Research Article

Self-Organization of K^+ -Crown Ether Derivatives into Double-Columnar Arrays Controlled by Supramolecular Isomers of Hydrogen-Bonded Anionic Biimidazolate Ni Complexes

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Anionic tris (biimidazolate) nickelate (II) ($[Ni(Hbim)_3]^-$), which is a hydrogen-bonding (H-bonding) molecular building block, undergoes self-organization into honeycomb-sheet superstructures connected by complementary intermolecular H-bonds. The crystal obtained from the stacking of these sheets is assembled into channel frameworks, approximately 2 nm wide, that clathrate two cationic K^+ -crown ether derivatives organised into one-dimensional (1D) double-columnar arrays. In this study, we have shown that all five cationic guest-included crystals form nanochannel structures that clathrate the 1-D double-columnar arrays of one of the four types of K^+ -crown ether derivatives, one of which induces a polymorph. This is accomplished by adaptably fitting two types of anionic $[Ni(Hbim)_3]^-$ host arrays. One is a $\Delta\Lambda-\Delta\Lambda-\Delta\Lambda \cdots$ network with H-bonded linkages alternating between the two different optical isomers of the Δ and Λ types with flexible H-bonded $[Ni(Hbim)_3]^-$. The other is a $\Delta\Delta\Delta-\Lambda\Lambda\Lambda \cdots$ network of a racemate with 1-D H-bonded arrays of the same optical isomer for each type. Thus, $[Ni(Hbim)_3]^-$ can assemble large cations such as K^+ crown-ether derivatives into double-columnar arrays by highly recognizing flexible H-bonding arrangements with two host networks of $\Delta\Lambda-\Delta\Lambda-\Delta\Lambda \cdots$ and $\Delta\Delta\Delta-\Lambda\Lambda\Lambda \cdots$.

1. Introduction

Self-assembled supramolecular architectures are currently of considerable interest owing to their intriguing network topologies and their potential applications in microelectronics, nonlinear optics, porous materials, and other technologies [1–10]. A tenet of crystal engineering, which belongs to supramolecular chemistry as well, is to control multidimensional network topologies in crystals constructed from molecular building blocks that are connected by means of mutual interactions of H-bonds and metal-coordination bonds [11–26]. For example, three-dimensional (3-D) molecular networks such as complicated (10,3)-*a* and (10,3)-*b* nets in crystals can also be produced in the field of crystal engineering by a rational design of artificial molecular building blocks [27–43].

In a previous report, we showed that 2,2'-biimidazolate monoanions ($Hbim^-$) was convenient for fabricating, via one-pot self-organization, controlled crystal structures that are not only coordinated to a transition metal ion but also connected to each other through intermolecular H-bonds of the complementary dual N-H $\cdots$ N type [44–50]. The self-organizing superstructures formed from the H-bonded networks of the transition metal complexes with $Hbim^-$ can be controlled in multidimensional networks by the molecular structures of the building blocks [51] or the existing counter ions [27, 52]. Thus, in the case of neutral building blocks, the superstructures form multidimensional networks such as 0-D H-bonded molecular dimers, 1-D linear and zigzag chains, 2-D honeycomb sheets, and 3-D helicates. These structures are constructed from the self-organisation of simple molecular building blocks, such as

FIGURE 1: Schematic representations of five superstructure networks formed from hydrogen-bonding $[\text{Ni}(\text{Hbim})_3]^-$ depending on the kind of counter cations.

