Coordination Chemistry Reviews
198 (2000) 205–218

www.elsevier.com/locate/ccr

Hydrogen bonded 2,2′-biimidazolate transition metal complexes as a tool of crystal engineering

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Received 26 March 1999; accepted 27 August 1999

Contents

Abstract

In the field of crystal engineering, many attempts have been made to control the molecular arrangements in crystal by simultaneous use of coordination bonds of a transition metal ion and complementary intermolecular hydrogen bonds. We obtained the first crystal structure of the hydrogen bonded metal complex of 2,2′-biimidazolate monoanion ligand Hbim$^-$ with Cu(II) as a neutral dimer metal complex. The hydrogen-bonded dimer structure indicates that the Hbim$^-$ ligand controls the crystal structure using not only the coordination to a transition metal ion as a bidentate chelate but simultaneously the formation of complemen-

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PII: S0010-8545(99)00223-4

tary intermolecular hydrogen bonds. We also found that the $Hbim^-$ ligand gave $[Ni(Hbim)_3]^-$ as a new building block for hydrogen-bonded self-assembling networks by one-pot synthesis to mix Ni(II) ion, counter cation and the ligand. The networks form zero-dimensional, one-dimensional, two-dimensional, and three-dimensional structures depending upon the kind of counter cations.

Keywords: Crystal engineering; Hydrogen bond; Metal complex; Nanostructure; Supramolecular chemistry

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1. Introduction

The unique strength, direction, and complementarity of noncovalent interactions such as hydrogen bonding and coordination bonding play a central role in the creation of a variety of molecular architectures for molecular self-assembly and molecular recognition in chemical, physical, and biological sciences [1,2]. The building blocks possessing such noncovalent interaction sites can produce one- (1-D), two- (2-D), and three-dimensional (3-D) molecular arrangements [3–5] with the long-range order. Control of such a dimensionality is essential to advance crystal engineering and to construct the desired molecular materials [6–8].

Complicated crystal structures composed of self-organizing networks can be formed by simultaneous use of complementary hydrogen bonds and coordination bonds [9]. As a preliminary experiment, we prepared a copper(II) complex, $[Cu^{II}(salenNMe_2)(Hbim)]_2$, with a dimer structure using 2,2′-biimidazolate, $Hbim^-$ as a bridging ligand with a π-conjugated system [10]. The crystal structure indicated for the first time that $Hbim^-$ ligand could be used for the formation of metal complexes having complementary intermolecular hydrogen bonds in the solid state.

We next designed a new anionic building block, tris-biimidazolate nickel(II) complex $[Ni(Hbim)_3]^-$, with the block possessing three complementary hydrogen-bonding sites. We found that simple one-pot procedures mixing nickel(II) ion, $Hbim^-$, and counter cation produce four types of hydrogen-bonded crystals based on the arrangement of the $[Ni(Hbim)_3]^-$, in which the nickel(II) center is linked by three $Hbim^-$ ligands: (1) a zero-dimensional dot structure with no complementary hydrogen bond, (2) a 1-D hydrogen-bonded zigzag ribbon, (3) a 2-D hydrogen-bonded honeycomb sheet and (4) a 3-D supra-cross-catenated network [11].

2. $Hbim^-$ ligands as a candidate for transition metal complexes with hydrogen bond

As 2,2′-biimidazole (H_2bim) is a bidentate chelating ligand with multi-proton donor sites, it is able to coordinate to a transition metal with three reversible types of protonated and deprotonated modes: neutral (H_2bim), mono-deprotonated (monoanion, $Hbim^-$), and di-deprotonated (dianion, bim^{2-}) types [12] (Fig. 1). The H_2bim ligand itself, which has a *trans* configuration in crystal, forms the

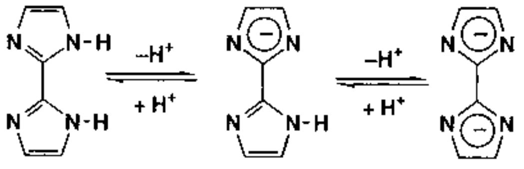
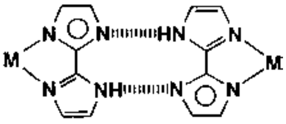


Fig. 1. 2,2′-biimidazole with three reversible types of protonated and deprotonated mode.

complementary hydrogen-bonded network with 1-D linear chains [13], as shown in Fig. 2. A metal complex with the configuration H_2bim, as a bidentate chelate ligand; however, can not form the complementary hydrogen bonds between the ligands. In such a case, the hydrogen-bonding sites of the H_2bim ligand in a metal complex are not used for a complementary intermolecular hydrogen bond, but are used for the hydrogen bonds with counter ions and solvent molecules in crystal [14]. Among the three types of protonated states of H_2bim ligand, the Hbim$^-$ ligand can form both a complementary intermolecular hydrogen bond of binary NH···N type and a coordination bond with metal ions as shown in complex **1**. Oro and coworkers proposed the dimer structure shown in this diagram, built up by a palladium(II) complex (**2**) containing only one Hbim$^-$ ligand, as the complex was observed to have a higher molecular weight in solution than that calculated [19b].



