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### Varieties of Crystalline Architecture by Using Hydrogen Bonding in Biimidazolate Metal Complex Systems. Part 4: Channel Structures

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## VARIETIES OF CRYSTALLINE ARCHITECTURE BY USING HYDROGEN BONDING IN BIIMIDAZOLATE METAL COMPLEX SYSTEMS. PART 4: CHANNEL STRUCTURES

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**Abstract** The crystal structure of  $[\text{Ni}(\text{Hbim})_3](\text{PTMA}) \cdot 3\text{MeOH}$  (**1**) ( $\text{Hbim}^-$  = mono diprotonated 2,2'-biimidazolate and  $\text{PTMA}^+$  = phenyltrimethyl-ammonium cation) has been determined. The structure consists of Ni(II) centers hexacoordinated by three 2,2'-biimidazolate ( $\text{Hbim}^-$ ) ligands in an octahedral arrangement. The crystal packing structure of complex **1** forms channel structures having the hole about  $\sim 9 \text{ \AA}$  along the  $c$  axis.

### INTRODUCTION

Microporous crystals such as zeolites are important materials for molecular sieves, shape-selective catalysts, ion-exchangers and many other applications.<sup>1,2</sup> An ultimate goal in the syntheses of these compounds is the control of size, shape, and (hydrophilic or hydrophobic) character of micropores. Although zeolites and other inorganic porous materials exhibit tremendous structural diversity, porous or channel solids based on organic building blocks are rare.<sup>3,4</sup>

We have demonstrated that the strategy of the crystallization using the trisbiimidazolate nickel(II) complex,  $[\text{Ni}(\text{Hbim})_3]^-$ , can be used to assemble a wide variety of ordered three-dimensional structures and that these assemblies have some of the desirable properties of microporous structures related inorganic materials such as channel structures.

## 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<sub>2</sub>bim was synthesized by literature method.<sup>4</sup>

#### [Ni(Hbim)<sub>3</sub>](PTMA)·3MeOH (**1**)

A suspension of H<sub>2</sub>bim (0.4 g, 3 mmol) and phenyltrimethylammonium bromide [(PTMA)Br] (0.22 g, 1 mmol) in methanol (60 cm<sup>3</sup>) was added to a methanol solution (5 cm<sup>3</sup>) 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<sup>3</sup>) of Ni(ClO<sub>4</sub>)·6H<sub>2</sub>O (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. Crystals of complex **1** were very fragile and rapidly lost solvent, hence elemental analysis of **1** was not satisfactory.

## RESULTS AND DISCUSSION

### Crystal Structure

The crystal data of [Ni(Hbim)<sub>3</sub>](PTMA)·3MeOH (**1**) is formula C<sub>30</sub>H<sub>41</sub>N<sub>13</sub>Ni<sub>2</sub>O<sub>3</sub>, orthorhombic, space group *Pccn* (No. 56), *a* = 19.8670(6) Å, *b* = 23.663(1) Å, *c* = 14.7899(6) Å, *V* = 6952.9(4) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calc}}$  = 1.319g/cm<sup>-3</sup>, Cu-K $\alpha$  radiation,  $\lambda$  = 1.54178 Å, 4.0 < 2 $\theta$  < 120°, 7249 reflections were collected, of which 2414 unique reflections ( $F_0 > 3.0 \sigma(F_0)$ ) were used for refinement (389 parameters), converging to *R* = 0.086 and *R<sub>w</sub>* = 0.089. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.71 and -0.50 eÅ<sup>-3</sup>, respectively. All calculations were performed using the teXsan crystallographic software package.<sup>5</sup>

The crystal of compound **1** consists of  $\Delta$  and  $\Lambda$  enantiomers of [Ni(Hbim)<sub>3</sub>]<sup>-</sup>, cations of PTMA<sup>+</sup> and methanol molecules. Four [Ni(Hbim)<sub>3</sub>]<sup>-</sup> complexes and four PTMA cations form a ring structure (Figure 1). The ring structures stack along the *c* axis running the length of the crystal to create a large channel structure. The inside of the channel structures is hydrophilic and filled with hydrogen bonded MeOH, as shown in Figure 1. The columns of MeOH molecules exit in the channel structures along the *c* axis. Each component of [Ni(Hbim)<sub>3</sub>]<sup>-</sup> complex is linked to one neighbor of the

$[\text{Ni}(\text{Hbim})_3]^-$  complex by a direct hydrogen bonding of NH-N types of Hbim<sup>-</sup> ligands to create distorted dimer arrangement, which connect the ring structure.

These observations are important because they suggest that intelligent application of the strategy of  $[\text{Ni}(\text{Hbim})_3]^-$  building blocks can be used to build an unlimited range of ordered three-dimensional organic and metallic networks with some of the desirable properties of zeolites and related inorganic materials, including high structural integrity, potentially large void volumes, and adjustable microporosity.

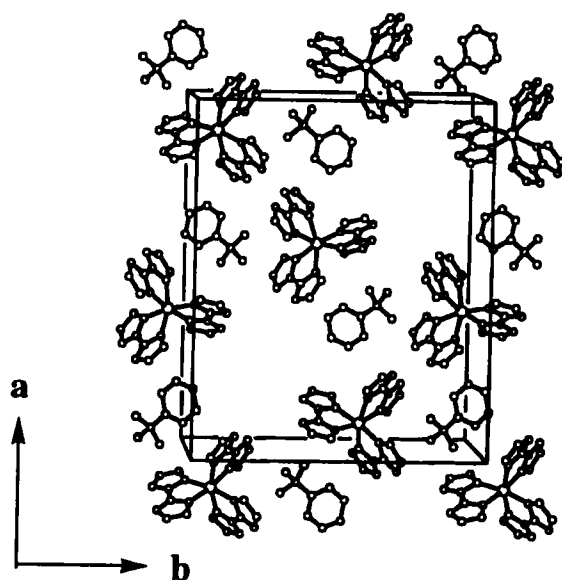


FIGURE 1 Packing structure of complex 1 along *a* and *b* axis.

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## REFERENCES

1. R. Szostak, Molecular Sieves, (Van Nostrand Reinhold, New York, 1989).
2. M. E. Davis, R. F. Lobo, Chem. Mater., **4**, 756 (1992).
3. X. Wang, M. Simard and J. D. Wuest, J. Am. Chem. Soc., **116**, 12119 (1994).
4. B. F. Abrahams, B. F. Hoskins, R. Robson, Nature, **369**, 727 (1994).
5. teXsan, Crystal Structure Analysis Package. Molecular Structure Corp. (the Woodlands, TX, 1985 and 1992).