Design and Structural Extension of a Supramolecular Inclusion-Compound Host Made by the Formation of Dimers of Isonicotinic Acid and Thiocyanato Coordinating Bridges

Ryo Sekiya and Shin-ichi Nishikiori*[a]

Abstract: A new host design for an inclusion compound with a preference for large planar aromatic guest molecules has been proposed. Our host design includes a rectangular cavity made using a long and a short building block based on the concept of supramolecular chemistry. The long building block facilitates the inclusion of large guests, and the short building block prevents the formation of an interpenetrated structure, which is often observed in frameworks with large void spaces. The long building block is made when dimers of 4-pyridinecarboxylic acid (isoH) form through hydrogen bonding between the two carboxylic acid moieties. This isoH dimer can link two transition metal centers using the N atoms at both ends to act as a long building block. For the short building block, the thiocyanato ion was used. This makes a bent bridge between two metal centers to form a 1D double-chain $[M(SCN)_2]_\infty$ complex. From the self-assembly of isoH, SCN^- and Ni^{2+}, a 2D network of $[Ni(SCN)_2(isoH)_2]_\infty$, in which the 1D $[Ni(SCN)_2]_\infty$ complexes are linked by the isoH dimers, is built up. The rectangular cavity is formed as a mesh within the 2D network. The crystal of our inclusion compound has a layered structure of 2D networks, and a 1D channel-like cavity penetrating the layered 2D networks is formed where guests may be included. Moreover, our host design has the advantage of easy extension of the host structure. Replacement of isoH with another component and use of three components is possible for making the long building block. In the latter case, a linear spacer having two carboxy groups is inserted into the isoH dimer to form a long building block with a trimer structure. Based on our host design, a series of new inclusion compounds were synthesized. The crystal structures of three compounds were determined by single crystal X-ray diffraction. These were a biphenyl inclusion compound $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}C_{12}H_{10}$ (the basic case), a 9,10-dichloroanthracene inclusion compound $[Ni(SCN)_2(acrylH)_2]\cdot\frac{1}{2}C_{14}H_8Cl_2$, where isoH is replaced with 3-(4-pyridinyl)-2-propenoic acid (acrylH), and a perylene inclusion compound $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}C_{20}H_{12}$, whose long building block is a trimer inserted with fumaric acid ($fumaricH_2$) as a linear spacer.

Keywords: crystal engineering · host–guest systems · hydrogen bonds · self-assembly · supramolecular chemistry

Introduction

Solid-state supramolecular chemistry and material science have shown quite spectacular advances over the last two decades. At the present time, supramolecular chemistry is one of the most prosperous fields in the whole of chemistry, and recent advances can be divided into three areas. The first aims at the construction of multi-dimensional supramolecular structures through self-assembly of various kinds of building blocks, from the viewpoint of structural interest.[1–3] The second targets particular solid state phenomena such as metallic conductivity,[4] superconductivity,[5] non-linear optical behavior[6] and molecular magnetism[7] invoked from the accumulation of composite organic molecules in a requisite manner. The third studies supramolecular inclusion compounds.[8, 9] Perhaps an ultimate purpose of the construction of such inclusion compounds is their chemical and/or physical properties, which originate from the structural arrangement of guests formed inside their structures. This is the purpose of the second category, and such inclusion compounds are constructed by multi-dimensional structures of the first category. The third category has an important application in combining the first and the second. A considerable amount of effort has been devoted to the former two categories, and many interesting and sophisticated compounds have been synthesized. In the last case, however, two problems still remain unsolved. The most troublesome obstacle is interpenetration.[2, 3, 10] Even though a host may have a desirable cavity size

[a] Prof. S.-i. Nishikiori, R. Sekiya
Department of Basic Science
Graduate School of Arts and Sciences, The University of Tokyo
Komaba, Meguro, Tokyo 153-8902 (Japan)
Fax: (+81) 3 5454 6569
E-mail: cnskor@mail.ecc.u-tokyo.ac.jp

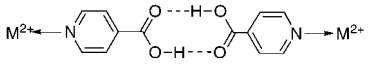
  0947-6539/02/0820-4803 $ 20.00+.50/0

for inclusion of a guest of interest at the appropriate stage of its design, in many cases the resultant compound has an interpenetrated structure and the guest is expelled from the cavity. In particular, use of a long building block, which is inevitable for constructing a large cavity suitable for a large guest, dramatically increases the possibility of forming such undesirable structures. The inclusion ability of these inclusion-compound hosts is significantly lowered or their guest species are restricted to small organic molecules such as solvents.[11–13] Another problem is the difficulty of controlling the construction of component molecules in the solid state. This difficulty comes from the fact that supramolecular structures are sensitive to many factors including the structure of component molecules, the functional groups of guests and the nature of counter ions and solvents.[11n, 14] As a result, the formation of undesired closed-packed structures is often observed and polymorphism also frequently takes place.[15] To predict the resultant structure is therefore difficult.

We believe that solving these problems is important and indispensable for the development of solid-state inclusion chemistry. Our main theme in this study is to establish a strategy for constructing an inclusion-compound host having the ability to include large guest molecules without forming an interpenetrated structure, based on the concept of supramolecular chemistry. In the following sections, we present the strategy of our fundamental host design and further structural development of the host. The crystal structures of three new inclusion compounds, which were synthesized in accordance with our host design, will be discussed.

Results and Discussion

Host Design: Our fundamental strategy for constructing an inclusion-compound host consists of two parts: formation of a linear long building block by the most simple and easy method possible, and construction of a host lattice with no interpenetrated structure using this long building blocks. In order to construct a host with the ability to include large guest molecules, a long building block is necessary. However, such a long building block requires multi-step synthetic procedures for its preparation and has a large molecular weight combined with poor solubility in common organic solvents. The latter point may cause a serious problem in the preparation of a host lattice using such a long building block. In this regard, a small building block is advantageous. With these contradictory demands in mind, we have designed a long building block based on the following strategy. Essentially, our strategy is not to directly synthesize a long building block, but to construct it through self-assembly of two small components. For connecting the two components, a certain interaction between them is inevitable. Among the interactions used in constructing supramolecular structures, hydrogen bonding is attractive because of its highly directional nature and relatively high bonding energy.[16–18] In order to use hydrogen bonding more efficiently, we considered employing the double hydrogen bonds of a carboxylic acid dimer. The enthalpy of formation of a carboxylic acid dimer was estimated to be 29.3–31.4 kJ mol^{-1}.[19] In the absence of strong competing hydrogen-bonding groups, we could therefore expect the dimer to form.[20] The resultant dimer usually has a straight and planar structure.[21] This predicted dimer structure is an indispensable factor for the construction of a pre-designed long building block. Considering the above, we first selected isonicotinic acid (4-pyridinecarboxylic acid, isoH) as a small component for making a long building block. As shown in Scheme 1, isoH can dimerize through the formation of a carboxylic acid dimer. The resultant molecular structure is long and planar. Both distal pyridyl N atoms of the dimer can coordinate to transition metal centers so that the isoH dimer acts as a bridging ligand, in the same way as 4,4′-bipyridine, a well known bridging ligand used in constructing multi-dimensional structures.[22]



Scheme 1. An isonicotinic acid (isoH) dimer as a building block.

