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ONE-DIMENSIONAL HETEROBIMETALLIC COMPLEX BRIDGED BY 2,2'-BIBENZIMIDAZOLATE LIGAND

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Abstract We have studied the crystal structure of a Cu(II) complex $[Cu(bbim)_2]({}^{n}Pr_4N)(Na)\cdot MeOH$ (**1**) [where $bbim^{2-}$ = di-deprotonated 2,2'-bibenzimidazolate and ${}^{n}Pr_4N^{+}$ = tetra-n-propylammonium cation] with two $bbim^{2-}$ as a di-deprotonated ligand for the first time. The X-ray crystal analysis shows that this Cu(II) complex consists of one-dimensional infinite chains with an alternate bonding sequence of Cu(II) and Na(I) bridged by the $bbim^{2-}$ ligand. Interestingly, Cu(II) ion in this complex has a distorted tetrahedral coordination structure. The interaction between these infinite chains is separated by ${}^{n}Pr_4N^{+}$ cations.

INTRODUCTION

Particular attention has been devoted recently to the development of rational synthetic routes to polymeric coordination complexes of new bridged ligands, because they are of interest in connection with materials science, for their potential properties such as electrical conductivity[1] and molecular magnetism.[2]

Since 2,2'-biimidazole (H_2bim) is a bidentate ligand with multi-proton donor properties, it can coordinate to transition metal ions as three types: neutral (H_2bim), mono-deprotonated ($Hbim^{-}$), and di-deprotonated (bim^{2-}) forms.[3,4] It was reported that 2,2'-bibenzimidazole (H_2bbim) has the same function toward transition metal ions as does the H_2bim ligand.[4] Also it is known the di-deprotonated ($bbim^{2-}$) form of this ligand can potentially behave as an effective two-electron donor[5] to give an oxidized form (bbim) as shown in Figure 1.

This $bbim^{2-}$ ligand can be not only a building block for one-dimensional heterobimetallic complexes as the bridges of two metal ions but also behave as a function ligand having multi-electron donor properties. So it seems an interesting materials challenge to prepare the coordination polymer using $bbim^{2-}$ bridged derivatives because it is possible to realize models for the electrical conductivity and molecule-based magnetism having the mutual interaction of dπ-pπ mixed electrons. As the first step, we

succeeded in preparing and characterizing the compound **1** by X-ray crystal structure analysis, which consisted of one-dimensional infinite chains with an alternate bonding sequence of Cu(II) and Na(I) bridged by the $bbim^{2-}$ ligand.

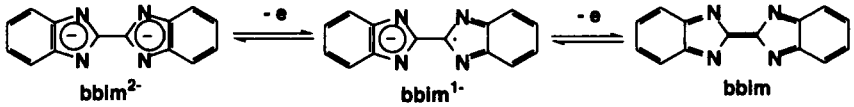

FIGURE 1 Oxidized forms of the $bbim^{2-}$ ligand.

RESULTS AND DISCUSSION

The starting material of $[Cu(H_2bbim)_2]Cl_2$ was synthesized according to literature .[6] The methanol solution of the compound **1** and tetra-n-propylammonium bromide with a 1 : 1 stoichiometric ratio reacted with an excess NaOMe alkaline solution and the mixture became black-brown to yield the compound **1** within a few days as black crystals.

The single-crystal structure of $[Cu(bbim)_2]({}^{n}Pr_4N)(Na)\cdot MeOH$ (**1**) was solved using standard direct methods techniques. The crystal data of the compound **1** is of formula $C_{41}H_{48}N_9CuNaO$, orthorhombic with space group *Pbcn* (No. 60), a = 11.0981(7) Å, b = 16.458(1) Å, c = 21.9897(7) Å, V = 4016.5(3) $Å^3$, Z = 8, and ρ_{calc} = 1.235 g/cm^{-1}. With Cu-Kα radiation, λ = 1.54178 Å, and $4.0 < 2\theta < 120°$, 4277 reflections were collected, of which 2015 unique reflections ($F_o > 3.0\,\sigma(F_o)$) were used for refinement (237 parameters), converging to R = 0.078 and R_w = 0.080. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.87 and -0.78 $eÅ^{-3}$, respectively. All calculations were performed using the teXsan crystallographic software package.[7]

Crystal Structure

The structure consists of infinite chains by heterometal complexes of the binuclear anions, $[Cu(bbim)_2(Na)]^-$, and ${}^{n}Pr_4N^+$ cations and methanol molecules. This is the first example of binuclear metal complexes bridged by the di-deprotonated bibenzimidazolate, which is characterized by X-ray crystal structure analysis. The X-ray crystal structure showed that the compound **1** is of one-dimensional infinite chain structures along the *a* axis which were built up of alternate copper(II) and sodium(I) ions bridged by $bbim^{2-}$ of multi-deprotonated and multi-electron transferred ligands as shown in Figure 2. Each one-dimensional chains built up of alternate heterometal ions has no

mutual interaction between $bbim^{2-}$ ligands, and copper(II) ions in terms of crystal structure. This is because the interaction between these infinite chains is separated by $^{n}Pr_4N^+$ cations.

In Figure 2 is also shown the inner coordination of a copper(II) ion and sodium(I) ion, and the $bbim^{2-}$ bridged dianion. The Cu(II) ions of the complex **1** are bound at the unusually distorted tetrahedral N_4 donor site comprised of two $bbim^{2-}$ ligands. The dihedral angle between the two $bbim^{2-}$ ligands is 130.33°. The Na(I) ions have five-coordinated structure comprised of the distorted tetrahedral N_4 donor site and the oxygen of a methanol molecule.

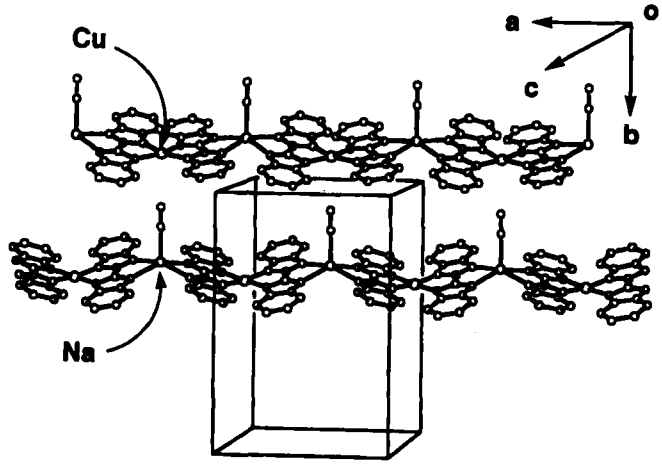

FIGURE 2 One-dimensional chain structures along the *a* axis of the compound 1.

CONCLUSION

We synthesized the first prototypical example of binuclear metal complexes bridged by the di-deprotonated bibenzimidazolate and characterized the crystal structure by X-ray diffraction. It turned out that the complex **1** forms one-dimensional infinite chains with an alternate bonding sequence of Cu(II) and Na(II) bridged by the $bbim^{2-}$ ligand. The interchain interaction was not found in terms of the crystal structure. Chemistry bridged between the multi-deprotonation property of $bbim^{2-}$ and multi-functionality of intriguing heterometallic complexes is underway.

ACKNOWLEDGMENT

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