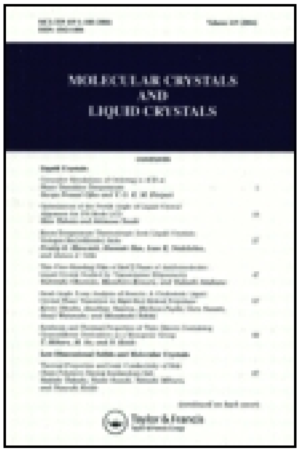

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Crystal Structure and Magnetic Characterization of a Building Block for Quasi One-Dimensional Heterobimetallic Polymeric Complexes Bridged by 2,2′-Bibenzimidazolate Ligands

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CRYSTAL STRUCTURE AND MAGNETIC CHARACTERIZATION OF A BUILDING BLOCK FOR QUASI ONE-DIMENSIONAL HETEROBIMETALLIC POLYMERIC COMPLEXES BRIDGED BY 2,2'-BIBENZIMIDAZOLATE LIGANDS

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Abstract We have synthesized $[^{63}Cu(bbim)_2](^nBu_4N)_2$(1)by 2,2'-bibenzimidazolate ligands (bbim) with multi-proton donor property as a building block of models for quasi one-dimensional heterobimetallic polymeric complexes with dp-pp interaction. The study of the molecular and electronic structures of **1** and the non-deprotonated form of **1**, in terms of crystal structure analysis and magnetic characterization by single-crystal ESR spectroscopy, has been carried out. The angular dependence of the Cu(II) hyperfine ESR spectra of **1** showed that the parallel orientation ($B_0 \parallel$ c axis) gave both the maximum copper hyperfine splitting (84×10^{-4} cm^{-1}) and the maximum anisotropic g value ($g_{\parallel} = 2.218$). The findings show that the copper(II) ion is bound at the site of a tetragonally distorted tetrahedral field, being in accord with the molecular structure of the donor site with the distorted tetrahedral symmetry as obtained by the X-ray crystal analysis. Superhyperfine structures due to the nitrogen atoms of bbim^{2-} dianion were detected in the $g_{\perp}$ region of the ESR spectrum of $[^{63}Cu(bbim)_2](^nBu_4N)_2$ in a frozen glass.

INTRODUCTION

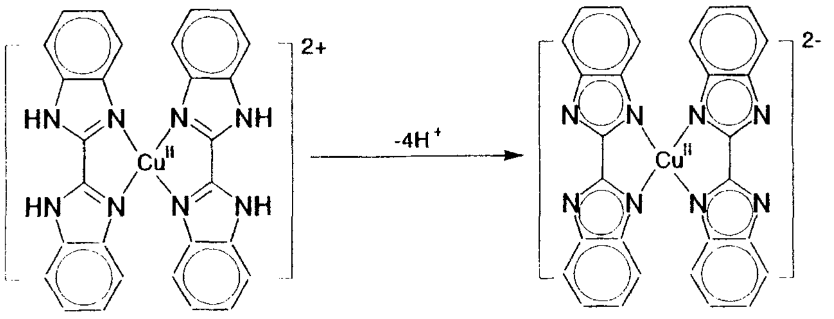
The quest for multifunctionality molecular based materials has been the focus of current topics in materials science and chemistry. Particularly, low-dimensional molecule-based materials with electric conductivity and magnetism are an intriguing issue because of the fluctuation of charge and spin. Quantum cooperative phenomena associated with the proton transfer induced or triggered by external perturbation have attracted attention to be novel supra-multifunctionality, recently.

We have designed a bidentate ligand with multi-proton donor property as a building block of models for quasi one-dimensional heterobimetallic polymeric complexes. We have synthesized **1** as a candidate for the building block to study the molecular and electronic structures of **1**, concentrating on the occurrence of charge transfer in the metal-ligand bond. For this purpose the crystal structure analysis of **1** and magnetic characterization of the metal binding site have been made by using the X-ray diffraction method and single-crystal ESR spectroscopy, respectively.

