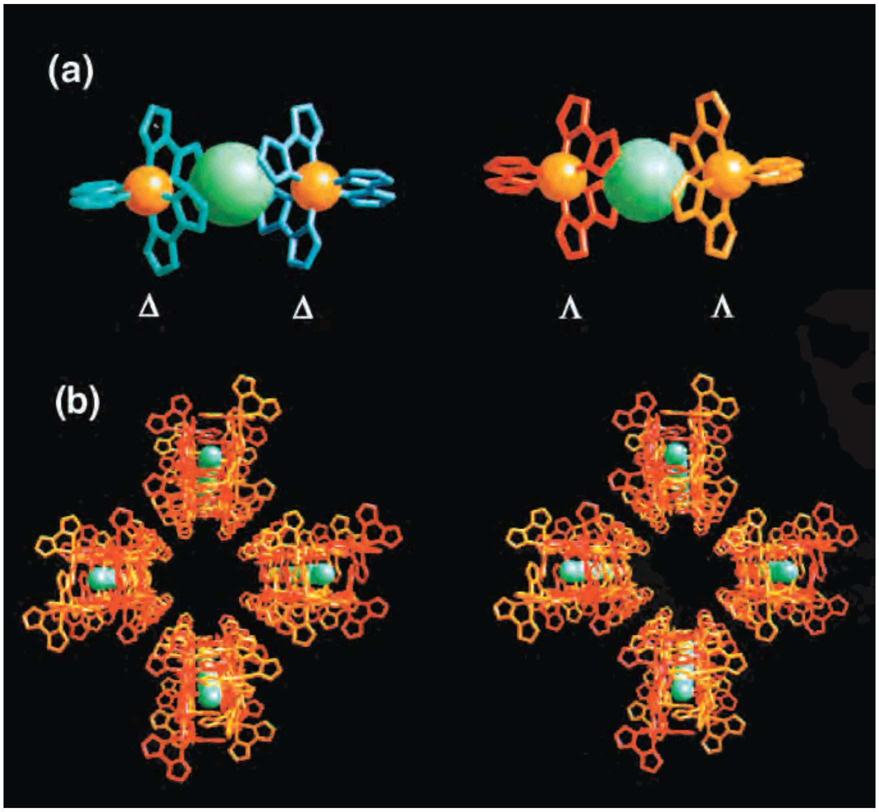

Figure 3. (a) A view of the structure showing a trinuclear building unit **2** containing crystal **B**. The structures are constructed from homochiral units with two Δ-isomers (blue and light-blue) or two Λ-isomers (red and yellow) of **1**. Green and orange indicate Cs(I) ions and Ni(II) ions, respectively. (b) A perspective stereoview along the *c* axis showing a larger right-handed 8_7 helix constructed from four smaller right-handed 4_1 helices.

~34 Å (Figure S 3-2, Supporting Information). Selective ion exchange in MeOH solution for Cs^+ with retention of the crystal **B** structure failed.

The superstructure formation of crystal **B** can be attributed to the cooperative use of $N^nPr_4^+$ and Cs^+ cations. The $N^nPr_4^+$ ions occupy the void spaces created by the interpenetration of each independent chiral 3-D net with Δ or Λ isomers of **1**. The use of other alkali metals with $N^nPr_4^+$ produces only 1-D zigzag ribbons within the crystal, as described in a previous paper.[7] The large ionic radius and high polarizability are important in the formation of this new, more complicated, structure. It is believed that the Cs^+ ion is bound to the deprotonated imidazolate site of the $Hbim^-$ ligand by using electrostatic π-interactions in both crystals **A** and **B**. The binding distances range from 3.188(10) to 3.62(1) Å for the Cs−C bond and 3.323(10) to 3.607(8) Å for the Cs−N bond in crystal **A**, and 3.368(6) to 3.565(7) Å (Cs−C) and 3.342(5) to 3.643(6) Å (Cs−N) in crystal **B**. It is believed that the crystal structures presented are the first where the structure was formed from an interaction between a Cs^+ ion and an imidazolate ring. The bond distances found in crystals **A** and **B** are similar to those in different complexes. A cesiocarbazole−pmdta complex with a multihapto interaction for the aromatic five-membered ring with an N atom, reported by Gregory,[9a] exhibits Cs−C bond distances of 3.233(6)−3.473(7) Å and Cs−N distances of 3.102(6)−3.360(5) Å. A triple-decker cesocene, reported by Harder,[9b] having multihapto interactions between two Cs^+ and three cyclopentadienyl (Cp) rings, has Cs−C distances from 3.313(6) to 3.385(5) Å. The crystal **A** and **B** can be kept forms stably in only each reactive mother liquors and in other solvent are decomposed. The TGA trace of crystal **A** reveals one mass loss at 376 °C, corresponding to chemical decomposition (31.1%). However, that of crystal **B** shows a mass loss at 163 °C by measurement on DTA, corresponding to one MeOH molecule (observed 2.51%, calculated 2.53%), followed by another mass loss at 323 °C, corresponding to decomposition (46.1%). The final residues of crystal **A** and **B** at 600 °C were black and amorphous.

This report clearly has shown that an electrostatic π-bonding interaction can form between a Cs^+ ion and an imidazolate ring in **1**. Furthermore, when Cs^+ and $N^nPr_4^+$ were used at the same time, an intricate 3-D racemate structure with (10,3)-a nets was formed by the 4_1 double helices wrapping around a 1-D column of Cs^+ ions. Finally, the current work may possibly be a general route to formation of 2-D and helical structures by controlling the assembly of only D_3-symmetric building blocks with different optical activity.[13]

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, four figures showing ORTEP diagrams, and other figures. Crystallographic data for **A** and **B** in CIF format. This material is avalable free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal **A**: A suspension of H_2bim (0.40 g, 3 mmol), CsCl (1.68 g, 10.0 mmol), and $CsOH \cdot H_2O$ (2.00 g, 12.0 mmol) was added to methanol (60 cm^3) and heated under reflux until the ligand had dissolved. To the resulting solution was added $NiCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol) in methanol (40 cm^3) dropwise, and the mixture was heated under reflux for 15 min. The insoluble components were removed by filtration, and the filtrate was allowed to stand at room temperature. After renewed filtration of white precipitate, blue prisms were obtained from the filtrate after several days. Crystal **B**: This crystal was obtained in a way similar to that employed for crystal **A** except that N^nPr_4Br (0.27 g, 1.0 mmol) was used instead of CsCl.