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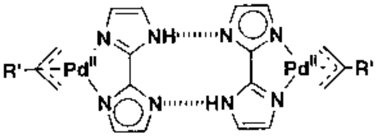


2 (R′=Me,H)

Conventional synthesis of metal complexes focusing on proton dissociation of a H_2bim ligand has been practiced in the past [15]. Many transition metal complexes

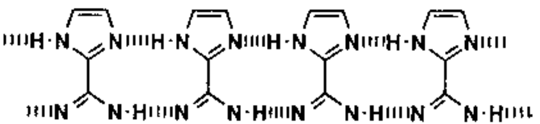
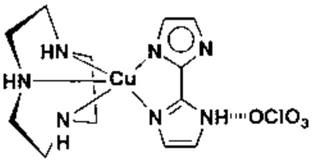


Fig. 2. 1-D hydrogen-bonded chain in crystal of 2,2′-biimidazole with *trans* configuration.

containing Hbim$^-$ ligands have also been prepared, but few crystal structures have been determined by X-ray crystal analysis. A coordination polymer $\{[Fe^{II}(Hbim)_2]\}_n$ which affords the first example of bridging Hbim$^-$ ligands, was created by direct coordination between two vacant coordination sites of Fe^{II} ion and the N atom [16]. In this case, the metal complex forms no complementary intermolecular hydrogen bonds of Hbim$^-$ ligand as in complex **1**.

We have identified the crystal structure of $[Cu^{II}(tacn)(Hbim)](ClO_4)MeOH$ (**3**) (tacn = 1,4,7-triazacyclononane) [10]. The Cu(II) ion is bound to five nitrogen-donor sites to give a distorted square-pyramidal coordination. The metal complex moiety has a + 1 charge and the counter ion ClO_4^- is a kind of proton acceptor; therefore, the Hbim$^-$ ligand forms the intermolecular hydrogen bonds with ClO_4^- and no complementary hydrogen bonds between the Hbim$^-$ as shown in Fig. 3. This is a common feature in cationic transition metal complexes.



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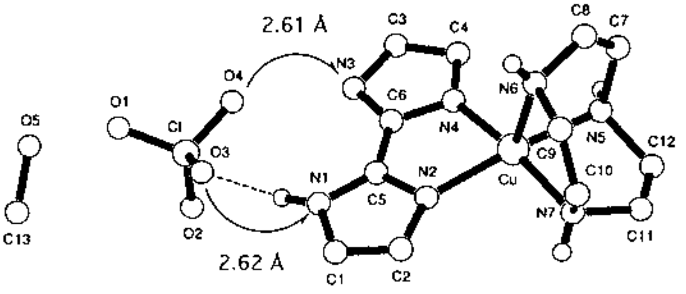
3. Hydrogen-bonded dimer structure

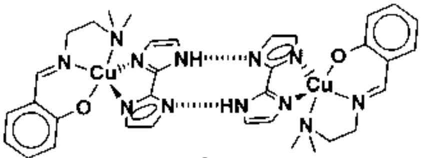
To preclude the interaction with counter anions, and to construct the complementary hydrogen bonded dimer as in complex **1**, we chose the copper(II) complex of the mononegative, tridentate ligand *N*-salicylidene-*N*′,*N*′-dimethylethylenedi-



Cu - N(2), 2.01(1) Å; Cu - N(4), 2.02(1)Å; Cu - N(5), 2.02(1)Å; Cu - N(6), 2.23(1)Å; Cu - N(7), 2.02(1)Å; N(1) - C(1), 1.38(2)Å; Cu - C(2), 1.34(2)Å; N(5)-O(2), 2.88(2)Å; N(6)-O(2), 2.93(1)Å; N(7)-O(1), 2.78(2)Å; N(1)-O(3), 2.63(1)Å; and N(3)-O(4), 2.63(2) Å.

Fig. 3. ORTEP view of the complex $[Cu^{II}(tacn)(Hbim)](ClO_4){\cdot}MeOH$ (**3**).

amine (salenNMe$_2$) in place of the neutral, triazamacrocycle ligand of tacn in complex **3**. Thus, a neutral complex of a copper(II) with Hbim$^-$ and salenNMe$_2$, [Cu^{II}(salenNMe$_2$)(Hbim)]$_2$ (**4**), was designed and synthesized [10]. The desired neutral complex was obtained by treatment of [Cu(salenNMe$_2$)(H$_2$bim)]ClO$_4$ with an equimolar amount of Me$_4$NOH in ethanol in 26% yield.



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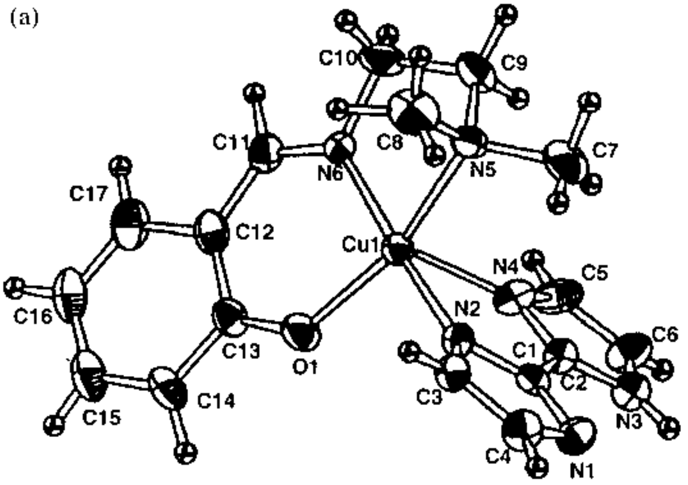
In this system, the tridentate ligand cannot donate a hydrogen bond and the methyl groups suppress the coordination of a solvent molecule to axial coordination positions [17]. However, an equatorial coordination position is available for binding to the Hbim$^-$ ligand. An ORTEP view of complex **4** is shown in Fig. 4 (a) along with the numbering scheme.

