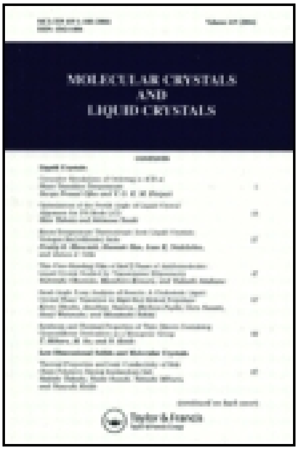

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Double Channel Structures Based on Hydrogen Bonding Networks of 2,2′-Biimidazolate Nickel(II) Complexes

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DOUBLE CHANNEL STRUCTURES BASED ON HYDROGEN BONDING NETWORKS OF 2,2'-BIIMIDAZOLATE NICKEL(II) COMPLEXES

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Abstract The [Ni(Hbim)3][K-DCH(18-crown-6)] (K-DCH(18-crown-6) = potassium *cis-syn-cis* -dicyclohexano-18-crown-6; Hbim = mono-deprotonated 2,2'-biimidazolate} is synthesized and the crystal structure is characterized by X-ray crystal analysis. (Crystal data: monoclinic, *C2/m*, a = 19.077(3) Å, b = 29.074(3) Å, c = 9.769(3) Å, β = 110.39(2)°, V = 5078(1) Å^3, Z = 4) The crystal structure is characterized as a double channel structure. The larger channels of the two are produced by stacking 2D-honeycomb sheets of [Ni(Hbim)3]$^-$ complexes and the inner small channels is built up by two potassium-crown ether complexes which occupy the cavity of the large outer channel.

INTRODUCTION

There is enormous current interest in the design of molecular building blocks that can assemble into structures of nanometer scale dimensions.[1,2] An important goal in this developing field has been the creation of molecular building blocks that allow the controlled formation of different one- (1D), two- (2D) and three- (3D) dimensional shapes to give designed materials such as microporous crystals with channels having zeolite properties.[3,4]

We have found that a particularly fruitful strategy for the generation of such materials is the use of the building block of [Ni(Hbim)3]$^-$, which consists of three 2,2'-biimidazolate ligands and a nickel(II) metal ion. The building blocks can form the complementary double NH-N types of hydrogen bonds between the blocks. We found that the [Ni(Hbim)3]$^-$ forms a wide variety of ordered three-dimensional superstructures with the intermolecular complementary hydrogen bonded networks using two enantiomers Δ and Λ types of the block. The formed superstructures are dependent on the kinds of counter cations used for the constructions. For example, the formation of one-dimensional zigzag chain structures[5] and double interlocking polycatenate structures[6] have been reported. In this report, selecting the [K-DCH(18-crown-6)]$^+$ as a cation, we succeeded to realize a superstructure of the molecular block of [Ni(Hbim)$_3$]$^-$, with unique intermolecular hydrogen bonded networks. The complex forms crystals with double channel structures, as shown in Figure 1. The channels are built up by stacking the *ab* plane sheets with double holes formed by two cations and six [Ni(Hbim)$_3$]$^-$ units along the *c* axis. The diameter of this larger outer channel formed by Ni-biimidazolate complexes is about 18 Å. Inside of the channel is occupied with two smaller cations, [K-DCH(18-crown-6)]$^+$. These two cations also produce a channel structure of about 7 Å diameter. The latter channel contains several MeOH and water molecules.

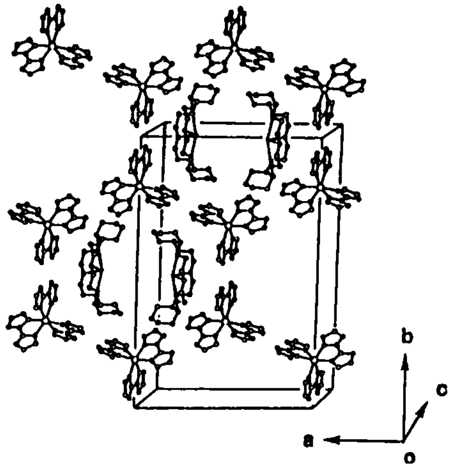

FIGURE 1 Double channel structures of complex **1**.

CRYSTAL STRUCTURE

The crystal data of [Ni(Hbim)$_3$][K-DCH(18-crown-6)]·3MeOH·2H$_2$O (**1**) is formula, $C_{41}H_{67}O_{11}N_{12}NiK$, monoclinic, space group *C*2/m (No. 12), *FW* = 1001.84, a = 19.077(3) Å, b = 29.074(3) Å, c = 9.769(3) Å, β = 110.39(2)°, V = 5078(1) Å^3, Z = 4, $\rho_{\chi alc}$ = 1.310 g/cm^{-1}, Cu-Kα radiation, λ = 1.54178 Å, $4.0 < 2\theta < 120°$, 4004 reflections were collected, of which 3874 unique reflections ($I_o > 3\sigma(I_o)$) were used for refinement (287 parameters), converging to R = 0.056 and R_w = 0.053. The structure of complex **1** was solved by heavy-atom Patterson methods[7] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed in calculation. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and -0.30 eÅ^{-3}. All calculations were performed using the teXsan[8] crystallographic software package. The final atomic coordinates of compound **1** are given in Table 2.