EXPERIMENTAL

The starting material of $[Cu(H_2bbim)_2](ClO_4)_2$ was synthesized according to a literature-based[1] but modified method. The methanol solution of a 1:2 stoichiometric ratio of $[Cu(H_2bbim)_2](ClO_4)_2$ and n-tetrabutylammonium perchlorate reacted with an excess methanol solution of the potassium t-butoxide alkaline, as shown in Scheme below. The mixture became black-brown to yield the black crystals of the compound **1** within a few days. The corresponding ^{63}Cu-enriched compounds have been prepared for the purpose of accurate ESR measurements.

$$[Cu(H_2bbim)_2](ClO_4)_2 \xrightarrow[^{t}BuOK/MeOH]{^{n}Bu_4NClO_4} [Cu(bbim)_2](^{n}Bu_4N)_2\cdot 2H_2O$$



The single-crystal structure of [^{63}Cu(bbim)$_2$](^{n}Bu$_4$N)$_2$•2H$_2$O(**1**) was solved by using standard direct methods techniques. The crystal data of **1** is orthorhombic with space group P2$_1$2$_1$2(No.18), a=17.860(5) Å, b=20.274(4) Å, c=8.708(4) Å, V=3153(1) Å^3, Z=2, and r$_{calc}$=1.134g/cm. With Mo-Ka radiation, l=0.71069 Å, and 6.0°<2q<50.1°, 3,192 reflections were collected, of which 2,482 unique reflections (I>2.0d(I)) were used for refinement (339 parameters), converging to R=0.114 and R$_w$=0.114. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.46 and -0.39 e / Å^3, respectively. All calculations were performed by means of the *teXsan* crystallographic software package[2].

Single-crystal ESR measurements of the complex **1** were made on a Bruker ESP300 ESR spectrometer and a JEOL FE-2XG ESR spectrometer both operating at X-band. For the measurement of the angular dependence of hyperfine ESR structures a two-circle goniometer was used.

RESULTS AND DISCUSSION

Crystal Structure

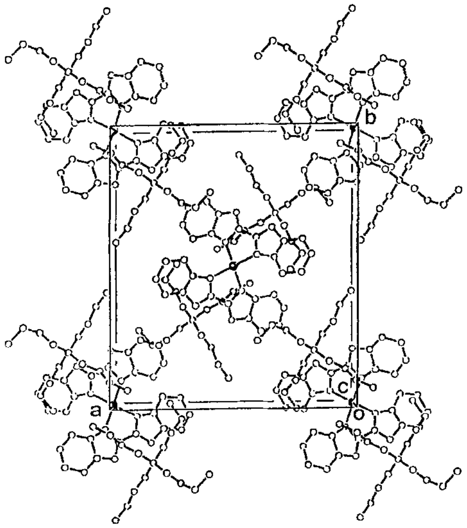


FIGURE 1 Projection of the crystal structure of **1** onto the *ab* plane.

The crystal structure of the unit cell of **1** consists of a copper(II) complex dianion $[Cu(bbim)_2]^{2-}$, two $^nBu_4N^+$ cations, and two water molecules of crystallization. Figure 1 shows the projection of the complex dianion $[Cu(bbim)_2]^{2-}$ onto the crystallographic *ab* plane, where the cations and water molecules are eliminated to have a clear view of the inner coordination of copper(II) ions and two $bbim^{2-}$ dianions.

Figure 2 depicts an ORTEP view of the molecular structure of 1, showing that the copper(II) ion is bound at the unusually distorted tetrahedral N_4 donor site. The dihedral angle between the two $bbim^{2-}$ ligands is 37 degree. The ligand field symmetry and electronic spin structure of the copper(II) binding site are discussed below in connection with the observed copper(II) hyperfine structure.

