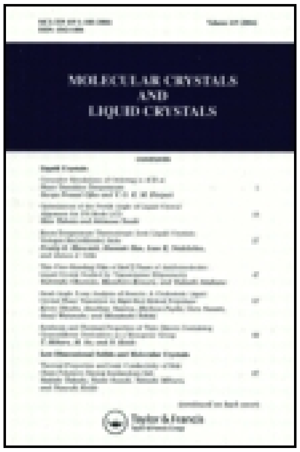

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Inclusion Compounds of K$^+$-Crown Ether Derivatives Introduced by Trisbiimidazolate Nickel(II) Complex with Large Channel Structures

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INCLUSION COMPOUNDS OF K+-CROWN ETHER DERIVATIVES INTRODUCED BY TRISBIIMIDAZOLATE NICKEL(II) COMPLEX WITH LARGE CHANNEL STRUCTURES

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Abstract [Ni(Hbim)$_3$][K-cryptand] (K-cryptand = potassium cryptand monocation; Hbim = mono-deprotonated 2,2'-biimidazolate] is synthesized and its crystal structure is characterized by X-ray crystal analysis. (Crystal data: monoclinic, *C*2/c (No. 15), a = 18.966(2) Å, b = 19.059(2) Å, c = 25.469(2) Å, β = 103.201(8)°, V = 8962(1) Å^3, Z = 8) It has a unique channel structure built up by stacking two-dimensional honeycomb sheets.

INTRODUCTION

The field of supramolecular chemistry has advanced to a stage at which we are able to select building blocks self-assembling into structures with specific network topologies. 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 shape of 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. Here we report the crystal structure of trisbiimidazolate nickel(II) complex ($[Ni^{II}(Hbim)_3]^-$ (Hbim = 2,2'-biimidazolate monoanion) with potassium-crown ether derivative as a counter cation, which forms a wide variety of ordered three-dimensional superstructures with the intermolecular complementary hydrogen bonded networks using two enantiomers Δ and Λ types as blocks. In Figure **1** we showed a two-dimensional hexagonal sheet structure constructing of $[Ni^{II}(Hbim)_3]^-$ building blocks and K^+-cryptand complexes.

EXPERIMENTAL

Crystal Structure

The crystal data of $[Ni(Hbim)_3][K\text{-Cryptand}]\cdot MeOH$ (**1**) are as follows: formula, $C_{38}H_{59}KN_{14}NiO_8$, monoclinic, space group *C*2/c (No. 15), $FW = 937.77$ $a = 18.966(2)$ Å, $b = 19.059(2)$ Å, $c = 25.469(2)$ Å, $\beta = 103.201(8)°$, $V = 8962(1)$ Å^3, $Z = 8$, $\rho_{calc} = 1.390$ g/cm^{-1}, Cu-Kα radiation, $\lambda = 1.54178$ Å, $6.0 < 2\theta < 113.7°$, 6238 reflections were collected, of which 3582 unique reflections ($I_0 > 3\sigma(I_0)$) were used for refinement (532 parameters), converging to $R = 0.066$ and $R_w = 0.059$. 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 0.79 and -0.55 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**.

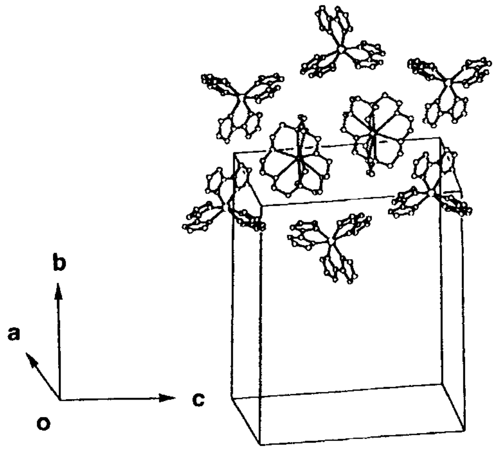

FIGURE 1 Crystal structure of $[Ni^{II}(Hbim)_3]^-$ building blocks and K^+-cryptand complexes.

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

Distances			
Ni(1) - N(1)	2.143(7)	Ni(1) - N(3)	2.097(7)
Ni(1) - N(5)	2.148(7)	Ni(1) - N(7)	2.098(7)
Ni(1) - N(9)	2.151(6)	Ni(1) - N(11)	2.098(7)
K(1) - O(1)	2.865(7)	K(1) - O(2)	2.868(7)
K(1) - O(3)	2.857(7)	K(1) - O(4)	2.802(7)
K(1) - O(5)	2.810(8)	K(1) - O(6)	2.799(8)
K(1) - N(13)	2.954(9)	K(1) - N(14)	2.928(8)
Angles			
N(1) - Ni(1) - N(3)	79.1(3)	N(1) - Ni(1) - N(5)	105.2(2)
N(1) - Ni(1) - N(7)	94.0(3)	N(1) - Ni(1) - N(9)	86.4(3)
N(1) - Ni(1) - N(11)	163.0(3)	N(3) - Ni(1) - N(5)	90.6(3)
N(3) - Ni(1) - N(7)	165.2(3)	N(3) - Ni(1) - N(9)	100.4(3)
N(3) - Ni(1) - N(11)	95.7(3)	N(5) - Ni(1) - N(7)	78.6(3)
N(5) - Ni(1) - N(9)	165.5(3)	N(5) - Ni(1) - N(11)	90.9(3)
N(7) - Ni(1) - N(9)	92.1(3)	N(7) - Ni(1) - N(11)	94.4(3)
N(9) - Ni(1) - N(11)	78.6(3)	O(1) - K(1) - O(2)	59.0(2)

