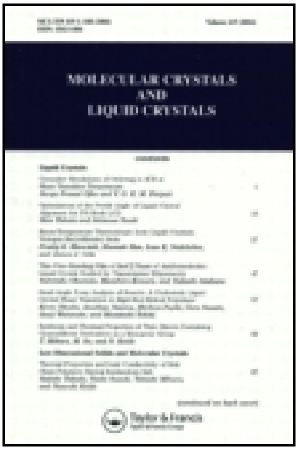

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Crystal Structure and Magnetic Characterization of a Building Block For One-Dimensional Heterobimetallic Poly- Meric Complexes Bridged by 2,2′-Bibenzimidazolate Ligands

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

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Abstract We have designed a bidentate ligand with multi-proton donor property as a building block of models for one-dimensional heterobimetallic complexes. We have synthesized $[Cu(bbim)_2](^nBu_4N)_2$ (1) as a candidate for the building block of such one-dimensional complexes. The crystal structure analysis of 1 and magnetic characterization by single-crystal ESR spectroscopy have been carried out. The crystal data is as follows: orthorhombic, $P2_12_12$, a = 17.860 Å, b = 20.274 Å, c = 8.704 Å, Z = 2. ^{63}Cu-enriched compound of 1 has also been synthesized for single-crystal ESR spectroscopy. ESR measurements of non-magnetically diluted single crystals of 1 have shown that Cu(II) ions are in the tetrahedral ligand field with great tetragonal distortion, being in accord with the molecular structural data on 1 by the X ray analysis.

INTRODUCTION

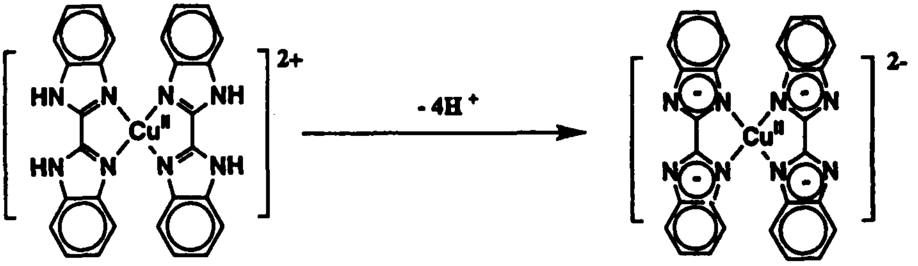
The quest for multifunctionality molecular based materials has been the focus of current topics in materials science and chemistry. Particularly, low-dimensional molecular based materials with electric conductivity and magnetism are an intriguing issue because of the fluctuation of charge and spin. Quantum 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 one-dimensional heterobimetallic complexes. We have synthesized $[Cu(bbim)_2](^nBu_4N)_2$ (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 $[Cu(bbim)_2](^{n}Bu_4N)_2 \cdot 2H_2O$ (1) was solved by using standard direct methods techniques. The crystal data of 1 is orthorhombic with space group $P2_12_12$ (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 ρ_{calc} = 1.134g/cm. With Mo-Kα radiation, λ = 0.71069 Å, and $6.0° < 2\theta < 50.1°$, 3,192 reflections were collected, of which 2,482 unique reflections ($I > 2.0\ \sigma(I)$) 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 -0.39e/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 ESP 300 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

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 twe 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.