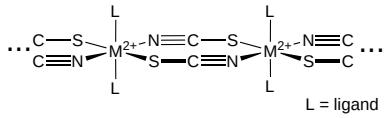
Next, we attempted to make a rectangular cavity using this isoH dimer. Our survey of recent works dealing with interpenetrated structures revealed that large square and polyhedral cavities constructed with long building blocks often provoke self-inclusion and interpenetration.[3, 10] To avoid such problems, we examined the possibility of a rectangular cavity, which is formed as a mesh in a 2D network and is framed by two long and two short building blocks.[23] The short dimension of a rectangular cavity prevents it from forming an interpenetrated structure of the 2D networks, and the long dimension contributes to the enlargement of its cavity space. At the same time, the dimensions may generate a guest preference of the cavity. The whole crystal structure of our inclusion compound is a layered structure of 2D networks. This layered structure forms a 1D arrangement of rectangular cavities and a 1D channel-type cavity penetrating the layered 2D networks formed there.

In order to make a rectangular cavity, we chose a SCN^- ion as a short building block. SCN^- ions can work as ambidentate ligands between transition metal centers to form a 1D double-chain structure as shown in Scheme 2.[24] If a divalent metal ion with an octahedral coordination form (M^{2+}) is used as a transition metal center, the $[M(SCN)_2]_\infty$ 1D complex has no

Abstract in Japanese:

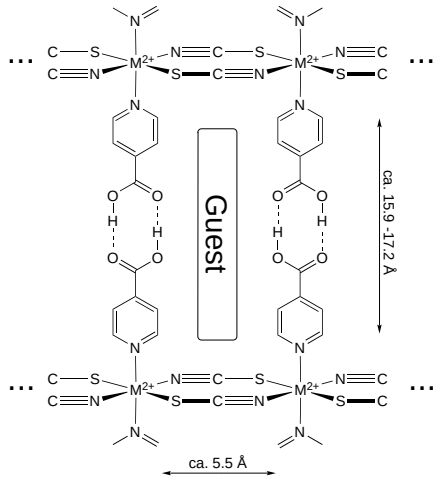
我々は、架橋チオシアン酸イオンとニッケルイオンから成る一次元錯体と水素結合によるイソニコチン酸二量体との自己集積により形成される新しい超分子包接体ホストの設計および合成をおこなった。この包接体ホストは、イソニコチン酸二量体が一次元錯体内のニッケルイオン間を架橋することで形成される二次元ネットワークが積層することで構築される。二次元ネットワーク中に 16.24 Å×5.5 Å の大きさを持つキャビティが形成され、この中にビフェニルをはじめ様々な芳香族化合物が包接された。また、このホストはイソニコチン酸二量体を 3-(4-ピリジル)-2-プロペン酸二量体に置き換えるか、イソニコチン酸二量体の間にフマル酸をスペーサーとして組み込み一種の三量体を形成させることで、キャビティの大きさを容易に拡張することが出来る。キャビティの大きさは前者が 20.98 Å×5.5 Å、後者は 23.72 Å×5.5 Å であり、9,10-ジクロロアントラセンとペリレンがそれぞれ包接された。

  0947-6539/02/0820-4804 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 20



Scheme 2. A 1D $[M(SCN)_2]_\infty$ complex formed with double chains of SCN^-.

electronic charge and the axial coordination sites of the metal ions are available to the isoH dimers. We expected a 2D network, as shown in Scheme 3, to be constructed by self-assembly of the two building blocks and M^{2+} ions. Rectangular cavities are formed as meshes of the 2D network. The



Scheme 3. A 2D network formed from isoH dimer building blocks and 1D $[M(SCN)_2]_\infty$ complexes.

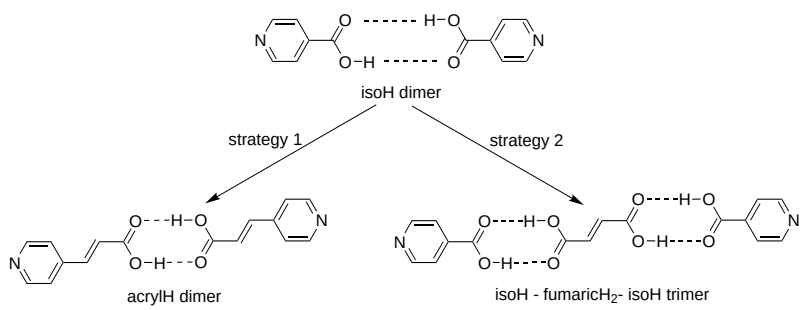
dimension of the long side of the rectangular cavity is 16–17 Å, which is the length of the isoH dimer building block, and that of the short side is 5–6 Å, which is the length of the SCN^- double bridge. The width of the rectangular cavity is expected to be narrow enough to prevent the formation of an interpenetrated structure and wide enough to accept a planar aromatic guest molecule.

Structural extension of host: Given the success of our method, namely the preparation of a long bridging block by self-assembly of small building blocks, we tried to develop the structure of the host. In the self-assembly process, the key feature is a carboxy group on the small building block. We first chose isoH as a small building block, because isoH is considered to be the simplest and most fundamental case. However, another choice was possible. In a subsequent step, we used 3-(4-pyridinyl)-2-propenoic acid (acrylH)[25] as a small building block. AcrylH is longer than isoH, forming as a result a dimer that is longer than the isoH dimer, as shown in Scheme 4. The resultant 2D network containing the acrylH dimer and the $[M(SCN)_2]_\infty$ 1D complex has rectangular cavities with greater height.