[a] Estimated standard deviations are given in parentheses.

Preparation

The synthetic method of the building block **1** ([Ni(Hbim)$_3$][K-Cryptand]·MeOH) was used as the procedure of a 'one-pot' self-assembly in methanol solution to form the nickel complex with hydrogen-bonded network. Complex **1** of the new building block was obtained by refluxing the mixture of the 2,2'-biimidazole (H_2bim) (1.5 mmol), cryptand (0.5 mmol) and ptassium*tert*-butoxide (1.0 g) in MeOH (30 cm^3) followed by the addition of the methanol solution (20 cm^3) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol). The reaction mixture was heated for 15 minutes and filtered. The filtratre was cooled slowly to room temperature and left over night. The resulting blue-violet crystalline precipitate was filtered and air-dried. In suitable for single-crystal X-ray diffraction studies were extracted from the crystals. The selected bond distances and angles of complex **1** is given in Table **1**. In Figure **1**, the crystal structure of **1** shows that the desired coordination and aggregation has been achieved with the nickel atom being coordinated to two Hbim$^-$ ligands as *cis*-isomers, which are involved in binary NH-N hydrogen bond arrangements with other building blocks.

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

atom	x	y	z	B_{eq}
Ni(1)	0.18665(8)	0.06281(7)	0.17997(6)	2.69(3)
K(1)	0.0172(1)	-0.3122(1)	0.03384(8)	4.07(6)
O(1)	0.1511(4)	-0.3054(4)	0.0001(3)	5.7(2)
O(2)	0.0235(4)	-0.3452(4)	-0.0749(3)	5.1(2)
O(3)	0.0554(4)	-0.4231(4)	0.1106(3)	6.9(2)
O(4)	-0.0867(4)	-0.4118(3)	0.0456(3)	5.2(2)
O(5)	0.0343(5)	-0.1974(4)	0.1049(3)	7.6(3)
O(6)	-0.0764(5)	-0.1968(4)	0.0131(3)	6.9(3)
O(7)	0.8391	0.0124	0.6200	23.5(7)
O(8)	0.5000	0.2119	0.2500	39.2(10)
N(1)	0.1726(4)	0.1388(3)	0.2387(3)	2.7(2)
N(2)	0.1693(4)	0.2551(4)	0.2504(3)	3.3(2)
N(3)	0.2486(4)	0.1464(3)	0.1613(3)	2.6(2)
N(4)	0.2913(4)	0.2524(4)	0.1839(3)	3.8(2)
N(5)	0.2835(4)	0.0066(3)	0.2168(3)	2.8(2)
N(6)	0.3230(4)	-0.0997(3)	0.2448(3)	3.4(2)
N(7)	0.1445(4)	-0.0202(3)	0.2175(3)	2.9(2)
N(8)	0.1682(4)	-0.1194(4)	0.2666(3)	3.8(2)
N(9)	0.0807(4)	0.0932(3)	0.1353(3)	2.8(2)
N(10)	-0.0083(4)	0.0688(4)	0.0658(3)	3.5(2)
N(11)	0.1796(4)	0.0086(3)	0.1072(3)	2.6(2)
N(12)	0.1097(4)	-0.0184(4)	0.0253(3)	3.6(2)
N(13)	0.1543(6)	-0.3039(7)	0.1165(4)	7.6(4)
N(14)	-0.1179(4)	-0.3234(5)	-0.0488(4)	5.0(3)
C(1)	0.1261(5)	0.1525(5)	0.2712(4)	3.4(3)
C(2)	0.1239(5)	0.2230(5)	0.2777(4)	4.0(3)
C(3)	0.3009(5)	0.1604(5)	0.1341(3)	3.0(2)
C(4)	0.3268(5)	0.2249(5)	0.1473(4)	4.1(3)
C(5)	0.1965(5)	0.2014(5)	0.2273(3)	2.8(2)
C(6)	0.2443(4)	0.2025(5)	0.1910(3)	2.8(2)
C(7)	0.3536(5)	0.0006(5)	0.2143(4)	3.3(2)
C(8)	0.3793(4)	-0.0648(5)	0.2314(4)	3.6(2)
C(9)	0.0816(5)	-0.0423(5)	0.2290(4)	3.9(3)
C(10)	0.0975(5)	-0.1030(5)	0.2599(4)	4.2(3)
C(11)	0.2672(5)	-0.0562(5)	0.2358(3)	2.8(2)
C(12)	0.1946(4)	-0.0684(5)	0.2404(3)	2.7(2)
C(13)	0.0193(5)	0.1270(5)	0.1419(4)	3.5(3)
C(14)	-0.0360(5)	0.1132(5)	0.0994(4)	4.1(3)
C(15)	0.2173(5)	-0.0336(5)	0.0822(4)	3.8(3)
C(16)	0.1750(5)	-0.0495(5)	0.0315(4)	4.5(3)
C(17)	0.0630(5)	0.0587(5)	0.0891(3)	2.8(2)
C(18)	0.1152(5)	0.0157(4)	0.0715(4)	2.5(2)
C(19)	0.2120(7)	-0.2847(8)	0.0897(6)	9.6(5)
C(20)	0.2128(6)	-0.3221(7)	0.0395(6)	8.1(4)
C(21)	0.1515(6)	-0.3416(6)	-0.0469(5)	6.8(4)