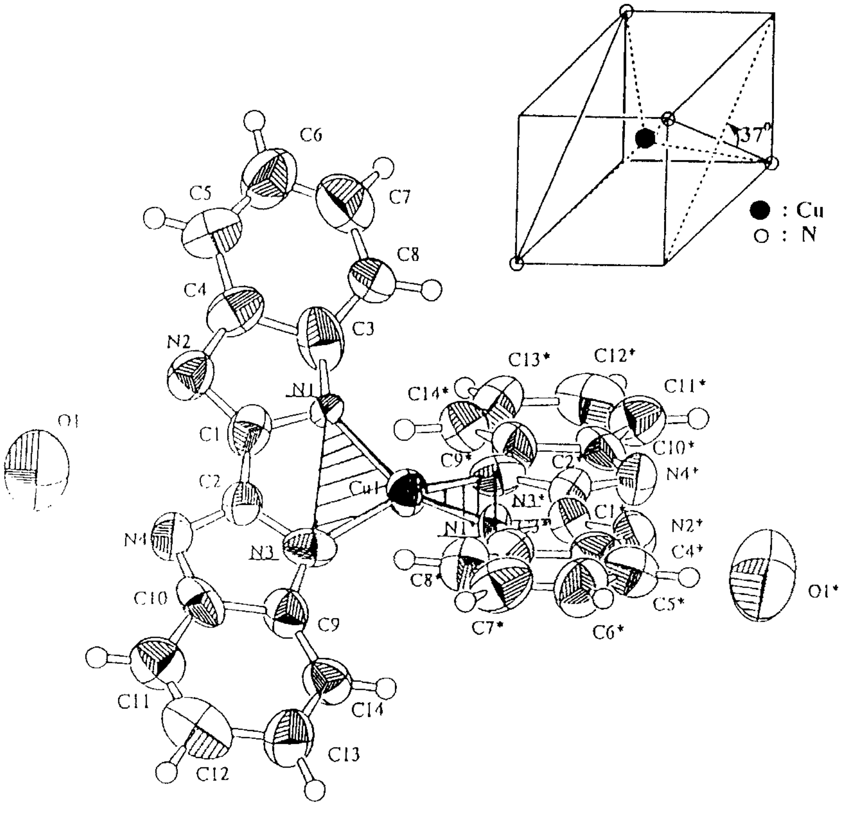


FIGURE 2 ORTEP view of the molecular structure of **1**. Only $[Cu(bbim)_2]^{2-}$ is depicted.

The two water molecules of crystallization form hydrogen bonding with the nitrogen atoms of the two bbim^{2-} ligands. Each hydrogen bonding takes place with the two nitrogen atoms on the other side which do not participate in the coordination with the copper(II) ion. The Cu(II)-Cu(II) distance between the nearest neighboring $[Cu(bbim)_2]^{2-}$ is 8.71 Å, suggesting the possible appearance of the copper(II) hyperfine structure in the ESR spectra of a non-magnetically diluted single crystal of **1**.

Electronic Spin Structure of the Metal Binding Site

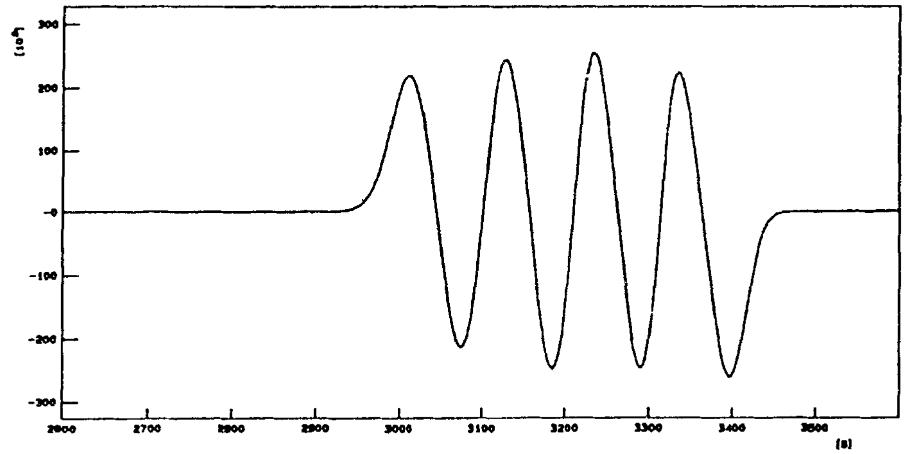


FIGURE 3 Copper hyperfine structure observed from the single crystal of **1** at 4K.

Figure 3 shows a typical copper(II) hyperfine ESR spectrum observed at 4K from a single crystal of **1**. The angular dependence of the spectra measured in the crystallographic-axis system showed the crystallographic site splitting in accordance with the orthorhombic symmetry and Z=2. The parallel orientation ($B_0 \parallel$ c axis) gave both the maximum copper hyperfine splitting(84×10^{-4} cm^{-1}) and the maximum anisotropic g value ($g_{\parallel}=2.218$). These findings indicate that the copper(II) binding site is in a ligand field of axial symmetry and that the symmetry axis is parallel to the c axis.

The observed axial g value and isotropic copper(II) hyperfine splitting (29×10^{-4} cm^{-1}) in the perpendicular orientation of static magnetic field also show that the copper(II) ion is bound at the site of a tetragonally distorted tetrahedral field, being in accord with the molecular structure of the donor site with the distorted tetrahedral symmetry (pseudotetrahedral symmetry), as obtained by the X-ray crystal analysis. The results from the single-crystal ESR measurements of **1** indicate that the ground-state electronic configuration for the copper(II) ion is $|(z^2)(\bar{z}^2)\cdots(yz)(\overline{yz})(xy)|$ in terms of d-orbitals.

A useful semiempirical relationship by Yokoi and Addison[3] has been applied to estimate the dihedral angle(w) in pseudotetrahedral symmetry(Table 1). The observed value for $g_{\parallel}$ has given 37 degrees, being in good agreement with the value from the X-ray analysis.