The primary coordination sphere of complex **4** is pseudo-square pyramidal with the tridentate Schiff base. It has N(2) of the Hbim$^-$ monoanion defining the equatorial plane and N(4) of the coordinated Hbim$^-$ ligand occupying one of the axial positions. The Hbim$^-$ ligand acts as a chelate ligand employing both equatorial and axial ligations [17,18].

The most important intermolecular interaction found in the crystal packing is formation of the dimeric hydrogen bonding [N(1)–N(3) 2.83(10) Å] as in complex **1** (Fig. 4 (b)). The two Hbim$^-$ skeletons connected by the hydrogen bonds of double NH···N types are coplanar to each other. The shortest Cu···Cu distance is 6.72 Å between the dimeric units along the *a* axis. The Cu···Cu distance through the hydrogen-bonded ligands in a dimeric unit is 10.60 Å. We measured magnetic susceptibility on powered samples in the range of 2.5–270 K. A weak antiferromagnetic interaction between Cu(II) ions ($\mu_{\mathrm{eff}} = 1.86$ μB (270 K), 1.70 μB (2.5 K)) was observed, which is caused by dipole–dipole interaction between the dimeric units. The exchange interaction in a hydrogen-bonded dimeric unit is presumed to be very weak, since the Cu–Cu distance is so long.

In the literature, complementary hydrogen-bonded neutral metal complexes containing a Hbim$^-$ ligand were proposed, but no crystal structures were reported [19]. For example, the neutral complexes such as [M(CO)$_2$(Hbim)] and [M(COD)(Hbim)] [19a], [Pd(η^3-2-RC$_3$H$_4$)(Hbim)](R = H, Me) [19b], [Mn(CO)$_2$(Hbim)L$_2$] [19c], [Mn(η^5-C$_5$H$_5$)(CO)$_2$(Hbim)] and [Rh(η^5-C$_5$H$_5$)Cl(Hbim)] [19d], [MH(CO)(PPh$_3$)$_2$(Hbim)] (M = Ru, Os) [19f], and [OsCl(η^2-H$_2$)(Hbim)(P^{i}Pr$_3$)$_2$] [19h] are presumed to form the dimer structure but no X-ray crystal analyses were performed. The structures of such complexes were tentatively assigned from the analysis of IR spectra; that is to say, the IR spectra showed medium strong signals around 1800 ~ 1900 cm^{-1}. The signals are assigned to 2γ(NH) secondary bending vibration [20]. Furthermore, the IR spectra showed a broad absorption band around 2500 cm^{-1}, which is assigned to intermolecular



Cu(1) - O(1), 1.933(6) Å; Cu(1) - N(2), 1.970(6) Å; Cu(1) - N(4), 2.365(7) Å; Cu(1) - N(5), 2.082(6) Å; Cu(1) - N(6), 1.962(6) Å; N(1) - C(1) , 1.344(9) Å; N(1) - C(4), 1.38(1) Å; N(1)-N(3), 2.83(10) Å.

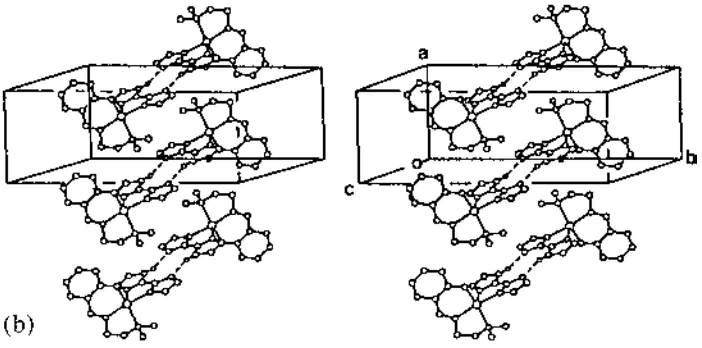


Fig. 4. (a) ORTEP view of the hydrogen-bonded dimer complex $[Cu^{II}(salenNMe_2)(Hbim)]_2$ (**4**). (b) Stereoview of crystal-packing for complex **4**. The dotted lines represent complementary intermolecular hydrogen bondings.

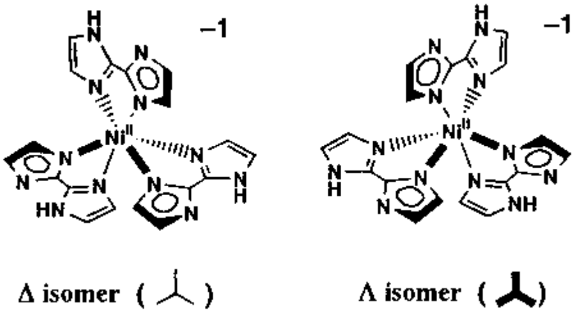
hydrogen-bonded N–H stretching. The signal of ν(NH) stretching vibration is shifted ca. 500 cm^{-1} toward low frequency by general hydrogen bonds. Those complexes are believed to form intermolecular hydrogen-bonded dimers between $Hbim^-$ ligands. The IR spectrum of complex **4** possesses all these characteristic features. Therefore the assignments of the dimeric structures mentioned above are partly confirmed by X-ray crystal structure analysis of complex **4**.