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

atom	x	y	z	B_{eq}
C(22)	0.0874(7)	-0.3236(6)	-0.0897(4)	6.8(4)
C(23)	-0.0390(8)	-0.3321(7)	-0.1152(5)	7.6(4)
C(24)	-0.1059(7)	-0.3557(6)	-0.0966(5)	6.9(4)
C(25)	0.1760(7)	-0.3724(9)	0.1422(7)	10.7(6)
C(26)	0.1157(9)	-0.4077(8)	0.1551(5)	10.4(5)
C(27)	-0.0060(7)	-0.4547(6)	0.1223(5)	7.5(4)
C(28)	-0.0614(6)	-0.4730(6)	0.0756(5)	6.5(4)
C(29)	-0.1433(6)	-0.4278(6)	0.0004(5)	6.8(4)
C(30)	-0.1720(6)	-0.3605(6)	-0.0271(5)	6.6(4)
C(31)	0.1449(8)	-0.247(1)	0.1544(5)	11.4(6)
C(32)	0.1034(10)	-0.1819(9)	0.1282(6)	11.1(6)
C(33)	-0.0029(10)	-0.1348(7)	0.0820(6)	9.8(5)
C(34)	-0.0756(9)	-0.1499(7)	0.0531(6)	9.4(5)
C(35)	-0.1462(7)	-0.2063(7)	-0.0190(6)	8.5(5)
C(36)	-0.1446(7)	-0.2527(7)	-0.0660(5)	8.0(4)
C(37)	0.7946	-0.0159	0.5770	15(1)
C(38)	0.778(1)	0.033(1)	0.6292(9)	6.9(6)
C(39)	0.4521	0.1554	0.2336	54(1)

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

RESULTS AND DISCUSSIONS

Crystal Structure of Complex 1

The crystal of complex **1** consists of the trisbiimidazolate mononuclear Ni(II) complex anion ([Ni(Hbim)$_3$]$^-$), the potassium cryptand cation ([K-Cryptand]$^+$), and the methanol molecule with ratio of 1 : 1 : 1. The methanol molecule is free from the coordination and is captured in the crystal lattice 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 most important interaction found in the crystal structure of the [Ni(Hbim)3][K-Cryptand] (1) is intermolecular hydrogen bondings to form the large distorted hexagonal channel structures produced by stacking of the 2D-honeycomb sheet structures. The 2D-honeycomb sheet structures are built up by the complementary hydrogen bonding with NH-N type of $Hbim^-$ between the alternate arrangement of Δ and Λ 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. A Cavity in 2D honeycomb sheets is included two K-Cryptand cations and distorted at ellipsoidal structures by induced fitting of the two cations.

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REFERENCES

1. J. W. MacDonald and G. M. Whitesides, Chem. Rev., 94, 2383 (1994).
2. M. J. Zaworotko, Chem. Soc. Rev., 23, 283 (1994).
3. G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, Nature, 374, 792, (1995).
4. J. S. Moore and S. Lee, Chem. Ind., 556 (1994).
5. M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 213 (1996).
6. M. Tadokoro, K. Isobe, H. Uekusa, Y. Ohashi and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 221 (1996).
7. R. M. Barrer, In Inclusion Compounds, J. L. Atwood J. E. D. Davies and D. D. MacNicol, Eds. (Academic Press: London, 1984) Vol.1 p191.
8. P. T. Beurskens, G. Admiraal, G. Beurskens, W. p. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smykalla, C. PATTY, 1992. Structure Analysis Programs with Intelligent Control (Rigaku Crop., Tokyo, Japan, 1991).