metal complexes with mono coordination of Hbim^- , dual coordination of *trans*- and *cis*-configurations, and ternary coordination of *racemic* and *optical-resolution* compounds of Δ - and Λ -configurations, respectively. On the other hand, building blocks with ternary coordination of Hbim^- such as a $[\text{Ni}(\text{Hbim})_3]^-$ produce multidimensional host anionic superstructures with H-bonded networks based on Δ - and Λ -optical isomers that depend on a variety of counter-cations. Some relatively large cations such as $[\text{K-DCH}(18\text{-crown-6})]^+$ (DCH(18-crown-6) dicyclohexyl 18-crown-6), $[\text{K}-(\text{Cryptand})]^+$, and $[\text{PPh}_4]^+$ (tetraphenyl phosphonium) lead to a honeycomb sheet network (Figure 1(c)) formed from alternating linkages between Δ - and Λ -optical isomers of $[\text{Ni}(\text{Hbim})_3]^-$. The sheet stacking of these isomers in

crystal is arranged in parallel with the cavities to form 1-D channel formations approximately 2 nm in width and filled with a double-columnar array of the cations. Other small alkyl ammonium cations such as NMe_4^+ , N^nPr_4^+ , and NEt_4^+ , as well as a mixture of N^nPr_4^+ and Cs^+ , induce $[\text{Ni}(\text{Hbim})_3]^-$ to self-organise into other superstructures in crystal, such as a 0-D water molecule-mediated trigonal sheet (Figure 1(a)), a 1-D zigzag ribbon (Figure 1(b)) with an alternating arrangement of Δ - and Λ -isomers, an expanded honeycomb sheet inserted with the neutral H_2bim (Figure 1(d)), and a (10,3)-a net with double helicates (Figure 1(e)). However, we have also found $[\text{Ni}(\text{Hbim})_3]^-$ to form cation-stuffed channel structures stacked, for example, with honeycomb sheets (Figure 1(c)) by the use of the

relatively small cations of a planar $[\text{PEPY}]^+$ (4-phenylethyl pyridinium) and a flexible $[\text{TMEA}]^+$ (trimethyl ethynyl ammonium) [53]. Thus, the channel spaces can be filled with ionic pairs with a ClO_4^- anion and two cations such as $[(\text{PEPY})_2 \cdot \text{ClO}_4]^+$ and $[(\text{TMEA})_2 \cdot \text{ClO}_4]^+$, respectively. Since they are not completely filled with, only two cations to be smaller volume than the pore sizes of the hexagonal channel formed from six $[\text{Ni}(\text{Hbim})_3]^-$. Here, we have demonstrated that three new crystals 2–4, with a crystal structure similar to those of $\{[\text{Ni}(\text{Hbim})_3][\text{K-DCH}(18\text{-crown-6})]\}_n$ (crystal 1) and $\{[\text{Ni}(\text{Hbim})_3][\text{K-(Cryptand)}]\}_n$ (crystal 5), are also self-organised into a guest-included channel formation constructed from the stacking of honeycomb sheets. The stackings for crystals 1–5 are controlled by the K^+ crown-ether derivatives of potassium monocyclohexyl-18-crown-6 complex ($[\text{K-MCH}(18\text{crown6})]^+$), potassium monobenzo-18-crown-6 complex ($[\text{K-MBZ}(18\text{crown6})]^+$), potassium cryptand complex ($[\text{K-cryptand}]^+$), and $[\text{K-DCH}(18\text{-crown-6})]^+$, respectively. Thus, anionic $[\text{Ni}(\text{Hbim})_3]^-$ not only aggregates into cation-stuffed channel formations with K^+ -crown ether complexes approximately 20 Å in diameter; their cationic arrays are also controlled in double-columnar structures by adaptably fitting flexible H-bonding networks formed from either of two different host sequences with the repeating units of $\Delta\Lambda-\Delta\Lambda-\Delta\Lambda \cdots$ or $\Delta\Delta\Delta-\Lambda\Lambda\Lambda \cdots$ (Figures 2(a) and 2(b)).

2. Results and Discussion

2.1. Syntheses. The self-organization of crystals 1–5 was performed under the same conditions as those of the one-pot procedures in MeOH with Ni^{2+} ions, H_2bim , potassium *n*-butoxide, and the relevant crown ether derivative to obtain five types of blue or violet crystal, respectively. In preparation with cryptand, two polymorphs of the violet and blue crystals 4 and 5 were grown from the same batch solution of MeOH. All crystal structures of crystals 1–5 were identified by X-ray crystallographic analysis. Each was confirmed to consist of a cation-stuffed channel framework that included one of the four types of K^+ -crown ether complexes. On the other hand, preparations based on $[\text{K-(18-crown-6)}]^+$ with a nonsubstituted simple crown ether and $[\text{K-DBZ}(18\text{-crown-6})]^+$ (potassium dibenzo-18-crown-6 complex) with a large steric hindrance of phenyl groups have no known crystal structure at present. This suggests that each one of the two cationic complexes cannot be accommodated in the hexagonal cavity as a unit of the channel framework in a crystal.