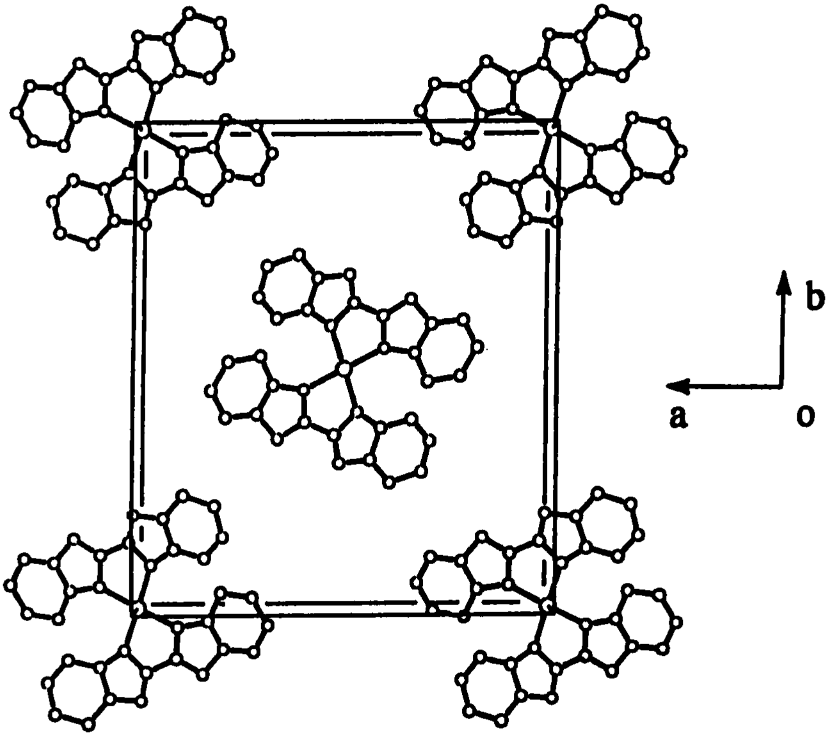


FIGURE 1 Projection of the crystal structure of 1 onto the *ab* plane.

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 will be discussed in connection with the observed ESR copper(II) hyperfine structure.

The two water molecules of crystallization form hydrogen bonding with the nitrogen atoms of the two $bbim^{-2}$ ligands. Each hydrogen bonding took 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 $[\mathrm{Cu(bbim)_2}]^{2-}$ 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**.

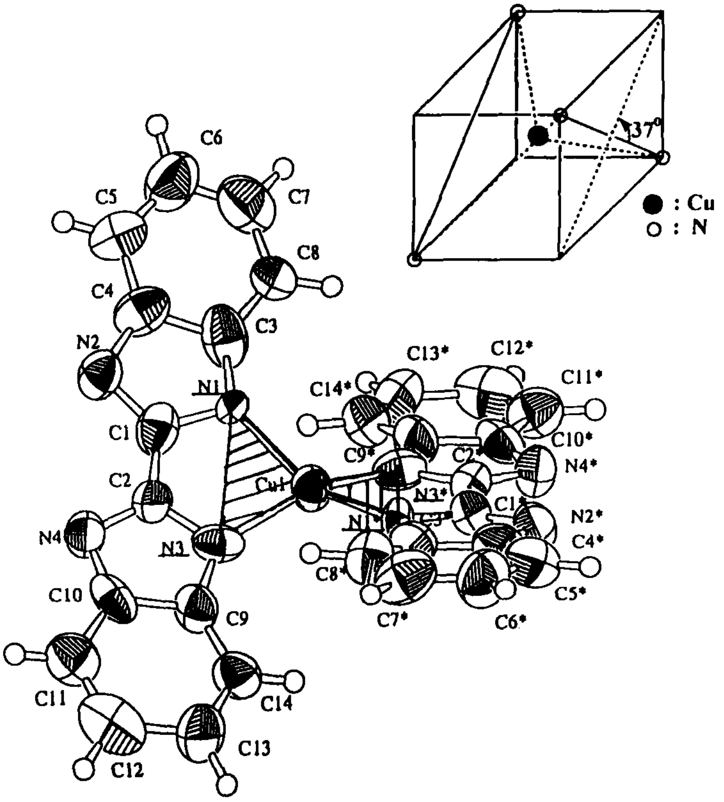


FIGURE 2 ORTEP oview of the molecular structure of **1**. Only $[\mathrm{Cu(II)(bbim)_2}]^{2-}$ is depicted.