RESULTS AND DISCUSSION

Structure of Complex 3

The crystal of complex **1** for X-ray analysis was obtained by slow evaporation of the filtrate from the reaction mixture in MeOH. An ORTEP view of complex **1** is shown in Figure 2 with the numbering scheme of non-hydrogen atoms. The selected bond distances and angles of complex **1** is given in Table 1. The crystal of complex **1** consists of the trisbiimidazolate mononuclear Ni(II) complex anion ($[Ni(Hbim)_3]^-$), the potassium *cis-syn-cis* -dicyclohexano-18-crown-6 cation ($[K\text{-}DCH(18\text{-crown-}6)]^+$), and methanol and water molecules with ratio of 1 : 1 : 3 : 2. One of three methanol molecules coordinate to the potassium ion in crown ether. Other two methanol and two water molecules are free from the coordination and are captured in the crystal lattice with intermolecular hydrogen bonds. These intermolecular hydrogen bonding distances can not be determined because of the large thermal vibration of both molecules.

The anion of $[Ni(Hbim)_3]^-$ contains the Ni(II) atom coordinated by three bidentate $Hbim^-$ ligands through the lone pairs of the imine nitrogen atoms of the imidazole rings. The Ni-N lengths of $[Ni(Hbim)_3]^-$ have similar distances and fall in the range of 2.046(6) - 2.118(7) Å. The coordination geometry is a distorted octahedron. The distortion is mainly resulted from small N-Ni-N bite angles of the range of 78° to 79° which are similar to those of $[Ni(bpy)_3]^{2+}$ (~ 79°)[9] and $[Ni(phen)_3]^{2+}$ (~ 79°)[10], although a bite angle of free bpy (2,2'-bipyridine) is 60° and the corresponding angle of free H_2bim (2,2'-biimidazole) only 41°: the bite angle as being interior to the intersection of two lines, each of which passes through the chelating nitrogen and bisects the ring incorporating that nitrogen.[11] Therefore, the distortion of the 2,2'-biimidazolate ligand in $[Ni(Hbim)_3]^-$ is much significant compared with that of the bpy ligand in $[Ni(bpy)_3]^{2+}$. In other word, a 2,2'-biimidazolate ligand is more flexible for coordination of metal ions than a bpy ligand.

The most important interaction found in the crystal structure of the $[K\text{-}DCH(18\text{-crown-}6)][Ni(Hbim)_3]$ (**1**) is intermolecular hydrogen bondings to form the microporous crystals with double channel structures along the *c* axis produced by stacking of the 2D-honeycomb sheet structures. The 2D-honeycomb sheet structures are built up by the complementary hydrogen bonding of NH-N type between the alternate arrangement of Δ and Λ type optical isomers of six building blocks of $[Ni(Hbim)_3]^-$ anions: N(2)*H(3)-N(4): 2.740(9) Å; N(2)H(3)-N(4)*: 2.740(9) Å; N(6)H(8)-N(6)*: 2.74(1) Å. The 2D-sheet structure is homeotypic with the CaCuP structure type.[12] The 2D-honeycomb sheets stack along the *c* axis to create the outer channel structures with diameter of the cavity of about 18 Å. The layers between 2D-sheet structures are separated by about

~4.3 Å (mean value of the shortest interlayer C-C distances). The small inner channels constructed with column structures formed in the outer channels by stacking of two potassium *cis-syn-cis* -dicyclohexano-18-crown-6 molecules to face each other along the *c* axis. The small channel structure is about 7 Å diameter, which contains MeOH and water molecules. Such double channel structure is stable even if MeOH and water solvents in the crystal lattice are removed.

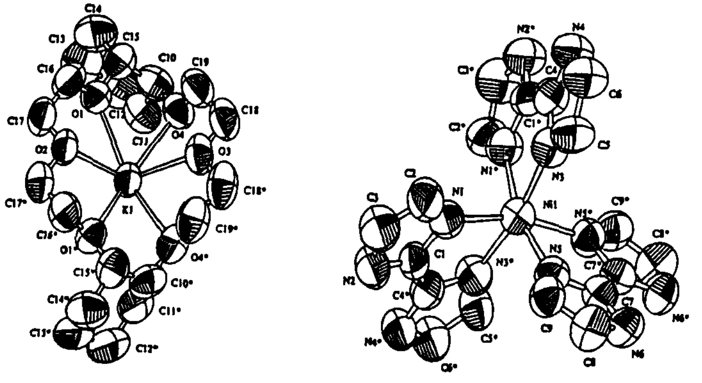

FIGURE 2 ORTEP view of complex **1**.

TABLE 1 Selected bond lengths (Å) and angles (deg) for compound (**1**)[a].