Moreover, it is possible to prepare a long bridging block by self-assembly of three components. As an example, we attempted to insert a fumaric acid molecule (fumaricH_2), which has two carboxy groups, into the isoH dimer as shown in Scheme 4. The fumaric acid molecule works as a linear spacer that connects two isoH molecules with a pair of double hydrogen bonds. The resultant trimer of isoH-fumaricH_2-isoH acts as a long bridging ligand. The insertion of the fumaric acid molecule causes a remarkable increase in the height of the rectangular cavity.

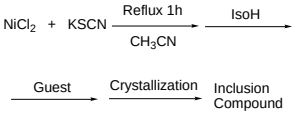
Synthesis: A series of new inclusion compounds with the chemical formula $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}G$ were obtained by the synthetic procedure outlined in Scheme 5. A small building block of isoH was used and Ni^{2+} provided the transition metal center.[26] The following were confirmed as molecules which it was possible to include as guests (G): anthracene,[26] naphthalene, naphthacene, phenanthrene, fluorene, 9-fluorenone oxime, biphenyl, *p*-terphenyl, mesitylene, styrene, 1,4-diethynylbenzene, thieno[3,2-*b*]thiophene, benz[*a*]-anthracene, anthraquinone, triphenylene, thianthrene, 9,10-dihydroanthracene, benzoic acid phenyl ester, azobenzene, pyrene, stylbene, 1,2,5,6-dibenzanthracene, chrysene, benzo[*a*]-pyrene, pentacene, quarter phenyl, diphenyl sulfide and 1,5-naphtalendiol. The inclusion compounds obtained were insoluble in common organic solvents except for aprotic solvents such as DMF and DMSO. The presence of the guests was confirmed by ^1H NMR spectra of their $[D_6]$DMSO solutions and the chemical formulae were determined by elemental analysis. Their IR spectra showed characteristic very strong absorptions at 2124 cm^{-1} and 1707 cm^{-1}. These indicate the presence of SCN^- and the carbonyl group of isoH, respectively. A broad absorption band observed in the range 2300–3400 cm^{-1} is presumed to originate from hydrogen bonds within the isoH dimer.

As examples of the host structures based on our host design, two more new types of inclusion compounds were synthesized: $[Ni(SCN)_2(acrylH)_2]\cdot\frac{1}{2}G$ (G = pyrene, 9,10-dichloroanthracene, phenanthrene, benz[*a*]anthracene, and coronene) and $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}G$ (G = perylene and naphthacene). These were obtained by preparative procedures similar to those shown in Scheme 5, but in the former case acrylH was used as a small building block instead of isoH and in the latter case fumaricH_2 was added as a linear



Scheme 4. Two strategies for structural extension from the isoH dimer building block by use of acrylH and fumaricH_2.

  0947-6539/02/0820-4805 $ 20.00+.50/0



Scheme 5. Procedure for the synthesis of an inclusion compound $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}G$.

spacer. Characterization was carried out by ^1H NMR, IR spectroscopy and elemental analysis similar to that performed on $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}G$.

Crystal structures: The crystal structures of a biphenyl inclusion compound $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}C_{12}H_{10}$ (**1**), a 9,10-dichloroanthracene inclusion compound $[Ni(SCN)_2(acrylH)_2]\cdot\frac{1}{2}C_{14}H_8Cl_2$ (**2**) and a perylene inclusion compound $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}C_{20}H_{12}$ (**3**) were determined by single crystal X-ray diffraction. Their hosts consist of 2D networks that are formed with the combination of long building blocks and $[Ni(SCN)_2]_\infty$ 1D double-chain complexes as predicted by Scheme 3. The structures of the long building blocks found in **1**–**3** are shown in Figure 1.

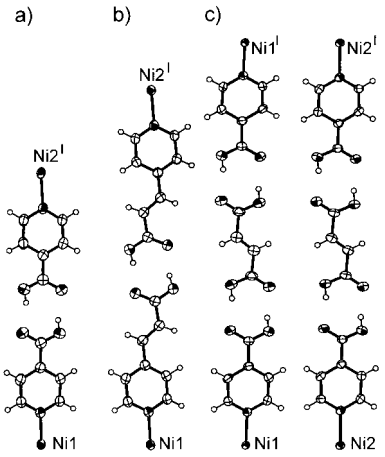


Figure 1. Structures of the long building blocks. a) Ni-isoH-isoH-Ni linkage in **1**. b) Ni-acrylH-acrylH-Ni linkage in **2**. c) Two Ni-isoH-fumaricH_2-isoH-Ni linkages in **3**. The Ni–Ni distances are 16.256(1) Å, 20.9826(8) Å and 23.722(5) Å for **1**, **2** and **3**, respectively. I = x, y, $z+1$.

The space group of **1** is $P\bar{1}$, and there are two crystallographically-independent Ni^{2+} ions which lie on independent inversion centers of the crystal. Each Ni^{2+} ion has an octahedral coordinated structure, in which two N atoms and two S atoms of two ambidentate SCN^- ligands occupy four equatorial sites. All SCN ligands form bent bridges between two Ni^{2+} ions to build up a 1D double-chain structure of $[Ni(SCN)_2]_\infty$ as shown in Scheme 2. The interval between two Ni^{2+} ions in the 1D complex is 5.5536(5) Å. The axial sites of the Ni^{2+} ion are coordinated by the pyridyl N atoms of isoH molecules from the upper and the lower side of the 1D complex. Two isoH molecules form an isoH dimer through double hydrogen bonds to their carboxy groups(Figure 1a). The isoH dimer links two Ni^{2+} ions in two adjacent 1D $[Ni(SCN)_2]_\infty$ complexes to form a linkage of Ni-isoH-isoH-Ni, whose length is 16.256(2) Å. The 1D $[Ni(SCN)_2]_\infty$ complex and the Ni-isoH-isoH-Ni linkage run along the b axis and the direction of [012], respectively, so that the $[Ni(SCN)_2(isoH)_2]_\infty$ 2D network spreads over the bc plane. These structural arrangements are shown in Figure 2a and 2b, which are projections along the bc plane and the b axis, respectively.