2.2. Crystal Structures. Figure 3 shows the structures of each hexagonal cavity as repeating units of stuffed channel frameworks that clathrate two K^+ -crown ether complexes for each of the crystals 1–5. Each of the hexagonal cavities is constructed from alternating linkages through H-bonds between the Δ and Λ optical isomers of six $[\text{Ni}(\text{Hbim})_3]^-$ molecules and contains two K^+ -crown ether complexes within it owing to the charge balance. As shown in Figure 3(a), it is interesting that only the *cis-syn-cis* structural isomer of $[\text{K-DCH}(18\text{crown6})]^+$ is included in a hexagonal cavity, despite

FIGURE 2: Schematic representations of two supramolecular isomers of (a) $\Delta\Lambda-\Delta\Lambda-\Delta\Lambda \cdots$ and (b) $\Delta\Delta\Delta-\Lambda\Lambda\Lambda \cdots$ sequences formed from $[\text{Ni}(\text{Hbim})_3]^-$.

the use of a commercial preparation with a mixture of structural isomers of the crown ethers including the *cis-anti-cis*, *cis-syn-trans*, *cis-anti-trans*, *trans-anti-trans*, and *trans-syn-trans* forms. The two K^+ -crown ether complexes are held to face each other in a saddle-shaped formation within the hexagonal cavity (distance between two K^+ ions in the crown ethers: 7.698(3) Å). The hydrophilic ether oxygens are aligned toward the outer wall of the cavity, whereas the two hydrophobic cyclohexyl groups are oriented toward the centre. Furthermore, stacking along the *c*-axis with two K^+ -crown complexes leads to the formation of a small channel space, which includes the solvent molecules (methanol and water). As a result, the channel consists of both a small inner channel due to the stacking of two K^+ -crown complexes and a large outer channel due to the hexagonal cavities (Figure 4(a)). Figures 3(b) and 3(c) show that each of the hexagonal cavities includes double stacking arrays along the *c*-axis for $[\text{K-MCH}(18\text{crown6})]^+$ and $[\text{K-MBZ}(18\text{crown6})]^+$, respectively. The hydrophilic ether oxygens, with their two K^+ -crown ether complexes, are positioned toward the outer wall of the cavity, and hydrophobic cyclohexyl and phenyl groups are each positioned around the centre of the hexagonal cavity. Therefore, their two complexes are aligned as stacked double-columnar structures in the channels, respectively, (Figures 4(b) and 4(c)). The two polymorphous crystals 4 and 5 induced by $[\text{K-cryptand}]^+$ also contain the stacked double-columnar structures, as shown in Figures 3(d) and 3(e). In the stacking channels of both 4 and 5, residual spaces (excluding the double columns) are occupied by a number of methanol molecules. One reason why $[\text{K-cryptand}]^+$ forms two polymorphs may be that it has a spherical structure. The results of these structural analyses have demonstrated that the vicinity of the outer wall in the channel is hydrophilic (Figures 4(d) and 4(e)). The honeycomb sheets in crystal 5 form at the deviated slide stack (Each honeycomb sheet stacks diagonally for the *ac* plane.) along the *c*-axis, as shown in Figure 6. The most important characteristic of $[\text{Ni}(\text{Hbim})_3]^-$ networks is that four K^+ -crown ether complexes are clathrated into the stacking channels, and crystallised as single crystals 1–5 by adaptably fitting flexible H-bonding distortions with the networks and sequential change between the $\Delta\Lambda-\Delta\Lambda-\Delta\Lambda$ and $\Delta\Delta\Delta-\Lambda\Lambda\Lambda$