4. New anionic building block $[Ni(Hbim)_3]^-$

In this way, we determined the first crystal structure of a hydrogen-bonded dimer bridging a transition metal ion by the complementary hydrogen bond between two $Hbim^-$ ligands in complex **4**. It was then planned to flexibly control the crystal structure by self-assembly using configurations of transition metal ions and complementary intermolecular hydrogen bonds. We designed a new anionic building block, a tris-biimidazolate nickel(II) complex (**5**) $[Ni^{II}(Hbim)_3]^-$, where the biimidazolate ligand with bidentate chelate ability possesses three complementary hydrogen-bonding sites. In fact, we found that a new, simple one-pot procedure mixing the Ni(II) ion, the $Hbim^-$ and a counter cation produces the self-assembling crystals with complementary hydrogen bonds based on building block **5**. It is possible to make up a variety of self-assembling networks with long-range orders depending upon the kind of counter cations [11].

As a common feature, all crystals contain anionic building block **5**, in which the central Ni(II) atom is coordinated by three bidentate $Hbim^-$ ligands through lone pairs of the imine nitrogen atoms in the imidazole rings. Building block **5** has an approximate point group D_3 symmetry, whose Δ and Λ isomers are illustrated in Fig. 5. The coordination geometry is a distorted octahedron. The distortion results from small N–Ni–N bite angles between 75 and 81°, which are similar to those of $[Ni(bpy)_3]^{2+}$ (79°) and $[Ni(phen)_3]^{2+}$ (79°) [21].

As shown in Fig. 6, we obtained four types of hydrogen-bonded and coordination-bonded molecular architectures of building block **5**: (1) a zero-dimensional (0-D) dot structure with no complementary hydrogen bonds, (2) a 1-D hydrogen-bonded zigzag ribbon, (3) a 2-D hydrogen-bonded honeycomb sheet, and (4) a 3-D supra-cross-catenated network. The results indicate formation of an unexpected example of 3-D supra-cross-catenated self-organization with counter-cation specificity, which shows unambiguously that nature surpasses our prediction or imagination for the mode of the self-assembly of building blocks.



Δ isomer

Λ isomer

Fig. 5. Λ and Δ isomers of building blocks $[Ni(Hbim)_3]^-$ (**5**) and their schematic symbols.

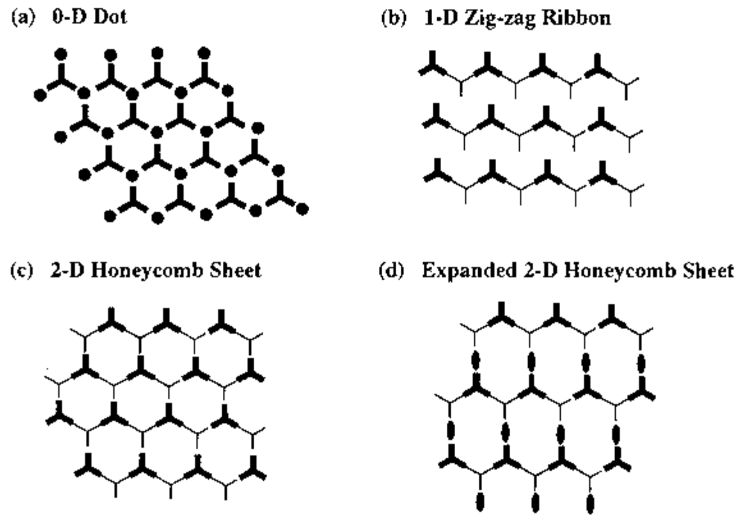


Fig. 6. Schematic representations of four types of the hydrogen-bonded networks using building blocks $[\mathrm{Ni(Hbim)_3}]^-$ (**5**). (●): a water molecule and (▮): a free 2,2′-biimidazole for intermediate spacers.

5. Multi-dimensional structures

The crystals, $[\mathrm{Ni^{II}(Hbim)_3}](\mathrm{NMe_4})\cdot 2\mathrm{H_2O}$ (**6**) and $[\mathrm{Ni^{II}(Hbim)_3}](\mathrm{NEt_4})\cdot 2\mathrm{H_2O}$ (**7**) built up by building block **5** with tetramethyl ammonium ion ($\mathrm{NMe_4^+}$) and tetraethyl ammonium ion ($\mathrm{NEt_4^+}$) as a counter cation are those with a ‘0-D dot’ structure. We have shown in Fig. 7 one crystal structure containing a $\mathrm{NEt_4^+}$ ion. Although the three hydrogen-bonding sites of **5** form no complementary hydrogen bonds between the ligands, what we call a 0-D structure, water molecules connect them to make a sheet arrangement by hydrogen bondings along the *ab* plane (Fig. 6(a)). The counter cation $\mathrm{NEt_4^+}$ occupies the cavity formed by three building block **5**.