Figure 2a shows the plane of the $[Ni(SCN)_2(isoH)_2]_\infty$ 2D network and biphenyl guests. In the 2D network, two kinds of rectangular meshes framed by the isoH dimer building blocks and the SCN^- bridges, one wide and one narrow, are

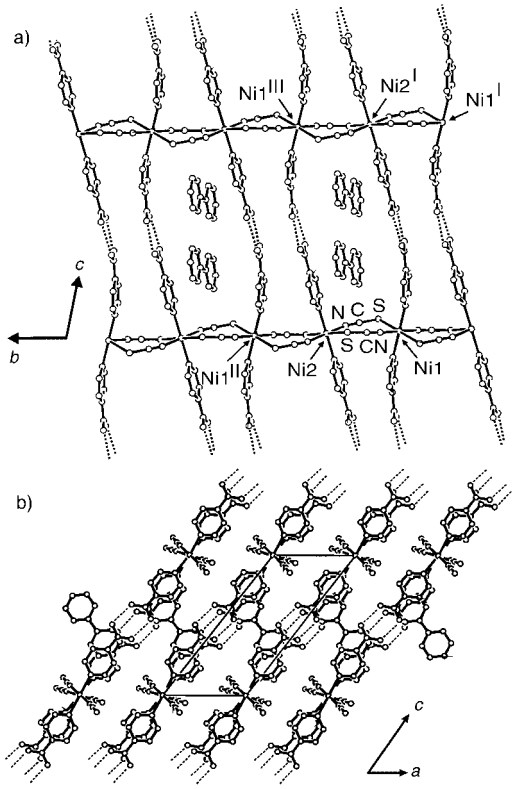


Figure 2. Crystal structure of $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}C_{12}H_{10}$ (**1**). a) A view projected onto the bc plane. A 2D network of $[Ni(SCN)_2(isoH)_2]_\infty$ and the biphenyl guests which are sandwiched by the 2D network are illustrated. b) A view along the b axis. The 2D $[Ni(SCN)_2(isoH)_2]_\infty$ networks are stacked along the a axis and biphenyl guests are arrayed in the 1D channel cavity penetrating the stacked 2D networks along the a axis. I = x, y, $z+1$; II = x, $y+1$, z; III = x, $y+1$, $z+1$.

generated. The isoH dimer building block is not completely flat but slightly waved. The two kinds of meshes are formed alternately along the b and the c axis as shown in Figure 2a. The wide mesh acts as a rectangular cavity, and includes a biphenyl molecule as a guest. On the other hand, the open space of the narrow mesh is occupied by the waved isoH dimers themselves so that the narrow mesh has no function as a cavity. The whole crystal structure of **1** is a layered structure of the 2D networks stacked along the a axis. Figure 2b shows this stacking scheme.

The molecular plane of the isoH dimer is almost perpendicular to the plane of the 2D network, and a biphenyl molecule, which has a planar structure, is sandwiched between the planes of four isoH dimers of two adjacent 2D networks. The molecular center of the biphenyl guest lies on an in-

  0947-6539/02/0820-4806 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 20

version center, being positioned at the midpoint between the two adjacent 2D networks. One benzene ring of the biphenyl guest is sandwiched by the isoH dimers of one 2D network, and the other benzene ring is sandwiched by the isoH dimers of another 2D network adjacent to the first one. This is repeated along the *a* axis in which direction the 2D networks stack. As a result, 1D channel cavities running along the *a* axis and penetrating the stacked 2D networks are formed; biphenyl guests are arrayed one-dimensionally there. Figure 2a shows the section of the 1D channel cavity and Figure 2b shows the arrangement of the biphenyl guests in the 1D channel cavity. These are related by the inversion centers of the crystal, so that the orientation of all guests is fixed to one direction.

The crystal structure of the 9,10-dichloroanthracene inclusion compound $[Ni(SCN)_2(acrylH)_2]\cdot\frac{1}{2}C_{14}H_8Cl_2$ (**2**) is very similar to that of **1** except for acrylH, which was replaced with isoH for extension of the host structure. The $[Ni(SCN)_2]_\infty$ 1D double-chain complex and the linkage of Ni-acrylH-acrylH-Ni run along the *b* axis and the direction of [012], respectively. A 2D network formed with the SCN^- bridges and the Ni-acrylH-acrylH-Ni linkages spreads over the *bc* plane. The lengths of the Ni-$(SCN)_2$-Ni and the Ni-acrylH-acrylH-Ni linkage are 5.5392(2) and 20.9826(8) Å, respectively. The structure of the Ni-acrylH-acrylH-Ni linkage is shown in Figure 1b. There is a wide mesh, which works as a rectangular cavity, and a narrow mesh with no function as a cavity in the 2D network, as is the case for **1**. The stacking scheme of the 2D networks, the formation of the 1D channel cavity and the arrangement of 9,10-dichloroanthracene guests in the 1D channel cavity are also same as was found for **1**. These similarities can be seen in Figure 3a and 3b, which show the host projected along the *bc* plane and also viewed along the *b* axis.

In $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}G$ (**3**), it was confirmed that a fumaric acid molecule works as a linear spacer between two isoH molecules as we aimed to achieve in our host design. The two carboxy groups of the fumaric acid connect two isoH molecules with a pair of double hydrogen bonds to make a long building block of a isoH-fumaricH_2-isoH trimer. This building block links two Ni^{2+} ions in two adjacent 1D $[Ni(SCN)_2]_\infty$ complexes to form a 2D network of $[Ni(SCN)_2(isoH)_2(fumaricH_2)]_\infty$. The whole crystal structure of **3** is a layered structure of the 2D networks similar to those found in **1** and **2**.

The space group of **3** is $P\bar{1}$. The unit cell contains two independent Ni^{2+} ions at independent inversion centers. There are two independent linkages of Ni-isoH-fumaricH_2-isoH-Ni, but their structures are very similar to each other as shown in Figure 1c. In both linkages, the center of the fumaricH_2 molecule lies on an inversion center of the crystal. The linkages run along the direction of the *c* axis so that they have the same length, 23.722(5) Å, which is the length of the *c* axis. The molecular planes of the linkages are slightly waved in an S-shape as shown in Figure 4. The $[Ni(SCN)_2]_\infty$ 1D complex extends along the *b* axis so that the $[Ni(SCN)_2(isoH)_2(fumaricH_2)]_\infty$ 2D network spreads over the *bc* plane. In the 2D network there is one kind of mesh framed by the SCN^- bridges and the two S-shaped linkages.

