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Varieties of Crystalline Architecture by Using Hydrogen Bonding in Biimidazolate Metal Complex Systems. Part 5: Double-Interlocking Honeycomb Sheet

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VARIETIES OF CRYSTALLINE ARCHITECTURE BY USING HYDROGEN BONDING IN BIIMIDAZOLATE METAL COMPLEX SYSTEMS. PART 5: DOUBLE-INTERLOCKING HONEYCOMB SHEET

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Abstract The crystal structures of $[Ni(Hbim)_3]_2(NEt_4)_2(H_2bim)\cdot MeOH$ (**1**) ($Hbim^-$ = mono diprotonated 2,2'-biimidazolate and NEt_4^+ = cation) has been determined. The structure was consists of Ni(II) centers hexacoordinated by three $Hbim^-$ ligands in octahedral arrangement. Complex **1** possesses an intermolecular H-bonding structure of interpenetrating polycatenane to give double-interlocking honeycomb sheet structures.

INTRODUCTION

Concurrent has been the development of three-dimensional networks based primarily on linking metal centers with rodlike or other essentially rigid bridging components.[1,2] An occasional product of this latter work has been the formation of interpenetrating, adamantyl-like networks.[3] Interleaved, extended networks incorporating flexible bridging units are, however, rare.[4-6] While the formation of such aggregates is fascinating, because of the size of the constituent molecules and their degrees of conformational freedom, it is difficult to identify the structural parameters in these building blocks responsible for self-assembly.

We report here the discovery of an unusual, new, flexibly bridged, interpenetrating polycatenane having double-interlocking honeycomb sheet structures, which making up trisbiimidazolate Ni(II) complexes, $[Ni(Hbim)_3]^-$, and free ligands of 2,2'-biimidazoles (H_2bim).

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 H_2bim was synthesized by literature method.[4]

$[Ni(Hbim)_3]_2(NEt_4)_2(H_2bim)\cdot MeOH$ (**1**)

A suspension of H_2bim (0.4 g, 3 mmol) and tetraethyl ammonium perchrolate (Et_4NClO_4) (0.22 g, 1 mmol) in methanol (60 cm^3) was added to a methanol solution (5 cm^3) of a 28% sodium methylate and 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; $C_{30}H_{42}N_{15}NiO$; Found: C, 52.02%; H, 6.16%; N, 30.32%, Calcd: C, 52.41%; H, 6.16%; N, 30.56%

RESULTS AND DISCUSSION

The crystal data of $[Ni(Hbim)_3]_2(NEt_4)_2(H_2bim)\cdot MeOH$ (**1**) is formula $C_{59}H_{80}N_{30}Ni_2O$, tetragonal, space group $P4_12_12$ (No. 92), a = 19.084(2) Å, c = 38.533(3) Å, V = 14034(2) $Å^3$, Z = 8, ρ_{calc} = 1.301 g/cm^{-1} , Cu-Kα radiation, λ = 1.54178 Å, $4.0 < 2\theta < 120°$, 6364 reflections were collected, of which 3122 unique reflections ($F_o > 3.0\ \sigma(F_o)$) were used for refinement (771 parameters), converging to R = 0.106 and R_w = 0.084. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.85 and -0.66 $eÅ^{-3}$, respectively. All calculations were performed using the teXsan crystallographic software package.[7]

The $[Ni(Hbim)_3(NEt_4)]_2(H_2bim)$ complex showed a complicated unique crystal structure. The crystal structure has four characteristic points. First, this has a zigzag one-dimensional chain structure having intermolecular hydrogen bonds similar to the structure, described in the complex $[Ni(Hbim)_3]^-$ with the $^nPr_4N^+$ cation.[8] The chain structure is comprised of alternate arrangements of Δ and Λ enamtiomers of the trisbiimidazolate nickel(II) anions. Second, free biimidazole ligands (H_2bim) connect the zigzag one-dimensional chains to give a honeycomb sheet structure by intermolecular hydrogen bonds (Figure 1). Third, the two pairs of the honeycomb sheets with perpendicular arrangement form a double interlocking structure. The orientation of the

intermolecular hydrogen bonding and the conformation around the nickel center play an important role for formation of the double interlocking structure. Finally, the unit of the interlocking double honeycomb sheets arrange in three-dimension to form an infinite interlocking structure of the double honeycomb sheets.

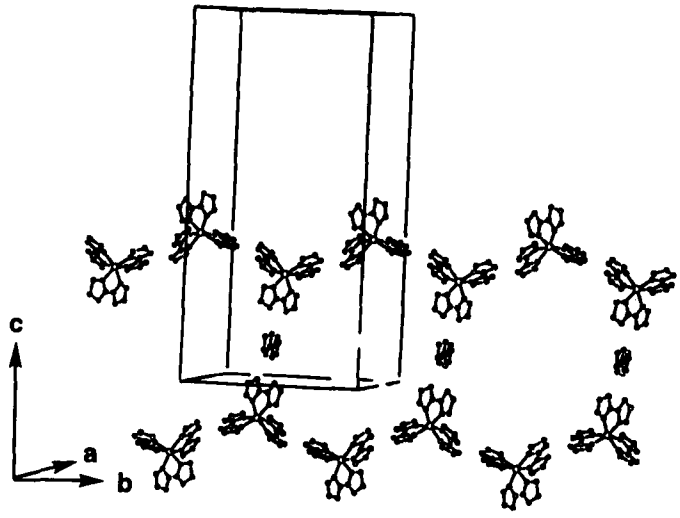

FIGURE 1 Honeycomb sheets structure of complex **1**.

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