FIGURE 3: Structural view of each hexagonal cavity for crystals 1–5. (a) The structure of the hexagonal cavity of 1 is constructed from nondistorted hydrogen bond connections of six $[\text{Ni}(\text{Hbim})_3]^-$ molecules with alternating $\Delta\Lambda$ – $\Delta\Lambda$ – $\Delta\Lambda$ sequences of the Δ (red sphere) and Λ (blue sphere) optical isomers and includes two $[\text{K-DCH}(18\text{-crown-6})]^+$. The frameworks of K^+ -crown ether derivatives and MeOH molecules are represented by the green ball-and-stick lines. The potassium and nickel (II) ions are drawn with yellow and magenta spheres, respectively. ((b) and (e)) The hexagonal cavities of 2 and 5, which are represented by H-bonded connections of the $\Delta\Delta\Delta$ – $\Lambda\Lambda\Lambda$ sequence with the distorted connection of the same optical isomers, include two $[\text{K-MCH}(18\text{-crown-6})]^+$ and two $[\text{K-cryptand}]^+$ molecules, respectively. (c) The hexagonal cavity of 3 that includes $[\text{K-MZB}(18\text{-crown-6})]^+$ is constructed from a sequence similar to that of 1 ($\Delta\Lambda$ – $\Delta\Lambda$ – $\Delta\Lambda$), although the hydrogen bonding connections are distorted. (d) The hexagonal cavity of 4 that includes $[\text{K-cryptand}]^+$, which is also a polymorph of 5, is constructed from the $\Delta\Lambda$ – $\Delta\Lambda$ – $\Delta\Lambda$ sequence.

FIGURE 4: Perspective views of the channel structures through each hexagonal cavity for crystals 1–5. Each hexagonal cavity is stacked to form the channel structures. The channel structures of all crystals are constructed from segregated stacking, that is, from different stacking columns of each of the Δ and Λ optical isomers of $[\text{Ni}(\text{Hbim})_3]^-$ along the channel axis. The Δ and Λ isomers of $[\text{Ni}(\text{Hbim})_3]^-$ are represented by the red and blue lines, respectively. The crown ether frameworks and MeOH molecules are shown in green. The potassium and nickel (II) ions are drawn as yellow and magenta spheres, respectively.

formations. Figure 5 shows the sequence structures of the $[\text{Ni}(\text{Hbim})_3]^-$ networks in each of the connected hexagonal cavities in crystals 1–5. As shown in Figures 5(a) and 5(e), two hexagonal cavities in crystals 1 and 5 are constructed

by hexagonal alignments almost without distortion, built up by the $\Delta\Lambda\text{--}\Delta\Lambda\text{--}\Delta\Lambda$ sequence of $[\text{Ni}(\text{Hbim})_3]^-$. In contrast, the hexagonal cavity of crystal 2 is constructed from the heavily distorted arrangements of $\Delta\Lambda\text{--}\Delta\Lambda\text{--}\Delta\Lambda$ in order

FIGURE 5: Views of honeycomb-sheet structures for crystals 1–5 are represented. Three sheet structures of crystals 1, 3, and 4 ((a), (c), and (d)) are constructed from alternating H-bonded connections with the $\Delta\Lambda-\Delta\Lambda-\Delta\Lambda$ sequence. In contrast, crystals 2 and 5 ((b) and (e)) are constructed from hydrogen-bonded connections with the $\Delta\Delta\Delta-\Lambda\Lambda\Lambda$ sequence between the two infinite $\Delta\Delta\Delta \cdots$ and $\Lambda\Lambda\Lambda \cdots$ zigzag chains. The Δ and Λ isomers of $[\text{Ni}(\text{Hbim})_3]^-$ are represented by red and blue lines, respectively. The crown ether frameworks and MeOH molecules are shown in green. The potassium and nickel (II) ions are drawn as yellow and magenta spheres, respectively.