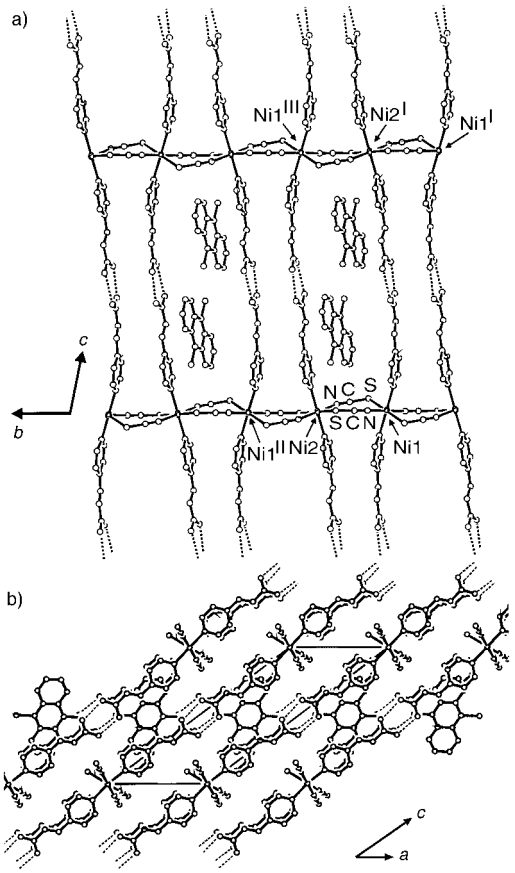


Figure 3. Crystal structure of $[Ni(SCN)_2(acrylH)_2]\cdot\frac{1}{2}C_{14}H_8Cl_2$ (**2**). a) A view projected on to the *bc* plane. The 2D network of $[Ni(SCN)_2(acrylH)_2]_\infty$ and 9,10-dichloroanthracene guests sandwiched by the 2D network are shown. b) A view along the *b* axis. The 2D $[Ni(SCN)_2(acrylH)_2]_\infty$ networks are stacked along the *a* axis, and 9,10-dichloroanthracene guests are arrayed in the 1D channel cavity penetrating the stacked 2D networks along the *a* axis. I = *x*, *y*, *z*+1; II = *x*, *y*+1, *z*; III = *x*, *y*+1, *z*+1.

The combination of the two S-shaped linkages generates wide and narrow parts in the mesh. The wide part of the mesh acts as a cavity and include a perylene guest molecule. The structure of the 2D network is shown in Figure 4, in which the structures of the mesh and the sandwiched perylene guest depicted. The center of the perylene guest lies on an inversion center which is located at the midpoint between two adjacent 2D networks stacked along the *a* axis. The perylene guest is sandwiched between the two adjacent 2D networks similarly to those seen in the cases of **1** and **2**. Figure 5 shows this structural arrangement. The length of the Ni-isoH-fumaricH_2-isoH-Ni linkage suggests potential ability to include guests larger than the guests of the $[Ni(SCN)_2(isoH)_2]_\infty$ and $[Ni(SCN)_2(acrylH)_2]_\infty$-type hosts. However, the waved structure of the long building block narrows the cavity space of the rectangular cavity.

The coordination structures of the Ni^{2+} ions in **1**, **2** and **3** were those such as may be observed in similar thiocyanato Ni complexes.[27] The lengths of Ni–N and Ni–S bonds in the 1D $[Ni(SCN)_2]_\infty$ complexes were in the ranges of 2.018(2)–2.045(8) Å, and 2.5102(9)–2.5642(6) Å, respectively. The bond angles of Ni-N-C and Ni-S-C were in the ranges

  0947-6539/02/0820-4807 $ 20.00+.50/0

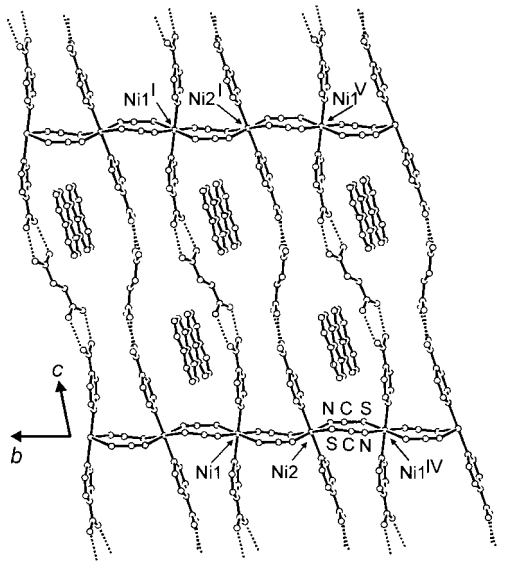


Figure 4. Crystal structure of $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}C_{20}H_{12}$ (**3**). A view projected on to the *bc* plane shows the structure of the 2D network of $[Ni(SCN)_2(isoH)_2(fumaricH_2)]_\infty$ and its rectangular cavity with wide and narrow gaps coming from the waved structure of the isoH-fumaricH_2-isoH trimer building blocks. The perylene guests are enclosed in the wide part of the cavity. I = x, y, $z+1$; IV = x, $y-1$, z; V = x, $y-1$, $z+1$.

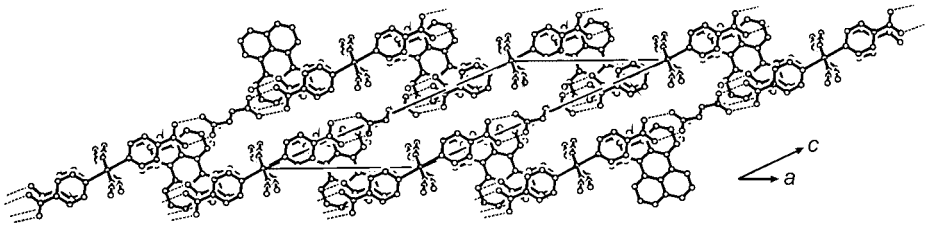


Figure 5. Crystal structure of $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}C_{20}H_{12}$ (**3**) viewed along the *b* axis. The 2D $[Ni(SCN)_2(isoH)_2(fumaricH_2)]_\infty$ networks are stacked along the *a* axis.

156.3(9) – 164.0(7)° and 97.94(16) – 101.95(10)°. The shortest distance between the guests and the long bridging blocks was found to be 3.430(6) Å for C(103) ··· C(22) in **1**, 3.393(5) Å for C(107) ··· C(22) in **2** and 3.271(18) Å for C(106) ··· O(204^{IV}) in **3** (IV: x, $y-1$, z), respectively. These data show the usual van der Waals contact. The lengths of the hydrogen bonds forming the carboxylic acid dimer structure are in the range 2.604(4) – 2.704(12) Å, normal for this type of hydrogen bond.[28] No structural abnormality was found in the guests of **1**, **2** and **3** except for slightly larger displacement factors due to thermal molecular motion.