TABLE 1 Estimated relationship between $g_{\parallel}$ and ω.

Complex	ω	$g_{\parallel}$	Reference
$Cu(P2A\text{-}H)_2$	0	2.182	3
$[Cu(bbim)_2](^nBu_4N)_2$	37	2.218	this work
$Cu(bipyam)_2(ClO_4)_2$ ′	56	2.244	3
$Cu(P2A\text{-}^tBu)_2$	60	2.254	3
$Cu[3,3',5,5'\text{-}Me_4(dpmn)_2]_2$	68	2.280	3
$Cu[Me_4Ga(dmpz)_2]_2$	72	2.316	3
Cs_2CuCl_2	74	2.384	3

Superhyperfine structures due to the nitrogen atoms of $bbim^{2-}$ dianion were detected in the $g_{\perp}$ region of the ESR spectrum of $[^{63}Cu(bbim)_2](^nBu_4N)_2 \cdot 2H_2O$ complex in dry MeOH-NaOMe (9:1) at 4K(Figure 4). The coupling constant for the superhyperfine interaction is 7×10^{-4} cm^{-1}, allowing us to evaluate MO parameters for **1**[4,5]. It turns out that the binding site is ionic compared with other Cu(II) complexes of the similar molecular distortion.

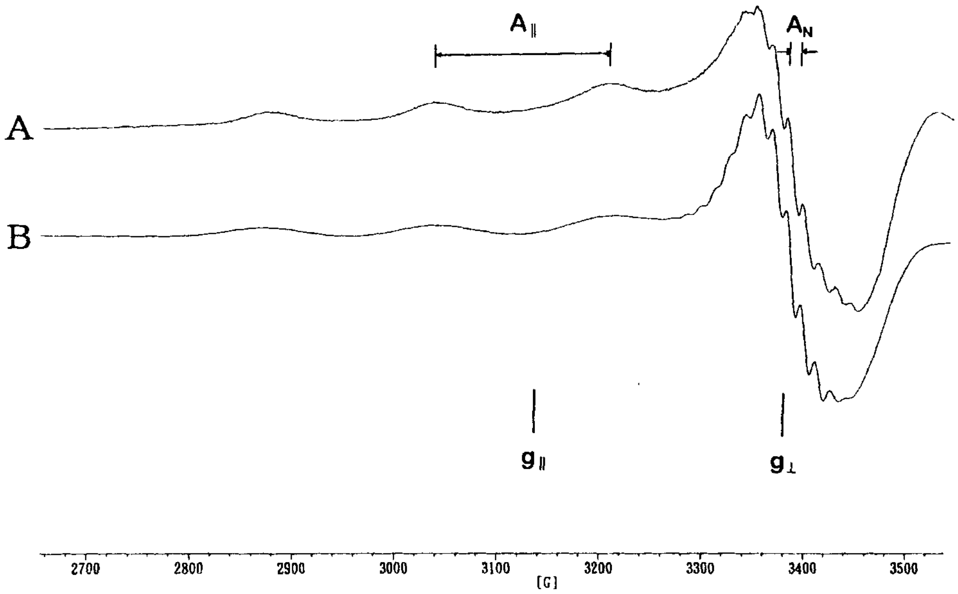


FIGURE 4 Experimental(A) and simulated(B) esr spectra of $[^{63}Cu(bbim)_2]$ $(^nBu_4N)_2 \cdot 2H_2O$(**1**) complex in dry MeOH-NaOMe(9:1). (A) observed at 4K. Agreement between the observed and simulated spectra shows the appearance of the superhyperfine splitting due to the *2,2'-bi-imidazole* nitrogen atoms in the $g_\perp$ region.

CONCLUSION

We have designed a building block with bidentate 2,2'-bibenzimidazolate ligands (bbim) with multi-proton donor capability and synthesized $[^{63}Cu(bbim)_2](^nBu_4N)_2 \cdot 2H_2O$(**1**) as a prototypical model for one-dimensional heterobimetallic complexes. Characterization of the molecular and electronic spin structures of the metal binding site **1** serves for the understanding of the properties of the polymeric complexes, whose synthesis is under way.

The X-ray crystal structure analysis and the single-crystal ESR study of **1** indicate that the binding site is of tetrahedral symmetry with great tetragonal distortion (pseudotetrahedral symmetry). This is partly due to the sizable ligand of the $bbim^{2-}$ dianion. Superhyperfine structures due to the nitrogen atoms of $bbim^{2-}$ dianion enable us to conclude that the binding site is ionic. The measurements of the non-deprotonated form of **1** are in progress.

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