The crystals, $[\mathrm{Ni^{II}(Hbim)_3}](\mathrm{N^{\mathit{n}}Pr_4})\cdot\mathrm{MeOH}$ (**8**), $[\mathrm{Ni^{II}(Hbim)_3}](\mathrm{N^{\mathit{n}}Bu_4})\cdot\mathrm{MeOH}$ (**9**) and $[\mathrm{Ni^{II}(Hbim)_3}](\mathrm{Etpy})\cdot\mathrm{MeOH}$ (**10**) containing tetra-*n*-propyl ammonium ion ($\mathrm{N^{\mathit{n}}Pr_4^+}$), tetra-*n*-butyl ammonium ion ($\mathrm{N^{\mathit{n}}Bu_4^+}$) and 1-ethyl pyridinium ion ($\mathrm{Etpy^+}$) ion, respectively, as a counter cation are among those with an 1-D zigzag ribbon structure. Fig. 8 shows the crystal structure of crystal **9**. One of the hydrogen-bonding sites oriented towards the *b* axis is blocked by hydrogen bonding with a methanol molecule. The other two sites are linked by complementary binary hydrogen bonds of NH···N type to produce a 1-D zigzag ribbon structure of building block **5** along the *a* axis (Fig. 6(b)). The counter cation $\mathrm{N^{\mathit{n}}Bu_4^+}$ occupies the cavity between the 1-D zigzag ribbons.

The crystals, $[\mathrm{Ni^{II}(Hbim)_3}][\mathrm{K{-}Cryp}]$ (**11**) and $[\mathrm{Ni^{II}(Hbim)_3}][\mathrm{K{-}DCH(18\text{-}crown\text{-}6)}]$ (**12**) containing a potassium cryptand complex ($[\mathrm{K{-}Cryp}]^+$) and a potassium

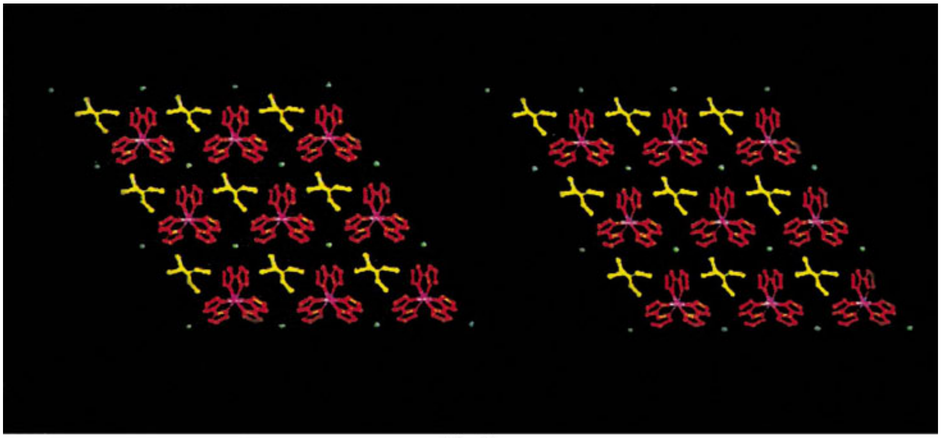


Fig. 7

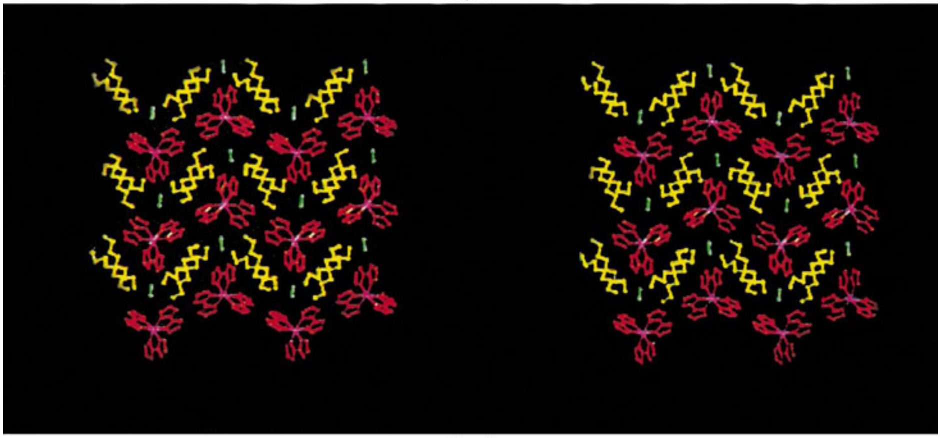


Fig. 8

Fig. 7. Stereoview of ‘zero-dimensional dot’ structure without complementary hydrogen bonds between the ligands in $[Ni(Hbim)_3][NEt_4]$ (**7**).
Fig. 8. Stereoviews of 1-D zigzag ribbon structure in $[Ni(Hbim)_3][N^nBu_4]$ (**9**).

cis-*syn*-*cis*-dicyclohexano-18-crown-6 complex ($[K–DCH(18\text{-crown-}6)]^+$)(Figs. 9(a) and 9(b)), as a counter cation are among those with a 2-D honeycomb sheet structure. Fig. 9(c) shows the 2-D honeycomb-sheet structure of crystal **11**. The characteristic structural feature is that they all have a microporous structure with a large diameter (Fig. 9(d)). All three hydrogen-bonding sites of building block **5** form complementary intermolecular hydrogen bonds. Two of the hydrogen-bonding sites make a 1-D hydrogen-bonded zigzag ribbon like crystal **9**. These ribbons are connected to each other by the remaining hydrogen-bonding site to form the 2-D honeycomb sheets along the *ab* plane (Fig. 9(e)). The six-membered building blocks are constructed by the alternate arrangement of Δ and Λ optical isomers (Fig. 6(c)). The 2-D sheet stacks along the *c* axis to produce the channel structures.

