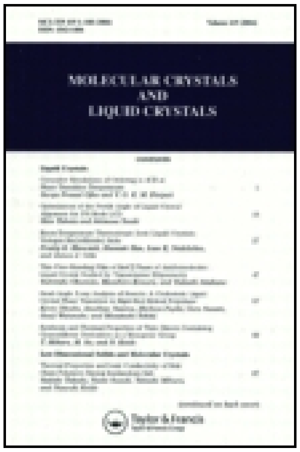

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DESIGEN OF ORGANIC STRUCTURE IN THE SOLID STATE: HYDROGEN BONDED MOLECULAR "ZIGZAG RIBBON" BUILT UP BY CIS-DIBIIMIDAZOLATE Ni(II) COMPLEXES

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Abstract The *cis*-[Ni(Hbim)$_2$(en)] (Hbim$^-$ = 2,2'-biimidazolate monoanion; en = ethylenediamine) (1) is synthesized and its crystal structure is characterized by X-ray crystal analysis (Crystal data: *monoclinic, P*2$_1$/n (No. 14), a = 8.970(2) Å, b = 16.872(3) Å, c = 12.389(2) Å, β = 91.82(2)°, V = 1874.0(6) Å^3, Z = 4). The crystal structure comprises one-dimensional zigzag-ribbon structures built up by alternate arrangements of Δ and Λ optical isomers of the building block 1. The zigzag-ribbon structure is supported by complementary intermolecular hydrogen bonds of Hbim$^-$ ligands contained the building block 1.

INTRODUCTION

Insight into the relationship between molecular and crystalline structures in organic solids will clarify the interactions that underline molecular recognition and self-assembly. This also helps to rationalize the macroscopic properties of organic materials in terms of microscopically molecular structures. We have previously shown how the application of molecular recognition principles using a 2,2'-biimidazolate mono anion (Hbim$^-$).[1] It is resulted in the crystal engineering of aggregates based on organic molecules of functional hybrid compounds with both metal configurations and intermolecular hydrogen bonds. In order to elucidate the role of functionalized organic molecules in formation of a superstructural solids, we have investigated some new ribbon structures with intermolecular hydrogen bonded zigzag arrangements, composed by new building blocks of *cis*-[Ni(Hbim)$_2$(L)] (Hbim$^-$ = 2,2'-biimidazolate monoanion; L = bidentate neutral chelate ligand). (Figure 1) It has the appropriate conformation to form stable metal complexes with a stereoisomer of *cis*- type. The building blocks also retain the ability to form complementary hydrogen bonds through NH-N moiety on the Hbim$^-$ ligand. Here we present the one-dimensional zigzag-ribbon structures and crystal packings of one of the building blocks (*cis*-[Ni(Hbim)$_2$(en)], (1)) (en = ethylenediamine).

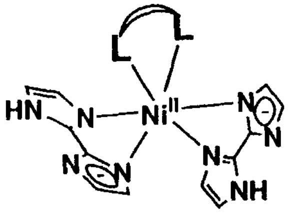


FIGURE 1 The new building block of *cis*-[Ni(Hbim)$_2$(L)].

EXPELIMENTAL

Preparation

For the synthetic method of the building block 1 (*cis*-[Ni(Hbim)$_2$(en)]) was used the procedure of a 'one-pot' self-assembly in methanol solution, by a combination of coordinate bond formation and intermolecular hydrogen bond, to form the nickel complex of organic molecule with hydrogen bonded network. An extended array consisting of complex **1** as a new building block was obtained by refluxing the mixture of the dissolved 2,2'-biimidazole (H_2bim) (2 mmol), ethylenediamine (1 mmol) and 28 % NaOMe methanol solution (1.5 g) in MeOH (30 cm^3) followed by the addition of the methanol solution (40 cm^3) of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol). The reaction mixture was heated for 15 minutes and filtered. The filtrate was cooled slowly to room temperature and left over night. The resulting blue-violet crystalline precipitate was filtered and air dried. Crystals suitable for single-crystal X-ray diffraction studies were collected from the precipitate. (Analysis of*cis*-[Ni(Hbim)$_2$(en)] $\cdot$MeOH; $C_{15}H_{22}N_{10}NiO$; Found: C, 42.73%; H, 5.29%; N, 33.16%, Calcd: C, 43.19%; H, 5.32%; N, 33.59%) The selected bond distances and angles of complex 1 is given in Table **1**. In Figure **2**, the X-ray crystal structure of complex 1 shows that the desired coordination and aggregation have been achieved by the nickel atom being coordinated to two Hbim$^-$ ligands as *cis*-isomers, which are in turn involved in an binary NH-N hydrogen bond arrangements with the other same building block.