FIGURE 6

to adaptably fit $[\text{K-MCH}(18\text{crown}6)]^+$, as shown in Figure 5(b). On the other hand, both hexagonal cavities of crystals 3 and 4 are constructed from arrangements with the $\Delta\Delta\Delta$ – $\Lambda\Lambda\Lambda$ sequences, which differ from the alternating $\Delta\Lambda$ – $\Delta\Lambda$ – $\Delta\Lambda$ sequences (Figures 5(c) and 5(d)). However, the arrangement of the hexagonal cavity in crystal 3 is heavily distorted to adaptably fit $[\text{K-MBZ}(18\text{crown}6)]^+$.

In this study, we identified five structures of crystals 1–5 induced by four K^+ -crown ether complexes. All of the crystals have stuffed channel frameworks with 1-D channels formed from $[\text{Ni}(\text{Hbim})_3]^-$. Each of the channels also includes a double-columnar array of the K^+ -crown ether complexes. The result indicates that $[\text{Ni}(\text{Hbim})_3]^-$ as a host molecule self-organizes into a stuffed channel framework, with widths of approximately two nanometres, induced by larger K^+ -crown ether complexes, similar to the urea crystal with guest-induced channel structures [54].

3. Conclusions

It is difficult to determine the positions and structures of guest molecules such as urea [54], zeolite [55], and MOF [56, 57], included in a nanoporous framework. This is because the resultant structures have a very robust porous framework made of an inorganic polymer such as aluminosilicate, owing to the heavy disordering of the included guest molecules. However, in a cation-clathrated porous framework formed from $[\text{Ni}(\text{Hbim})_3]^-$, as we have shown here, a crystal structure is obtained under conditions in which guest molecules have already been included in the nanochannels by one-pot synthesis. This is different from typical porous crystals such as zeolite, which do not have guest molecules. Thus, it is necessary not only to isolate the crystal of unstable nanoporous frameworks in advance, but also to fix the included guest cations by adaptable fitting of self-organised porous host frameworks formed from $[\text{Ni}(\text{Hbim})_3]^-$. The crystal structure of the included guest

molecules is clearly determined because adaptably fitting into the host H-bonding network prevents disordering of the guest molecules. In this study, we have compared five crystal structures induced by relatively large K^+ -crown ether derivatives. In contrast to host molecules that usually capture certain guest molecules in the well-known field of molecular recognition, the host arrays of $[\text{Ni}(\text{Hbim})_3]^-$ suggest a new host-guest chemistry because the self-organised supramolecular isomer, which is different from H-bonded superstructures, recognises certain guest molecules in the crystal. Here, K^+ -crown ether derivatives have been one-dimensionally arranged in the channel, the K^+ ion conductivity is not observed in the crystal. In the future, we hope that Li^+ ion-conductivity will be produced from an anionic nanochannel crystal that includes Li^+ -crown ether derivatives. Such a controlled crystal structure by induced fitting to $[\text{Ni}(\text{Hbim})_3]^-$ must be found as new structural-chemical investigation on the guest molecules included into a porous crystal.

4. Experimental Sections

4.1. Synthesis of $\{[\text{Ni}(\text{Hbim})_3]/[\text{K-DCH}(18\text{-crown-6})]\cdot\text{MeOH}\cdot\text{H}_2\text{O}\}_n$ (I). A suspension of H_2bim (0.13 g, 1.0 mmol), $\text{DCH}(18\text{crown}6)$ (0.12 g, 0.31 mmol), and KO^tBu (0.30 g, 2.6 mmol) was added to methanol (30 cm^3) and heated under reflux until the ligand dissolved. $\text{Ni}(\text{ClO}_4)_4\cdot 6\text{H}_2\text{O}$ (0.11 g, 0.31 mmol) in methanol (20 cm^3) was added dropwise to the resulting solution, 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. Blue prisms were obtained from the filtrate after several days. Elemental analysis: Calcd for $[\text{Ni}(\text{Hbim})_3][\text{K-DCH}(18\text{crown}6)]\cdot 1.5\text{H}_2\text{O}$ ($\text{C}_{38}\text{H}_{52}\text{N}_{12}\text{O}_{6.5}\text{NiK}$): C, 50.90%; H, 6.07%; N, 18.74%; Found: C, 50.85%; H, 5.86%; N, 18.77% (dried in vacuo for 6 h at

100°C). IR (KBr) 2937 cm⁻¹ (ν (CH)), ~2500 cm⁻¹ (br, ν (NH)), 1895 cm⁻¹ (br, 2 γ (NH)).