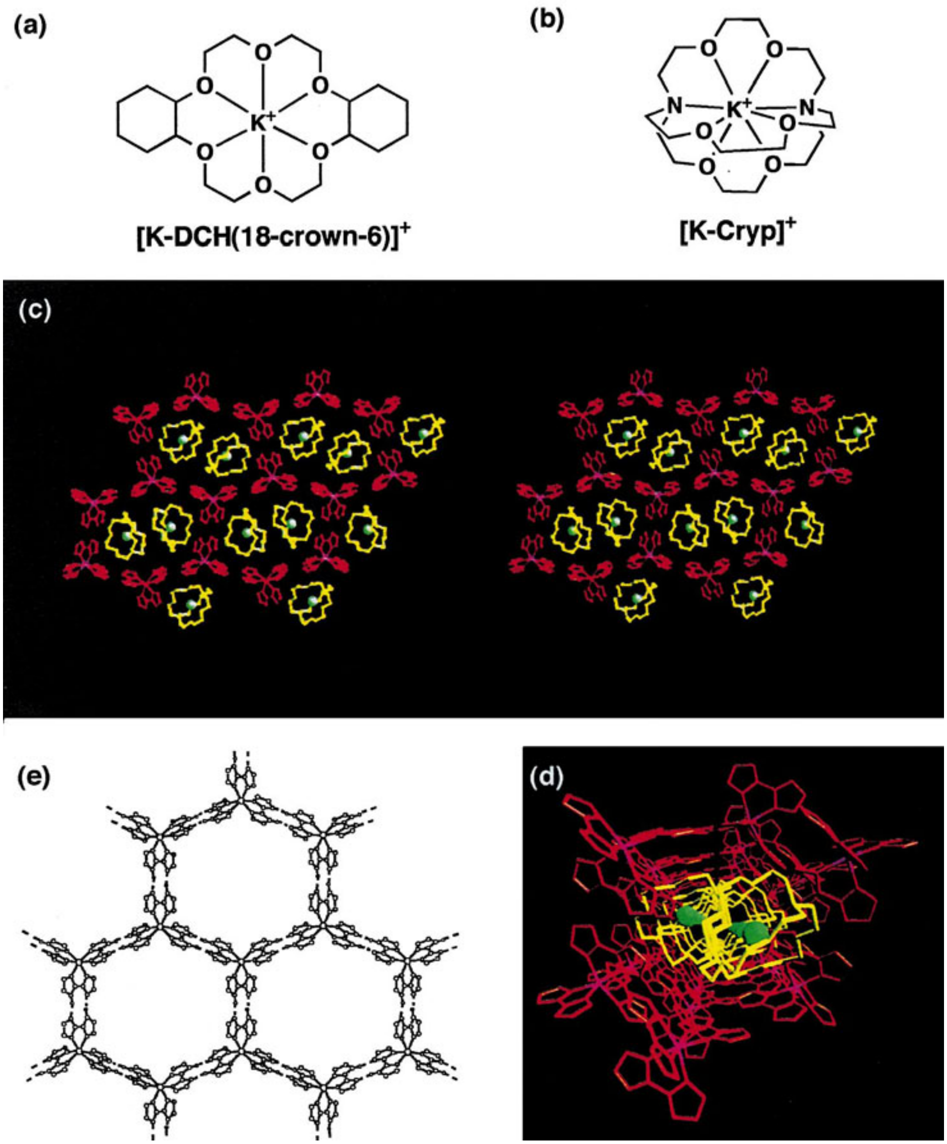


Fig. 9. (a) Potassium cryptand complex ($[K–Cryp]^+$) (b) Potassium *cis*-*syn*-*cis*-dicyclohexano-18-crown-6 complex ($[K–DCH(18\text{-crown-}6)]^+$). (c) Stereoview of 2-D honeycomb sheets in $[Ni(Hbim)_3][K–Cryp]$ (**11**). (d) Hydrogen-bonded network structure of a 2-D honeycomb sheet. (e) A perspective view of the microporous structure with a large channel formed by six $[Ni(Hbim)_3]^-$ (**5**) building blocks and two K^+–cryptand complexes.

The crystals $\{[Ni^{II}(Hbim)_3](NEt_4)\}_2(H_2bim)$ (**13**) and $\{[Ni^{II}(Hbim)_3]$-$(NMeEt_3)\}_2(H_2bim)$ (**14**) containing a NEt_4^+ cation and a methyl-triethyl ammonium ion ($NMeEt_3^+$) as a counter cation are among those with a 2-D expanded honeycomb sheet structure. Fig. 10(a) shows this structure containing the crystal **14**. The crystal structure shows an unprecedented example of a 3-D supra-cross-catenated self-organization based on hydrogen-bonded networks of building block **5** (Fig. 6(d)). First, this crystal has a 1-D zigzag ribbon structure similar to crystal **11**. Next, free neutral H_2bim ligands connect that 1-D ribbon array by complementary hydrogen bonds to form an expanded 2-D honeycomb sheet structure. Then, the sheets interpenetrate each other with a perpendicular orientation to construct a cross double-interlocking catenate structure (Fig. 10(b)). Finally, the catenated structure is arranged in 3-D to form an infinite polycatenated structure (Fig. 10(c)).

6. Conclusions

We found that the $Hbim^-$ ligand has an important function of controlling crystal structures by one-pot self-assembly using simultaneously, both the configuration of a transition metal ion and a complementary intermolecular hydrogen bond. First, we proved that the $Hbim^-$ ligand can form a complementary hydrogen bond by X-ray crystal structure analysis of complex **4**. Based on this fundamental result, we utilized the $Hbim^-$ ligand to control the molecular arrangements in crystal by designing a new anionic building block **5**.