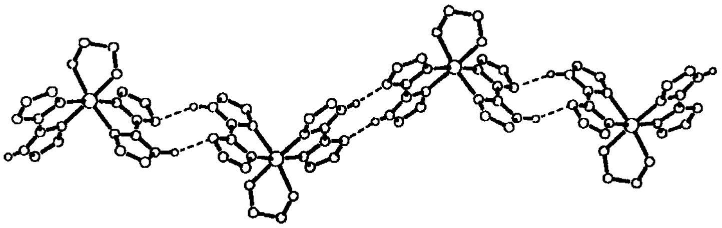
Crystal Structure

The crystal data of [Ni(Hbim)$_2$(en)]·MeOH (1) is formula, $C_{14}H_{18}N_{10}NiO$, *monoclinic*, space group $P2_1/n$ (No. 14), $FW = 385.06$, $a = 8.970(2)$ Å, $b = 16.872(3)$ Å, $c = 12.389(2)$ Å, $\beta = 91.82(2)°$, $V = 1874.0(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.365$ g/cm^{-1}, Cu-Kα radiation,λ = 0.71069 Å, $6.0 < 2\theta < 50.0°$. Reflections of 3426 were collected, of which 2726 unique reflections ($I_o > 3\sigma$ (I_o)) were used for refinement (321 parameters), converging to R = 0.038 and R_w = 0.041. The structure of complex 1 was solved by heavy-atom Patterson methods[2] 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 0.64 and -0.42 eÅ^{-3}. All calculations were performed using the teXsan[3] crystallographic software package. The final atomic coordinates of complex 1 are given in Table 2.

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

Distances			
Ni(1) - N(1)	2.122(3)	Ni(1) - N(3)	2.064(3)
Ni(1) - N(5)	2.127(3)	Ni(1) - N(7)	2.090(3)
Ni(1) - N(9)	2.133(4)	Ni(1) - N(10)	2.100(4)
Angles			
N(1) - Ni(1) - N(3)	79.6(1)	N(1) - Ni(1) - N(5)	98.4(1)
N(1) - Ni(1) - N(7)	172.7(1)	N(1) - Ni(1) - N(9)	88.7(1)
N(1) - Ni (1) - N(10)	97.3(1)	N(3) - Ni(1) - N(5)	92.7(1)
N(3) - Ni (1) - N(7)	93.4 (1)	N(3) - Ni(1) - N(9)	96.2(1)
N(3) - Ni(1) - N(10)	176.3(1)	N(5) - Ni(1) - N(7)	79.9(1)
N(5) - Ni(1) - N(9)	169.5(2)	Ni(1) - N(9) - C(14)	107.3(3)
N(5) - Ni(1) - N(10)	89.6(1)	N(7) - Ni(1) - N(9)	94.0(1)
N(7) - Ni(1) - N(10)	89.8(1)	N(9) - Ni(1) - N(10)	81.8(1)

[a] Estimated standard deviations are given in parentheses.



FUGURE 2 The crystal structure of one-dimensional "zigzag-ribbon" of the building block 1.

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

atom	x	y	z	B_{eq}
Ni(1)	0.12666(6)	0.21077(3)	-0.11347(4)	2.33(1)
O(1)	0.7785(4)	0.0553(2)	0.0271(3)	4.56(9)
N(1)	-0.0560(3)	0.2779(2)	-0.0586(3)	2.38(8)
N(2)	-0.1348(3)	0.4033(2)	-0.0213(3)	2.27(8)
N(3)	0.2229(3)	0.3216(2)	-0.1014(3)	2.34(8)
N(4)	0.2026(4)	0.4465(2)	-0.0484(3)	2.51(8)
N(5)	0.2176(4)	0.1747(2)	0.0394(3)	2.67(8)
N(6)	0.3729(4)	0.0890(2)	0.1190(3)	2.99(8)
N(7)	0.3237(4)	0.1568(2)	-0.1612(3)	2.54(8)
N(8)	0.5193(4)	0.0791(2)	-0.1064(3)	3.44(9)
N(9)	0.0397(4)	0.2244(2)	-0.2747(3)	3.23(9)
N(10)	0.0160(5)	0.1014(2)	-0.1281(3)	3.38(10)
C(1)	-0.2060(5)	0.2765(3)	-0.0408(3)	2.72(10)
C(2)	-0.2534(5)	0.3516(3)	-0.0180(3)	2.62(10)
C(3)	0.3585(5)	0.3583(3)	-0.1095(3)	2.8(1)
C(4)	0.3478(5)	0.4351(3)	-0.0771(4)	2.9(1)
C(5)	-0.0214(4)	0.3557(2)	-0.0457(3)	2.11(9)
C(6)	0.1313(4)	0.3769(2)	-0.0637(3)	2.21(9)
C(7)	0.1843(5)	0.1672(3)	0.1478(3)	3.1(1)
C(8)	0.2772(5)	0.1144(3)	0.1977(4)	3.3(1)
C(9)	0.4102(5)	0.1407(3)	-0.2482(4)	3.2(1)
C(10)	0.5270(5)	0.0940(3)	-0.2156(4)	3.6(1)
C(11)	0.3318(4)	0.1263(3)	0.0257(3)	2.59(10)
C(12)	0.3951(4)	0.1183(2)	-0.0797(3)	2.56(10)
C(13)	0.7721(6)	0.0883(3)	0.1338(4)	5.0(1)
C(14)	-0.0772(6)	0.1637(3)	-0.2924(4)	4.3(1)
C(15)	-0.0220(6)	0.0876(3)	-0.2428(4)	4.3(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 DISCUSSION