4.2. Synthesis of $\{[Ni(Hbim)_3][K-MCH(18-crown-6)] \cdot MeOH \cdot H_2O\}_n$ (2). This crystal was obtained by a method similar to that employed for 1; however, MCH(18crown6) (0.10 g, 0.31 mmol) was used instead of DCH(18crown6). Elemental analysis: Calcd for $[Ni(Hbim)_3][K-MCH(18-crown-6)] \cdot 3.5H_2O$ (C₃₄H₅₂O_{9.5}N₁₂NiK): C, 46.48%; H, 5.97%; N, 19.13%; Found: C, 46.48%; H, 5.50%; N, 18.87% (dried in vacuo for 6 h at 100°C). IR (KBr) 2938 cm⁻¹ (ν (CH)), ~2500 cm⁻¹ (br, ν (NH)), 1896 cm⁻¹ (br, 2 γ (NH)).

4.3. Synthesis of $\{[Ni(Hbim)_3][K-MBZ(18-crown-6)] \cdot MeOH\}_n$ (3). This crystal was obtained by a method similar to that employed for 1; however, MBZ(18crown6) (0.10 g, 0.31 mmol) was used instead of DCH(18crown6). Elemental analysis: Calcd for $[Ni(Hbim)_3][K-MBZ(18-crown-6)] \cdot H_2O$ (C₃₄H₄₁O₇N₁₂NiK): C, 49.35%; H, 4.99%; N, 20.31%; Found: C, 49.57%; H, 5.13%; N, 20.23% (dried in vacuo for 6 h at 100°C). IR (KBr) 2941 cm⁻¹ (ν (CH)), ~2500 cm⁻¹ (br, ν (NH)), 1899 cm⁻¹ (br, 2 γ (NH)).

4.4. Syntheses of $\{[Ni(Hbim)_3][K-cryptand] \cdot 2MeOH\}_n$ (4) and $\{[Ni(Hbim)_3][K-cryptand] \cdot MeOH\}_n$ (5). This crystal was obtained by a method similar to that employed for 1; however, cryptand (0.12 g, 0.31 mmol) was used instead of DCH(18crown6). Elemental analysis: Calcd for $[Ni(Hbim)_3][K-cryptand] \cdot H_2O$ (C₃₆H₅₃O₇N₁₄NiK): C, 48.49%; H, 5.99%; N, 21.99%. Found: C, 47.99%; H, 5.98%; N, 21.64% (dried in vacuo for 6 h at 100°C and analysed the mixture of 4 and 5). IR (KBr) 2940 cm⁻¹ (ν (CH)), ~2500 cm⁻¹ (br, ν (NH)), 1898 cm⁻¹ (br, 2 γ (NH)).

Crystal Data for 1. C₄₁H₆₇O₁₁N₁₂NiK, FW = 1001.85, *Monoclinic*, space group C2/m (number 12) with $a = 19.077(3)$ Å, $b = 29.074(3)$ Å, $c = 9.769(3)$ Å, $\beta = 110.39(2)^\circ$, $V = 5078(1)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.310$ g/cm³, $F(000) = 2128.00$. 314 parameters, $R_1 = 0.070$, $wR_2 = 0.152$, and GOF = 1.054 for all 1419 data ($I > 3\sigma(I)$); $\mu(\text{CuK}\alpha) = 18.38$ cm⁻¹; 3797 reflections collected; the values of the minimum and maximum residual electron densities are 0.36 and -0.28 eÅ⁻³, respectively.

