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Varieties of Crystalline Architecture by Using Hydrogen Bonding in Biimidazolate Metal Complex Systems. Part 2: One-Dimensional Linear Chains

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VARIETIES OF CRYSTALLINE ARCHITECTURE BY USING HYDROGEN BONDING IN BIIMIDAZOLATE METAL COMPLEX SYSTEMS. PART 2: ONE-DIMENSIONAL LINEAR CHAINS

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Abstract. We observed lower shifted $\nu(\text{NH})$ bands and higher shifted $2\gamma(\text{NH})$ overtone vibrations in $[\text{Cu}(\text{Hbim})_2]_n$ (**1**) (Hbim^- = mono deprotonated 2,2'-biimidazolate) in FT-IR spectroscopy. This observation demonstrated that complex **1** forms a hydrogen-bonding polymer with intermolecular NH-N hydrogen bonds between Hbim^- ligands to give a one-dimensional linear structure.

INTRODUCTION

In order to realize HBCT systems by using transition metal complexes it is requirement that metal complexes have not only the conjugated ligand systems but also an ability to construct the one-, two- or three-dimensional network systems with intermolecular hydrogen bonds.¹⁻⁵ We have already demonstrated that the Cu(II) complex $[\text{Cu}(\text{salenNMe}_2)(\text{Hbim})]_2$ with the one-deprotonated 2,2'-biimidazolate ligand (Hbim^-) can form the intermolecular hydrogen bonding dimer which has the complementary NH-N bond between the Hbim^- ligands.³

It should be considered that mononuclear transition metal complexes with two Hbim^- ligands are possible to form one-dimensional chain structures with intermolecular hydrogen bonds between Hbim^- ligands. The complex of $[\text{Cu}(\text{Hbim})_2]_n$ (**1**) was already prepared and reported as the insoluble polymer.^{6,7} Complex **1** was interesting to become a good candidate to be achieved the HBCT systems but not characterized on it in detail.

IR spectral data may support that complex **1** has a relatively strong intermolecular hydrogen bond of the NH-N type between ligands to form one-dimensional chain structures as shown in Figure 1.

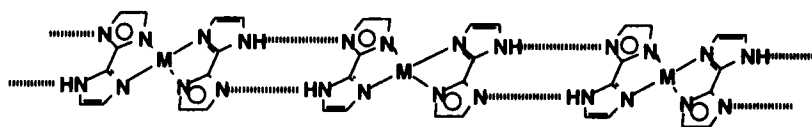


FIGURE 1 Hydrogen bonding one-dimensional linear chains.

EXPERIMENTAL

Measurement

The IR spectra were recorded in KBr discs on a Perkin-Elmer 180 spectrophotometer at 300 K.

Preparation

Complex **1** was prepared by the modified literature method.^{6,7} Complex **1** is probably polymeric and insoluble in common solvent, not giving any good crystals for X-ray analysis.

RESULTS AND DISCUSSION

The IR spectra of the complex **1** in KBr disk are shown in Figure 2. The IR spectra of free imidazole in CCl_4 show the $\nu(\text{NH})$ band around 3478 cm^{-1} ,⁸ which indicates no intermolecular hydrogen bonds for NH groups. While in the solid state the band is shifted to lower frequency around 2833 cm^{-1} .⁸ Such lower shift is due to an intermolecular hydrogen bonds of a NH-N type.¹⁰ The corresponding band in complex **1** is shifted much lower to 2525 cm^{-1} (2895 cm^{-1} for free 2,2'-biimidazole (H_2bim) in solid) as shown in Figure 2. This suggests that a strong NH-N hydrogen bonding is formed in complex **1**.

In general, free imidazoles show weak out-of-plane deformation $2\gamma(\text{NH})$ around 1800 cm^{-1} which is shifted to higher frequencies when they form strong NH-N hydrogen bonding in the solid state.¹² Complex **1** shows a similar deformation band, at a higher frequency (1899 cm^{-1}) in the strong intensity (Figure 2). Thus, the $2\gamma(\text{NH})$ bands and their intensity also supports that complex **1** has a strong hydrogen bond.¹³ Consequently, the IR spectra of complex **1** represents typical strong NH-N hydrogen bonding systems, which is manifested by the shifts of the $\nu(\text{NH})$ and, the intensity and

frequency of $2\nu(\text{NH})$. We conclude that complex **1** has the strong intermolecular hydrogen bonds of Hbim^- ligands with complementary two NH-N types and forms one dimensional linear chains, which are assembled by the intermolecular hydrogen bonds of Hbim^- ligands.

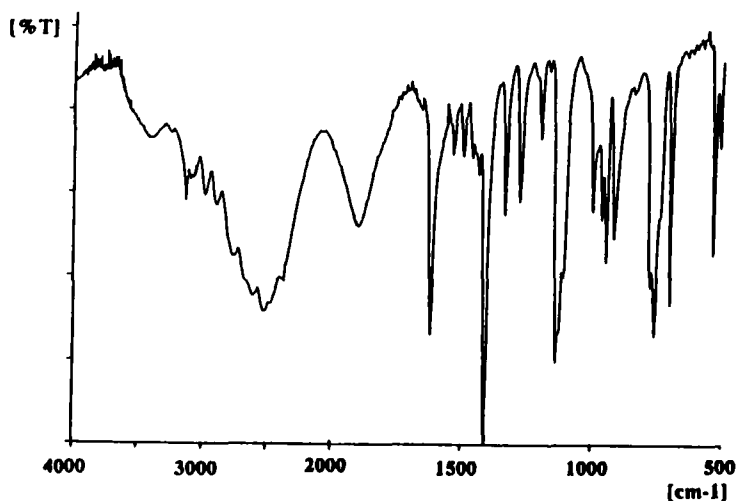


FIGURE 2 FT-IR spectra of complex **1** at room temperature in KBr disks.

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