Structure of Complex 1

The crystal of complex 1 consists of enamtiomers Δ and Λ of the *cis*-[Ni(Hbim)$_2$(en)] and a methanol molecule with ratio of 1 : 1. The most important linkage interaction found in the crystal packing is the formation of the intermolecular one-dimensional zigzag-ribbon linkages with complementary hydrogen bonds of two sites on *cis*-isomers, as shown in Figure 2. The intermolecular chain structures are made up of an alternate arrangement of Δ and Λ enamtiomers of Ni(II) building blocks. The methanol molecules are free from the coordination and captured in the crystal lattice with intermolecular hydrogen bonds between the neutral building blocks. Hydroxide groups of methanol molecules form intermolecular hydrogen bonds between a hydrogen atom of the ethylenediamine ligand and an nitrogen atom in one of two Hbim ligands in the building block forming the binary NH-N hydrogen bonds.

Two intermolecular hydrogen bondings between the Hbim$^-$ ligand units of *cis*-isomer comprises one short [N(4)···N(2)* or N(2)···N(4)* 2.751(5) Å, (* symmetry operator: -x -y -z)], and one long [N(6)···N(8)* or N(8)···N(6)* 3.003 Å, (* symmetry operator: -x -y -z)] linkages (a and b, respectively, in Figure 1). One long binary hydrogen bonding site (b) of the building block is distorted to be a consequence of the slight geometric mismatch according to intermolecular hydrogen bonds between the oxygen atom in the methanol molecule and the nitrogen atoms ot form binary hydrogen bonding site (O(1)-N(8) 2.839(4) Å)]. The other short intermolecular hydrogen bonds is approximately co-planar because the cooperative effect of the hydrogen bonds results in the relatively shorter and stronger N(H)···N interaction without interference.

The nickel atom is, as expected in the light of previous metal complexes formed with Hbim$^-$ ligand,[1] coordinated to the N(1), N(3), N(5), N(7), N(9) and N(10) centers. The complex has crystallographic D_3 symmetry, where the Λ and Δ isomers are illustrated in Figure 2. The coordination geometry is a distorted octahedral. The N(1)-Ni(1)-N(7), N(3)-Ni(1)-N(10) and N(5)-Ni(1)-N(9) angles are 172.7(1), 176.3(1)' and 169.5(2)', respectively, cf. 168.9, 170.5 and 170.3' in $[Ni(phen)_3]^{2+}$, [4]. The remaining N-Ni-N angles are in the range 79.6(1)-97.3(1)'. The Ni-N distances, Ni(1)-N(1) 2.122(3), Ni(1)-N(5) 2.127(3), Ni(1)-N(3) 2.064(3), Ni(1)-N(7) 2.090(3), Ni(1)-N(9) 2.133(4) and Ni(1)-N(10) 2.100(4) Å, are very similar to those in the related trisbiimidazolate nickel complex $[Ni(Hbim)_3]$[K-DHC(18-crown-6)] [2.112(7), 2.112(7), 2.046(6), 2.046(6), 2.118(7) and 2.118(7) Å].[5] Two imidazole rings in a Hbim$^-$ ligand are almost coplanar (ca. 7' twist about the single-bond linkage). The associated non-bonded N(1)···N(3), N(5)···N(7) and N(9)···N(10) separations (2.68, 2.71 and 2.77 Å, respectively) are almost the same and within the ranges previously observed.[5] However, the non-bonded N(2)···N(4) and N(6)···N(8) separations (3.14 and 3.13 Å), on the opposite side of a metal chelating site in the ligand, are deferent from those of metal chelating sites. The planes of the two coordinated Hbim$^-$ ligands are twisted by ca. 81.2' to each other.

Results

We have shown that, in a single step, the ligand Hbim$^-$ fulfills its bifunctional role by generating a transition-metal complex of a one-dimensional zigzag-ribbon network in part , self-assembled by a combination of metal coordination and intermolecular binary hydrogen bonds. In addition we have demonstrated that the same methodology can be extended to a range of organic assemblies by use of transition metal configurations.

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