Conclusion

We have proposed a strategy for constructing an inclusion-compound host. Specifically, a long building block is made by the dimer formation of two carboxy groups through double hydrogen bonding, and a host is formed by the combination of the long building blocks and thiocyanato coordinating bridges. Moreover, we have pointed out possibilities for extension of our host structure based on the concept of supramolecular chemistry, and have demonstrated two examples. In the first section of this paper we alluded to two problems in constructing a supramolecular inclusion compound host. The first is to avoid forming an interpenetrated structure, and the second is to control and predict the host structure. In respect of these points, our host design works well. No interpenetrated structure has been found in our preparative experiments. The formation of the long building blocks and the 2D network have usually been observed; the exception is when an aromatic species with a functional group stronger than a carboxy group and a SCN^- ligand with respect to forming a hydrogen bond and a coordinating bond has been used as a guest. However, in the case of fumaric acid being used as a linear spacer, the structural flexibility of the resultant long building block appeared and disturbed the expansion of the inclusion ability. In this regard, the second problem remains to be solved.

Besides the easy preparation, the predictable structure and the easy structural extension mentioned above, one of the remarkable properties of our host is its clear preference for planar aromatic guests. The inclusion of non-aromatic guests into our host has not been observed, and our host may accept large aromatics whose inclusion into existing hosts has been difficult due to their size. The complete orientational order of the included aromatic guests is also one of the properties of our host. The presence of strong anisotropy of the crystals originating in these structural features could be considered. These properties will be useful in the field of developing materials with interest in chemical and/or physical properties, such as chemical reactions in hosts, and optics.

Experimental Section

Preparation of $[Ni(SCN)_2(isoH)_2]\cdot\frac{1}{2}C_{12}H_{10}$ (1): KSCN (1.76 g, 18.1 mmol) was added with vigorous stirring to acetonitrile (100 mL) in which $NiCl_2\cdot 6H_2O$ (2.02 g, 8.5 mmol) was suspended, and the mixture refluxed for 1 h. Precipitated KCl was filtered off, and isonicotinic acid (2.09 g, 17.0 mmol) and biphenyl were added to the filtrate. Green crystals of the clathrate were obtained after slowly evaporating of the solvent over a period of a few days at ambient temperature. The crystals were collected, washed with acetonitrile, and dried in air. Elemental analysis calcd (%) for $C_{20}H_{15}N_4O_4S_2Ni$ (498.19): C 48.21, H 3.04, N 11.25; found: C 48.04, H 3.04, N 11.31.

Preparation of $[Ni(SCN)_2(acrylH)_2]\cdot\frac{1}{2}C_{14}H_8Cl_2$ (2): Green crystals of **2** were obtained by the same procedure used in the preparation of **1**, however, KSCN (2.15 g, 22.1 mmol), 3-(4-pyridyl)-2-acrylic acid[25] (2.6 g, 17 mmol) and 9,10-dichloroanthracene were used instead of KSCN (1.76 g, 18.1 mmol), isonicotinic acid and biphenyl, respectively. Elemental analysis calcd (%) for $C_{25}H_{18}N_4O_4ClS_2Ni$ (596.71): C 50.31, H 3.05, N 9.39; found: C 50.48, H 3.05, N 9.20.

Preparation of $[Ni(SCN)_2(isoH)_2(fumaricH_2)]\cdot\frac{1}{2}C_{20}H_{12}$ (3): KSCN (2.48 g, 2.5 mmol) was added with vigorous stirring to acetonitrile (100 mL) in which $NiCl_2\cdot 6H_2O$ (2.49 g, 10.1 mmol) was suspended. After refluxing the mixture for 1 h, precipitated KCl was filtered off, and isonicotinic acid (2.49 g, 20.2 mmol), fumaric acid (2.34 g, 20.2 mmol) and perylene were added. Brown crystals of the clathrate were obtained after slowly evaporating the solvent for a few days at ambient temperature. Elemental analysis calcd (%) for $C_{28}H_{20}N_4O_8S_2Ni$ (663.31): C 50.69, H 3.05, N 8.45; found: C 50.79, H 2.99, N 8.68.

0947-6539/02/0820-4808 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 20

X-ray Crystal structure determinations: The intensity data were collected on a Rigaku RAXIS-RAPID imaging plate area detector for **1** and **2** and on a Rigaku AFC-7R four-circular diffractometer for **3** using graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at ambient temperature. The crystal structures were solved by the direct method using the SHELXS-97 program[29] and refined by the successive differential Fourier syntheses and full-matrix least-squares procedure using the SHELXL-97 program.[30] Anisotropic thermal factors were applied to all non-hydrogen atoms. All hydrogen atoms were generated geometrically.

Crystal of 1: $C_{20}H_{15}N_4O_4S_2Ni$, $F_W = 498.19$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.5146(5)$ Å, $b = 11.107(1)$ Å, $c = 16.504(1)$ Å, $\alpha = 102.267(4)^\circ$, $\beta = 52.054(3)^\circ$, $\gamma = 96.638(4)^\circ$, $U = 1061.3(1)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 1.146$ mm^{-1}, $T = 293$ K. The intensity data collection was carried out for a $0.40 \times 0.20 \times 0.10$ mm green crystal in the range of $3.2 < 2\theta < 59.8^\circ$ with ω scan. Empirical absorption correction[31] was applied to 6026 reflections measured ($R_{int} = 0.021$), and 4747 independent reflections ($F_o > 4\sigma(F_o)$) were used for the analysis. The final reliability factors were $R1(F_o) = 0.0387$, $wR2(F_o^2) = 0.1103$ and GOF. = 1.111 for 283 parameters. The maximum and minimum electron density residues found in the final differential Fourier syntheses were +0.424 and −0.451 e Å^{-3}, respectively.

Crystal of 2: $C_{25}H_{18}N_4O_4ClS_2Ni$, $F_W = 596.71$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.2611(3)$ Å, $b = 11.0783(4)$ Å, $c = 21.3992(8)$ Å, $\alpha = 78.235(1)^\circ$, $\beta = 36.562(1)^\circ$, $\gamma = 81.068(1)^\circ$, $U = 1280.23(8)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 1.065$ mm^{-1}, $T = 293$ K. The intensity data collection was carried out for a $0.30 \times 0.10 \times 0.10$ mm green crystal in the range of $3.2 < 2\theta < 59.9^\circ$ with ω scan. Empirical absorption correction[31] was applied to 7195 reflections measured($R_{int} = 0.0280$), and 5678 independent reflections ($F_o > 4\sigma(F_o)$) were used for the analysis. The final reliability factors were $R1(F_o) = 0.0367$, $wR2(F_o^2) = 0.0903$ and GOF = 1.079 for 337 parameters. The maximum and minimum electron density residues found in the final differential Fourier syntheses were +0.431 and −0.419 e Å^{-3}, respectively.

