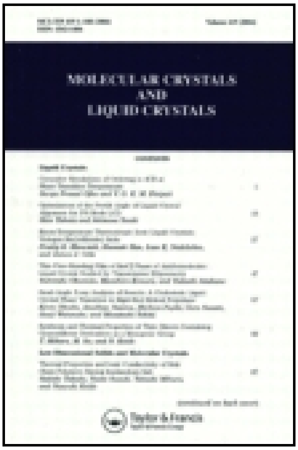

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Varieties of Crystalline Architecture by Using Hydrogen Bonding in Biimidazolate Metal Complex Systems. Part 3: Zigzag One-Dimensional Chains

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VARIETIES OF CRYSTALLINE ARCHITECTURE BY USING HYDROGEN BONDING IN BIIMIDAZOLATE METAL COMPLEX SYSTEMS.
PART 3: ZIGZAG ONE-DIMENSIONAL CHAINS

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Abstract The crystal structure of $[Ni(Hbim)_3](^nPr_4N)\cdot MeOH$ (**1**) ($Hbim^-$ = mono- deprotonated 2,2'-biimidazolate and $^nPr_4N^+$ = tetra-n-propyl-ammonium cation) has been determined. The structure was consists of Ni(II) centers hexacoordinated by three 2,2'-biimidazolate ($Hbim^-$) ligands in an octahedral arrangement. Complex **1** possesses an intermolecular hydrogen bonding structure of zigzag one-dimensional chains in which two of the three $Hbim^-$ ligands connect the metal complex units.

INTRODUCTION

Design of organic molecular crystals as a part of crystal engineering utilizing intermolecular hydrogen-bondings has been extensively studied.[1-3] We are exploring new ways to construct and control the alignment of component molecules by using transition-metal ions and intermolecular multi-point hydrogen bonds of 2,2'-biimidazolate ($Hbim^-$). The transition metal complexes with three $Hbim^-$ ligands have an ability to form a three-dimensional hydrogen bonding networks. We have found that the Ni(II) complexes having three 2,2'-biimidazolate ligands ($[Ni(Hbim)_3]^-$), as shown in Figure 1, with two enantiomers Δ and Λ of these trisbiimidazolate complexes, form a variety of crystal structure with intermolecular hydrogen bonding networks depending on the kinds of the cations.

EXPERIMENTAL

Preparation.

Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution. The ligand of H_2bim was synthesized by literature method.[4]

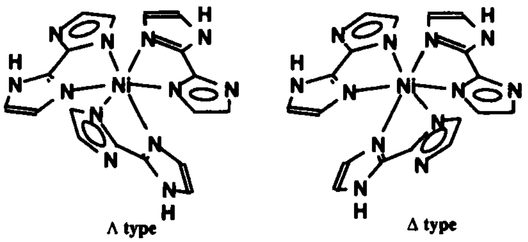

FIGURE 1 Trisbiimidazolate nickel (II) complex, $[Ni(Hbim)_3]^-$.

$[Ni(Hbim)_3](^nPr_4N)\cdot MeOH$ (**1**)

A suspension of H_2bim (0.4 g, 3 mmol) and tetra-n-propylammonium bromide ($^nPr_4NBr$) (0.27 g, 1 mmol) in methanol (60 cm^3) was added to a methanol solution (5 cm^3) of a 28% sodium methylate and the mixture was refluxed to dissolve ligands. To this solution was added dropwise to a methanolic solution (40 cm^3) of $Ni(ClO_4)\cdot 6H_2O$ (0.36g, 1 mmol), and the mixture was refluxed for 5 minutes. Insoluble precipitates were filtered and the filtrate was allowed to stand at room temperature to give blue prism crystals. Analysis; $C_{31}H_{47}N_{13}NiO$; Found: C, 54.51%; H, 6.53%; N, 27.34%, Calcd: C, 55.04%; H, 7.00%; N, 26.92%

CRYSTAL STRUCTURE

The crystal data of $[Ni(Hbim)_3](^nPr_4N)\cdot MeOH$ (**1**) is orthorhombic, space group $Pca2_1$ (No. 29), a = 18.667(2) Å, b = 23.723(6) Å, c = 16.786(1) Å, V = 7433.6(8) $Å^3$, Z = 4, Cu-Kα radiation, λ = 1.54178 Å, $4.0 < 2\theta < 120°$, 7729 reflections were collected, of which 2803 unique reflections ($F_o > 3\sigma(F_o)$) were used for refinement (808 parameters), converging to R = 0.084 and R_w = 0.064. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.53 and -0.56 $eÅ^{-3}$, respectively. All calculations were performed using the teXsan crystallographic software package.[5]

The The $[Ni(Hbim)_3]^-$ complex has an approximate point group D_3 symmetry, where the Λ and Δ isomers are illustrated in Figure 1. The crystal of compound **1** consists of enantiomers Δ and Λ of $[Ni(Hbim)_3]^-$, cations of $^nPr_4N^+$ and methanol molecules. The $^nPr_4N^+$ cations and the methanol molecule are free from the coordination and the methanol molecules are captured in the crystal lattice with intermolecular hydrogen bonds.

The most important intermolecular interaction found in the crystal packing is the formation of the zigzag chain structures with intermolecular hydrogen bonds of two NH-N types, as shown in Figure 2. The intermolecular chain structures are made up of an alternate arrangement of Δ and Λ enamtiomers of the Ni(II) anions. The other remaining Hbim⁻ ligand does not participate in the H-bonding chains and has an H-bonding interaction with MeOH from recrystallization solvent.

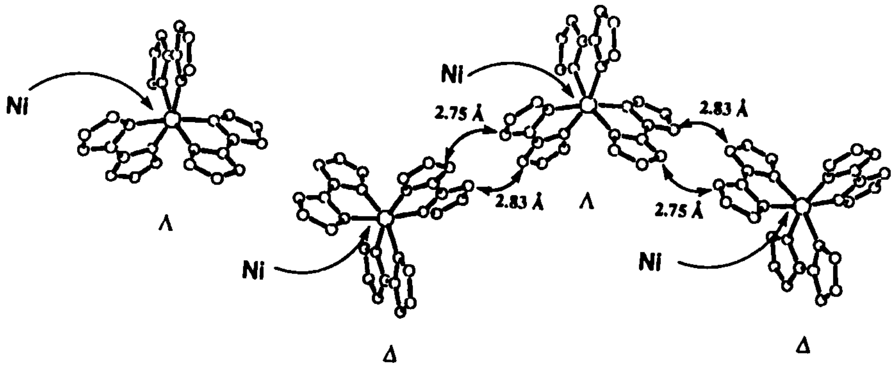

FIGURE 2 Structure of zigzag one-dimensional chains of complex **1**.

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