The production of the four types of molecular architecture by one-pot molecular self-organization of building block **5** evolves from three fundamental factors: (1) three complementary binary hydrogen-bonding sites, (2) Δ and Λ optical isomers in the chiral coordination mode, and (3) the kind of counter cations. Each crystal has a different kind of counter cation: alkyl pyridinium, alkyl ammoniums or crown ether derivatives, as shown in Table 1. Our results indicate that the mode of self-organization can be controlled by varying the kind of counter cation, although at this stage the prediction of the cation specificity is difficult. Interestingly, we have succeeded systematically in the organization of building block **5** for the creation of microporous structures with large channels containing counter cations $[K–Cryp]^+$ and $[K–DCH(18\text{-crown-}6)]^+$, and the 3-D double-interlocking polycatenate structures containing the counter cations NEt_4^+ and $NMeEt_3^+$. Our further study will be aimed at comprehending the mutual relationship between hydrogen-bonded super-

Table 1
Dimensionalities of crystal structures constructed by building blocks **5** depending upon the type of counter cations

Dimensionality	Counter cations
0	NEt_4^+ NMe_4^+
1	$N^nPr_4^+$ $N^nBu_4^+$ $Etpy^+$
2	$[K–Cryp]^+$ $[K–DCH\ (18\text{-crown-}6)]^+$
3	NEt_4^+ $NmeEt_3^+$

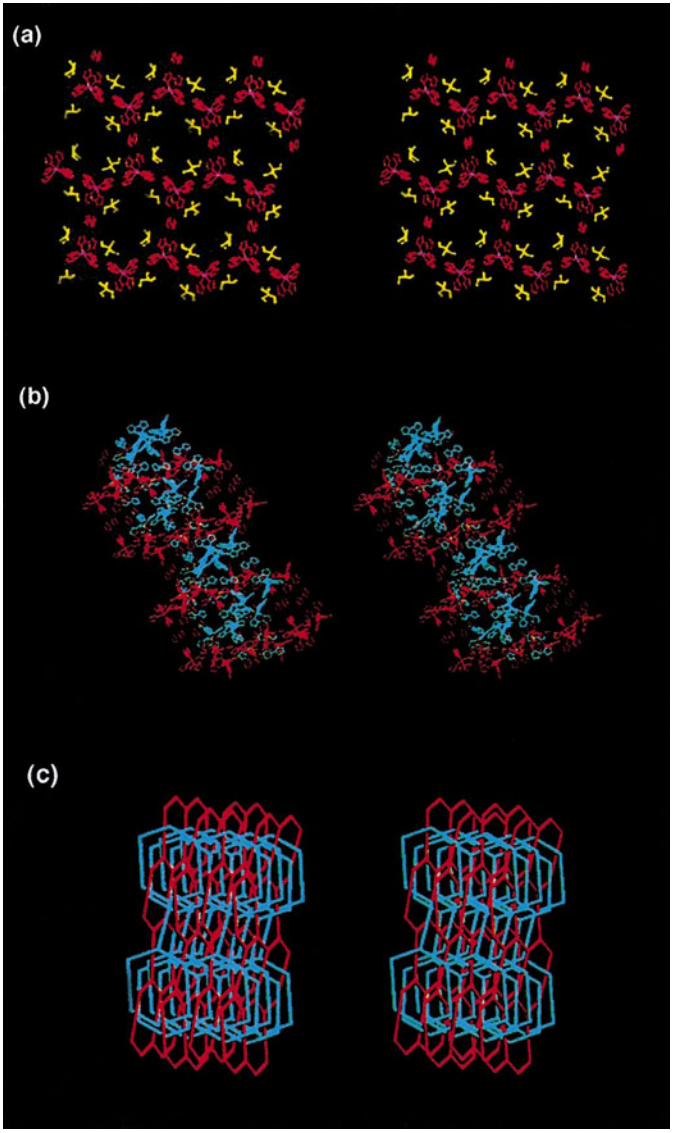


Fig. 10. (a) Stereoviews of 2-D expanded honeycomb sheet structure in $\{[Ni^{II}(Hbim)_3](NMeEt_3)\}_2(H_2bim)$ (**14**). The free neutral H_2bim ligands connect zigzag ribbons through complementary hydrogen bonds to form an expanded sheet structure. (b) A part of the polycatenate network for the crystal. (c) Schematic drawing of the polycatenate network for the crystal in three-dimension; the straight lines represent the distance between nickel ions in two $[Ni(Hbim)_3]^-$ (**5**) building blocks. A 3-D double-interlocking structure is formed by two sets of stacked honeycomb sheets (red and blue) that are perpendicular to each other.

structures of the building block and the kind or shape of component counter cations. Elucidation of the role of counter cations in self-assembly is important to predict the crystal structures and to understand the crystal structure engineering in these systems.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 10146103) on Priority Areas from the Ministry of Education, Science Sports and Culture, Japan. The authors thank the persons of the Analytical Center, Osaka City University, for the use of their 4-circle single crystal X-ray diffractometer and elemental analysis.