Crystal of 3: $C_{28}H_{20}N_4O_8S_2Ni$, $F_W = 663.31$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.383(3)$ Å, $b = 11.007(2)$ Å, $c = 23.723(5)$ Å, $\alpha = 78.60(2)^\circ$, $\beta = 38.61(2)^\circ$, $\gamma = 109.70(2)^\circ$, $U = 1367.4(4)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.922$ mm^{-1}, $T = 293$ K. The intensity data collection was carried out for a $0.20 \times 0.20 \times 0.20$ mm brown crystal in the range $5.54 < 2\theta < 60.0^\circ$ with ω-2θ scan. No absorption correction was applied to the 8342 reflections measured, and 4461 independent reflections ($F_o > 3\sigma(F_o)$) were used for the analysis. The final reliability factors were $R1(F_o) = 0.0489$, $wR2(F_o^2) = 0.0983$ and GOF = 1.06 for 391 parameters. The maximum and minimum electron density residues found in the final differential Fourier syntheses were +0.436 and −0.421 e Å^{-3}, respectively.

CCDC-186249 (**1**), 186250 (**2**) and 186251 (**3**) contain the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research(A) Project No. 12354008 from the Japan Society for the Promotion of Science.

[1] a) S. M. Contakes, T. B. Rauchfuss, *Angew. Chem.* **2000**, *112*, 2060–2062; *Angew. Chem. Int. Ed.* **2000**, *39*, 1984–1986; b) R. D. Schnebeck, E. Freisinger, B. Lippert, *Eur. J. Inorg. Chem.* **2000**, 1193–1200; c) G. De Munno, M. Julve, F. Nicolo', F. Lloret, J. Faus, R. Ruiz, E. Sinn, *Angew. Chem.* **1993**, *105*, 588–590; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 613–615; d) D. M. L. Goodgame, S. Menzer, A. M. Smith, D. J. Williams, *Angew. Chem.* **1995**, *107*, 605–607; *Angew. Chem. Int. Ed.* **1995**, *34*, 574–575; e) M. L. Tong, S. L. Zheng, X. M. Chen, *Chem. Eur. J.* **2000**, *6*, 3729–3738; f) C. He, B. G. Zhang, C. Duan, J. Li, Q. J. Meng, *Eur. J. Inorg. Chem.* **2000**, 2549–2554; g) F. A. Cotton, C. Lin, C. A. Murillo, *Inorg. Chem.* **2001**, *40*, 478–484.

[2] P. J. Hagrmann, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798–2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684.

[3] R. Robson in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 733–755.

[4] J. Ferraris, D. O. Cowan, V. V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.

[5] J. M. Williams, M. A. Beno, H. H. Wang, P. C. W. Leung, T. J. Emge, U. Geiser, K. D. Carlson, *Acc. Chem. Res.* **1985**, *18*, 261–267.

[6] W. Lin, O. R. Evans, R. G. Xiong, Z. Wang, *J. Am. Chem. Soc.* **1998**, *120*, 13272–13273.

[7] a) M. A. S. Goher, M. A. M. Abu-Youssef, F. A. Mautner, R. Vicente, A. Escuer, *Eur. J. Inorg. Chem.* **2000**, 1819–1823; b) X. Hao, Y. Wei, S. Zhang, *Chem. Commun.* **2000**, 2271–2272; c) R. E. D. Sesto, A. M. Arif, J. S. Miller, *Inorg. Chem.* **2000**, *39*, 4894–4902; d) M. M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, *J. Am. Chem. Soc.* **1997**, *119*, 4369–4379.

[8] a) M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397; b) O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861–2868.

[9] T. Iwamoto in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 644–690.

[10] S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.

[11] a) E. Weber, J. Ahrendt, M. Czugler, I. Csöregh, *Angew. Chem.* **1986**, *98*, 719–721; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 746–748; b) R. K. R. Jetti, F. Xue, T. C. W. Mak, A. Nangia, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1223–1232; c) X. P. Yang, D. M. Du, Q. Li, T. C. W. Mak, H. N. C. Wong, *Chem. Commun.* **1999**, 1607–1608; d) K. Tanaka, D. Fujimoto, A. Altreuther, T. Oeser, H. Irngartinger, F. Toda, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2115–2120; e) R. Thaimattam, F. Xue, J. A. R. P. Sarma, T. C. W. Mak, G. R. Desiraju, *J. Am. Chem. Soc.* **2001**, *123*, 4432–4445; f) F. C. Krebs, M. Jørgensen, *J. Org. Chem.* **2001**, *66*, 6169–6173; g) G. J. Kemperman, R. de Gelder, F. J. Dommerholt, P. C. Raemakers-Franken, A. J. H. Kiunder, B. Zwanenburg, *Eur. J. Org. Chem.* **2001**, 3641–3650; h) M. Szyrszyng, E. Nowak, M. Gdaniec, M. J. Milewska, A. Herman, T. Polonski, *J. Org. Chem.* **2001**, *66*, 7380–7384; i) M. Sugahara, K. Sada, M. Miyata, *Chem. Commun.* **1999**, 293–294; j) K. Beketov, E. Weber, J. Seidel, K. Köhnke, K. Makhkamov, B. Ibragimov, *Chem. Commun.* **1999**, 91–92; k) M. R. Caira, A. Horne, L. R. Nassimbeni, F. Toda, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1717–1720; l) A. T. Ung, D. Gizachew, R. Bishop, M. L. Scudder, I. G. Dance, D. C. Craig, *J. Am. Chem. Soc.* **1995**, *117*, 8745–8756; m) R. D. Sommer, A. L. Rheingold, A. J. Goshe, B. Bosnich, *J. Am. Chem. Soc.* **2001**, *123*, 3940–3952; n) K. Biradha, D. Dennis, V. A. MacKinnon, C. V. K. Sharma, M. J. Zaworotko, *J. Am. Chem. Soc.* **1998**, *120*, 11894–11903; o) K. Endo, T. Ezuhara, M. Koyanagi, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1997**, *119*, 499–505; p) J. A. Swift, A. M. Pivovar, A. M. Reynolds, M. D. Ward, *J. Am. Chem. Soc.* **1998**, *120*, 5887–5894; q) M. Akazome, T. Takahashi, K. Ogura, *J. Org. Chem.* **1999**, *64*, 2293–2300.