Distances	
Ni(1) - N(1) 2.112(7)	Ni(1) - N(1) 2.112(7)
Ni(1) - N(3) 2.046(6)	Ni(1) - N(3) 2.046(6)
Ni(1) - N(5) 2.118(7)	Ni(1) - N(5) 2.118(7)
K(1) - O(1) 2.833(6)	K(1) - O(1) 2.833(6)
K(1) - O(2) 2.734(8)	K(1) - O(3) 2.717(9)
K(1) - O(4) 2.843(7)	K(1) - O(4) 2.843(7)
K(1) - O(5) 2.76(2)	
Angles	
N(1) - Ni(1) - N(1) 102.2(4)	N(1) - Ni(1) - N(3) 95.1(3)
N(1) - Ni(1) - N(3) 78.6(3)	N(1) - Ni(1) - N(5) 90.5(3)
N(1) - Ni(1) - N(5) 164.1(3)	N(1) - Ni(1) - N(3) 78.6(3)
N(1) - Ni(1) - N(3) 95.1(3)	N(1) - Ni(1) - N(5) 164.1(3)
N(1) - Ni(1) - N(5) 90.5(3)	N(3) - Ni(1) - N(3) 170.0(4)
N(3) - Ni(1) - N(5) 91.0(3)	N(3) - Ni(1) - N(5) 96.8(3)
N(3) - Ni(1) - N(5) 96.8(3)	N(3) - Ni(1) - N(5) 91.0(3)
N(5) - Ni(1) - N(5) 78.9(4)	

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[a] Estimated standard deviations are given in parentheses.

TABLE 2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

atom	x	y	z	B_{eq}
Ni(1)	0.0000	0.17915(7)	0.0000	6.81(5)
K(1)	0.2847(2)	0.0000	0.8491(3)	8.12(8)
O(1)	0.2422(3)	0.0855(2)	0.7052(7)	8.7(2)
O(2)	0.1836(5)	0.0000	0.5703(9)	8.5(3)
O(3)	0.2073(5)	0.0000	1.0360(10)	10.2(3)
O(4)	0.2786(3)	0.0817(3)	1.0045(7)	9.3(2)
O(5)	0.6019(9)	0.0000	0.266(2)	20.2(6)
O(6)	0.393(1)	0.0707(8)	0.308(2)	37.7(9)
O(7)	0.421(3)	0.0000	0.174(7)	73(2)
O(8)	0.393(3)	0.0000	0.506(6)	62(1)
N(1)	-0.0383(4)	0.2248(2)	0.1269(8)	7.1(2)
N(2)	-0.1370(4)	0.2540(2)	0.1630(8)	7.9(2)
N(3)	0.1106(4)	0.1853(2)	0.1256(7)	7.0(2)
N(4)	0.2255(4)	0.2139(2)	0.1485(8)	7.5(2)
N(5)	-0.0123(3)	0.1229(2)	0.1275(7)	6.6(2)
N(6)	-0.0062(4)	0.0470(2)	0.1565(7)	6.8(2)
C(1)	-0.1123(5)	0.2295(3)	0.0712(9)	6.2(2)
C(2)	-0.0151(5)	0.2458(3)	0.259(1)	8.9(3)
C(3)	-0.0754(6)	0.2645(3)	0.282(1)	9.5(3)
C(4)	0.1523(5)	0.2102(3)	0.0672(9)	6.6(2)
C(5)	0.1607(5)	0.1722(3)	0.256(1)	8.2(3)
C(6)	0.2293(5)	0.1896(3)	0.2719(9)	8.2(3)
C(7)	-0.0044(4)	0.0823(3)	0.0706(8)	6.1(2)
C(8)	-0.0130(5)	0.0668(3)	0.2797(9)	7.7(3)
C(9)	-0.0173(5)	0.1125(3)	0.2596(10)	7.4(3)
C(10)	0.2930(7)	0.1219(4)	0.933(1)	10.5(4)
C(11)	0.3734(7)	0.1182(4)	0.943(1)	11.3(4)
C(12)	0.3941(7)	0.1601(5)	0.867(2)	14.0(5)
C(13)	0.3386(9)	0.1660(4)	0.713(2)	14.5(5)
C(14)	0.2590(8)	0.1702(4)	0.709(2)	13.6(5)
C(15)	0.2375(6)	0.1272(4)	0.779(1)	10.5(4)
C(16)	0.1799(7)	0.0807(4)	0.575(1)	11.0(4)
C(17)	0.1882(6)	0.0404(4)	0.491(1)	10.1(3)
C(18)	0.2019(6)	0.0407(5)	1.113(1)	11.8(4)
C(19)	0.2066(6)	0.0811(4)	1.022(1)	11.6(4)
C(20)	0.411(2)	0.093(1)	0.458(5)	55(1)
C(21)	0.540(3)	0.0000	0.165(5)	39(1)

$B_{eq} = 8/3\{p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos g + 2U_{13}aa^*cc^*\cos b + 2U_{23}bb^*cc^*\cos a)\}$

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