Crystal Data for 2. C₃₄H₅₁O₈N₁₂NiK, FW = 853.65, *Monoclinic*, space group P2₁/n (number 14) with $a = 8.780(1)$ Å, $b = 17.039(3)$ Å, $c = 28.327(2)$ Å, $\beta = 91.50(1)^\circ$, $V = 4236.3(9)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.338$ g/cm³, $F(000) = 1800.00$. 559 parameters, $R_1 = 0.075$, $wR_2 = 0.174$, and GOF = 1.117 for 3854 data ($I > 3\sigma(I)$); $\mu(\text{CuK}\alpha) = 20.57$ cm⁻¹; 6582 reflections collected; the values of the minimum and maximum residual electron densities are 0.48 and -0.86 eÅ⁻³, respectively.

Crystal Data for 3. C₃₅H₄₃O₇N₁₂NiK, FW = 841.60, *Monoclinic*, space group C2₁/n (number 14) with $a = 9.294(2)$ Å, $b = 25.183(5)$ Å, $c = 17.099(2)$ Å, $\beta = 95.64(1)^\circ$, $V = 3982(1)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.403$ g/cm³, $F(000) = 1760.00$.

544 parameters, $R_1 = 0.066$, $wR_2 = 0.179$, and GOF = 1.829 for all 3448 data ($I > 3\sigma(I)$); $\mu(\text{CuK}\alpha) = 21.65$ cm⁻¹; 4243 reflections collected; the values of the minimum and maximum residual electron densities are 0.22 and -0.22 eÅ⁻³, respectively.

Crystal Data for 4. C₇₄H₁₁₀O₁₄N₂₈Ni₂K₂, FW = 1811.46, *Monoclinic*, space group P-1 (number 2) with $a = 13.962(1)$ Å, $b = 25.636(3)$ Å, $c = 12.937(1)$ Å, $\alpha = 100.034(8)^\circ$, $\beta = 93.221(8)^\circ$, $\gamma = 101.778(7)^\circ$, $V = 4443.4(8)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.354$ g/cm³, $F(000) = 3824.00$. 1165 parameters, $R_1 = 0.094$, $wR_2 = 0.213$, and GOF = 1.511 for all 5963 data ($I > 3\sigma(I)$); $\mu(\text{CuK}\alpha) = 19.89$ cm⁻¹; 12427 reflections collected; the values of the minimum and maximum residual electron densities are 0.99 and -1.14 eÅ⁻³, respectively.

Crystal Data for 5. C₃₈H₅₉O₈N₁₄NiK, FW = 937.77, *Monoclinic*, space group C2/c (number 15) with $a = 18.966(2)$ Å, $b = 19.058(2)$ Å, $c = 25.469(2)$ Å, $\beta = 103.201(8)^\circ$, $V = 8962(1)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.390$ g/cm³, $F(000) = 3968.00$. 587 parameters, $R_1 = 0.074$, $R_w = 0.164$, and GOF = 1.189 for all 3530 data ($I > 3\sigma(I)$); $\mu(\text{CuK}\alpha) = 20.08$ cm⁻¹; 6033 reflections collected; the values of the minimum and maximum residual electron densities are 1.03 and -0.59 eÅ⁻³, respectively.

The data collection for crystals 1–5 was performed by a Rigaku AFC7R—the 4-circle single-crystal X-ray diffractometer based on Lorenz-polarization corrections and graphite monochromatic Cu-K α ($\lambda = 1.54178$ Å)—for all crystals. Their structures were then solved by using direct method techniques with the SIR92 [58] and full-matrix least-squares (DIRDIF99) refinement [59]. The hydrogen atom positions were fixed. Further details of the data collection and structure solution of crystals 1–5 are provided as crystal data in Supplementary Material available online at doi:10.1155/2012/216050. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-829900 (1), CCDC-829901 (2), CCDC-829897 (3), CCDC-829899 (4), and CCDC-829898(5). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ (fax: Int. Code (+44)1223/336-033; e-mail: deposit@chemcrs.cam.ac.uk).

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