[12] a) M. Miyata, K. Sada in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 147–176; b) P. Dastidar, I. Goldberg in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 305–350; c) F. Toda in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 465–516.

[13] J. Lipkowski in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 691–714.

[14] M. L. Tong, S. L. Zheng, X. M. Chen, *Chem. Eur. J.* **2000**, *6*, 3729–3738

[15] M. D. Hollingsworth, B. D. Santarsiero, K. D. M. Harris, *Angew. Chem.* **1994**, *106*, 698–701; *Angew. Chem. Int. Ed.* **1994**, *33*, 649–652.

[16] a) J. C. MacDonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383–2420; b) R. Taylor, O. Kennard, *Acc. Chem. Res.* **1984**, *17*, 320–326; c) G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed.* **1995**, *32*, 2311–2327; d) G. R. Desiraju, *Acc. Chem. Res.* **1996**, 29, 441–449; e) G. R. Desiraju, *Acc. Chem. Res.* **1991**, *24*, 290–296.

[17] a) S. S. Kuduva, D. C. Craig, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1999**, *121*, 1936–1944; b) P. Holý, J. Závada, I. Císaøová, J. Podlaha, *Angew. Chem.* **1999**, *111*, 393–395; *Angew. Chem. Int. Ed.* **1999**, *38*, 381–383.

[18] a) H. Koshima, S. Honke, *J. Org. Chem*. **1999**, *64*, 790 – 793; b) H. Koshima, S. Honke, J. Fujita, *J. Org. Chem*. **1999**, *64*, 3916 – 3921; c) K. Kinbara, Y. Harada, K. Saigo, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1339 – 2347; d) E. Batchelor, J. Klinowski, W. Jones, *J. Mater. Chem*. **2000**, *10*, 839 – 848; e) K. E. Schwiebert, D. N. Chin, J. C. MacDonald, G. M. Whitesides, *J. Am. Chem. Soc*. **1996**, *118*, 4018 – 4029; f) S. Palacin, D. N. Chin, E. E. Simanek, J. C. MacDonald, G. M. Whitesides, M. T. McBridge, G. T. R. Palmore, *J. Am. Chem. Soc*. **1997**, *119*, 11 807 – 11 816; g) M. Mazik, D. Bläser, R. Boese, *Chem. Eur. J*. **2000**, *6*, 2865 – 2873; h) C. B. Aakeröy, A. M. Beatty, D. S. Leinen, *Angew. Chem.* **1999**, *111*, 1932 – 1936; *Angew. Chem. Int. Ed.* **1999**, *38*, 1815 – 1819; i) C. B. Aakeröy, A. M. Beatty, D. S. Leinen, K. R. Lorimer, *Chem. Commun.* **2000**, 935 – 936; j) S. S. Kuduva, D. Bläser, R. Boese, G. R. Desiraju, *J. Org. Chem*. **2001**, *66*, 1621 – 2626; k) H. Suezawa, T. Yoshida, M. Hirota, H. Takahashi, Y. Umezawa, K. Honda, S. Tsuboyama, M. Nishio, *J. Chem. Soc. Perkin Trans. 2* **2001**, 2053 – 2058.

[19] a) X. Zhao, Y. Chang, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc*. **1990**, *112*, 6627 – 6634; b) L. A. Curtis, M. Blander, *Chem. Rev*. **1988**, *88*, 827 – 841.

[20] F. H. Allen, W. D. S. Motherwell, P. R. Raithby, G. P. Shields, R. Taylor, *New J. Chem.* **1999**, 25 – 34.

[21] L. Leiserowitz, *Acta Crystallogr. Sect. B* **1976**, *32*, 775 – 802.

[22] a) S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem.* **2000**, *111*, 2161 – 2164; *Angew. Chem. Int. Ed*. **2000**, *39*, 2082 – 2084; b) S. Subramanian, M. J. Zaworotko, *Angew. Chem.* **1995**, *107*, 2295 – 2297; *Angew. Chem. Int. Ed*. **1995**, *34*, 2127 – 2129.

[23] L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc*. **1998**, *120*, 2676 – 2677.

[24] a) R. G. Goel, W. P. Henry, M. J. Oliver, A. L. Beauchamp, *Inorg. Chem*. **1981**, *20*, 3924 – 3928; b) L. Tchertanov, C. Pascard, *Acta Crystallogr. Sect. B* **1997**, *53*, 904 – 915; c) G. Yang, H. G. Zhu, B. H. Liang, X. M. Chen, *J. Chem. Soc. Dalton Trans.* **2001**, 580 – 585.

[25] A. R. Katritzky, *J. Chem. Soc*. **1955**, 2581 – 2586.

[26] R. Sekiya, S. Nishikiori, *Chem. Commun*. **2001**, 2612 – 2613.

[27] a) M. Taniguchi, A. Ouchi, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3277 – 3278; b) R. Vincente, A. Escuer, J. Ribas, X. Solans, *J. Chem. Soc. Dalton Trans.* **1994**, 259 – 262; c) M. Monfort, C. Bastos, C. Diaz, J. Ribas, *Inorg. Chim. Acta* **1994**, *218*, 185 – 188; d) M. James, H. Kawaguchi, K. Tatsumi, T. W. Hambley, *Acta Crystallogr. Sect. C* **1998**, *54*, 1890 – 1811; e) A. Escuer, S. B. Kumar, F. Mautner, R. Vincente, *Inorg. Chim. Acta* **1988**, *269*, 313 – 316; f) T. K. Maji, I. R. Laskar, G. Mostafa, A. J. Welch, P. S. Mukherjee, N. R. Chaudhuri, *Polyhedron* **2001**, *20*, 651 – 655.

[28] D. Braga, F. Grepioni, P. Sabatino, G. R. Desiraju, *Organimetallics* **1994**, *13*, 3532 – 3543.

[29] G. M. Sheldrick, SHELXS-97, Program for the solution of crystal structures. University of Göttingen (Germany), **1997**.

[30] G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures. University of Göttingen (Germany), **1997**.

[31] PROCESS-AUTO, Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer, Rigaku Corporation, Tokyo (Japan), **1998**.

Received: May 24, 2002 [F4129]

  0947-6539/02/0820-4810 $ 20.00+.50/0