References

[1] J.-M. Lehn, Supramolecular Chemistry, VHC, Weinheim, 1995.
[2] (a) G.M. Whitesides, J.P. Mathias, C.T. Seto, Science 254 (1991) 1312. (b) J. Rebeck, Jr., Angew. Chem. Int. Ed. Engl. 29 (1990) 254.
[3] (a) S. Subramanian, M.J. Zaworotko, Coord. Chem. Rev. 137 (1994) 357. (b) O. Ermer, J. Am. Chem. Soc. 110 (1988) 3747.
[4] (a) M.C. Etter, Acc. Chem. Res. 23 (1990) 120. (b) C.B. Aakeröy, K.R. Seddon, Chem. Soc. Rev. 26 (1993) 397.
[5] I. Weissbuch, R.P. Biro, M. Lahav, L. Leiserowitz, Acta Crystallogr. Sect. B 51 (1995) 115.
[6] (a) G.R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam, 1989. (b) G.R. Desiraju, Angew. Chem. Int. Ed. Engl. 34 (1995) 2311.
[7] J.C. MacDonald, G.M. Whitesides, Chem. Rev. 94 (1994) 2383.
[8] (a) M.J. Zaworotko, Chem. Soc. Rev. 137 (1994) 283. (b) A.D. Burrows, C.-W. Chan, M.M. Chowdhry, J.E. McGrady, D.M.P. Mingos, Chem. Soc. Rev. 138 (1995) 329.
[9] M.M. Chowdhry, D.M.P. Mingos, A.J.P. White, D.J. Williams, Chem. Commun. (1996) 899.
[10] (a) M. Tadokoro, J. Toyoda, K. Isobe, T. Itoh, A. Miyazaki, T. Enoki, K. Nakasuji, Chem. Lett. (1995) 613. (b) M. Tadokoro, K. Isobe, A. Miyazaki, T. Enoki, K. Nakasuji, Mol. Cryst. Liq. Cryst. 278 (1996) 199.
[11] M. Tadokoro, K. Isobe, H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro, K. Nakasuji, Angew. Chem. Int. Ed. Engl. 38 (1999) 95.
[12] S.W. Kaiser, R.B. Saillant, W.M. Butler, P.G. Rusmussen, Inorg. Chem. 15 (1976) 2681.
[13] D.T. Cromer, R.R. Ryan, C.B. Storm, Acta Crystallogr. Sect. C 43 (1987) 1435.
[14] For example: (a) A.D. Mighell, C.W. Reimann, F.A. Mauer, Acta Crystallogr. Sect. B 25 (1969) 60. (b) I.G. Dance, A.S. Abushamleh, H.A. Goodwin, Inorg. Chim. Acta 43 (1980) 217. (c) C. Kirchner, B. Krebs, Inorg. Chem. 26 (1987) 3569. (d) A. Bencini, F. Mani, Inorg. Chim. Acta 154 (1988) 215. (e) S.-J. Liu, C.-C. Su, Polyhedron 15 (1996) 1141.
[15] For example: (a) F. Holmes, K.M. Jones, E.G. Torrible, J. Chem. Soc. (1961) 4790. (b) A.S. Abushamleh, H.A. Goodwin, Aust. J. Chem. 32 (1979) 513.
[16] M.A.M. Lorente, F. Dahan, Y. Sanakis, V. Petrouleas, A. Bousseksou, J.-P. Tuchagues, Inorg. Chem. 34 (1995) 5346.
[17] T.J. Kistenmacher, D.J. Szalda, C.C. Chiang, M. Rossi, L.G. Marzilli, Inorg. Chem. 17 (1978) 2582.
[18] D.J. Szalda, T.J. Kistenmacher, L.G. Marzilli, J. Am. Chem. Soc. 98 (1976) 8371.

[19] For example: (a) S.W. Kaiser, R.B. Saillant, W.M. Butler, P.G. Rasmussen, Inorg. Chem. 15 (1976) 2681. (b) R. Usón, J. Gimeno, L.A. Ora, J.M. Martínez de llarduya, J.A. Cabeza, J. Chem. Soc. Dalton Trans. (1983) 1729. (c) M.P. Gamasa, E. Garcia, J. Gimeno, J. Organomet. Chem. 307 (1986) 39. (d) L.A. Ora, D. Carmona, M.P. Lamata, A. Tiripicchio, F.J. Lahoz, J. Chem. Soc. Dalton Trans. (1986) 15. (e) D.P. Rillema, R. Sahai, P. Matthews, A.K. Edwards, R.J. Shaver, L. Morgan, Inorg. Chem. 29 (1990) 167. (f) M.P. Garcia, A.M. López, M.A. Esteruelas, F.J. Lahoz, L.A. Ora, J. Chem. Soc. Dalton Trans. (1990) 3465. (g) S.S. Kandil, L.H. Madkour, Spectrosc. Lett. 26 (1993) 535. (h) M.A. Esteruelas, F.J. Lahoz, L.A. Ora, E. Oñate, N. Ruiz, Inorg. Chem. 33 (1994) 787. (i) H. Kanno, S. Manriki, E. Yamazaki, S. Utsuno, J. Fujita, Bull. Chem. Soc. Jpn. 69 (1996) 1981. (j) M.A. Esteruelas, F.J. Lahoz, A.M. López, E. Oñate, L.A. Oro, N. Ruiz, E. Soda, J. Tolosa, Inorg. Chem. 35 (1996) 7811.

[20] Z. Malarski, L. Sobczyk, Spectrochem. Acta 48A (1992) 519.

[21] (a) A. Wada, C. Katayama, J. Tanaka, Acta Crystallogr. Sect. B 32 (1976) 3194. (b) B.A. Frenz, J.A. Ibers, Inorg. Chem. 11 (1972) 1109.