Electronic Spin Structure of the Metal Binding Site

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 $Z = 2$. Figure 4 shows a hyperfine spectrum with the static magnetic field $\mathbf{B}_0$ nearly along the c axis. The parallel orientation ($\mathbf{B}_0 \parallel$ c axis) gave both the minimum copper hyperfine splitting and the minimum

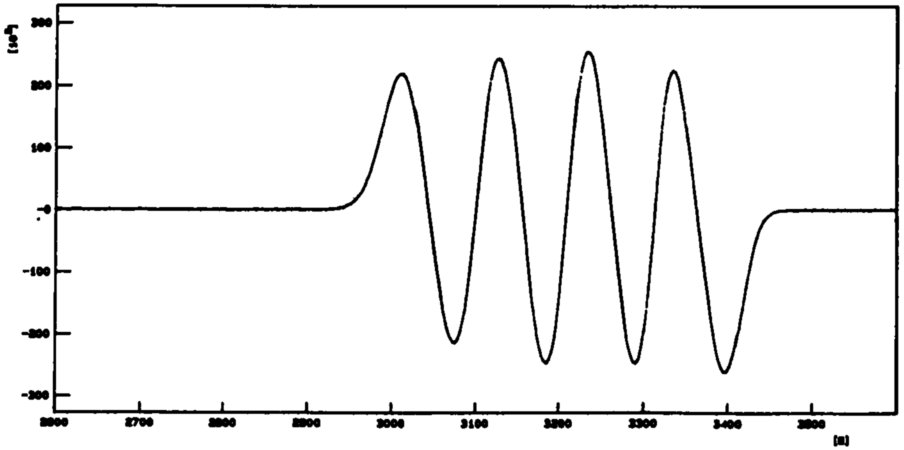


FIGURE 3 Copper hyperfine structure observed from the single crystal of 1 at 4 K.

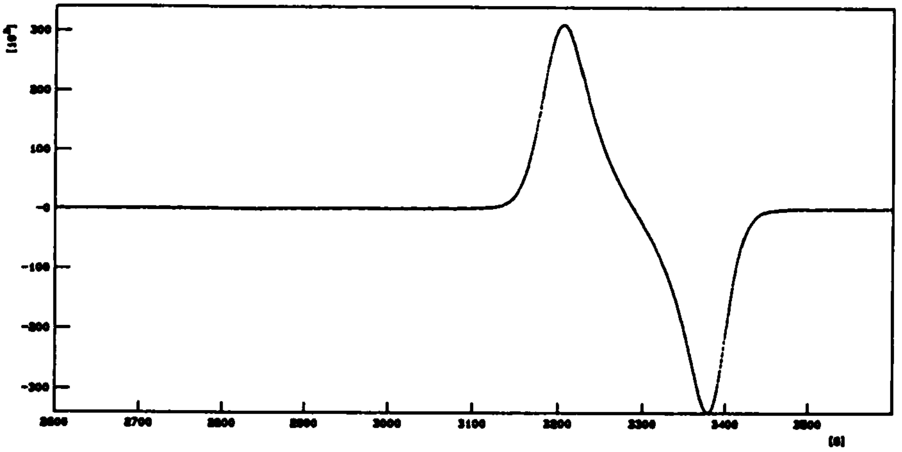


FIGURE 4 Copper hyperfine structure observed with the static magnetic field nearly parallel to the *c* axis.

anisotropic g value (g = 2.04). The isotropic behaviors of the g value (g_1= g_2= 2.04, g_3= 2.22) and the copper hyperfine splitting featured in the spectra measured in the *ab* plane. 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 g value and nearly vanishing copper(II) hyperfine splitting ($29\text{x}10^{-4}$ cm^{-1}) also show that the copper(II) ion 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 in pseudotetrahedral symmetry. The observed value for g_3 has given 37 degrees, being in good agreement with the value from the X-ray analysis.

Superhyperfine structures due to the nitrogen atoms of the bbim^{2-} dianion were not detected in any orientation of $\mathbf{B}_0$ with respect to the crystallographic abc axis system in a wide range from 4 K to ambient temperature. In order to observe ligand nitrogen hyperfine structures magnetically diluted single crystals are required.

CONCLUSION

We have designed a building block with bidentate 2,2'-bibenzimidazolate ligands with multi-proton donor capability and synthesized $[\mathrm{Cu(bimm)_2}](^n\mathrm{Bu_4N})_2\cdot 2\mathrm{H_2O}$ (1) as prototypical models for one-dimensional heterobimetallic complexes. It has been required to characterize the molecular and electronic spin structures of the metal binding site despite that 1 is a monometallic complex.

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. In order to know the occurrence of charge transfer in the crystal state of 1, detailed analyses of the copper(II) hyperfine structure appearing in the single-crystal ESR spectra of 1 are in progress. The ^{63}Cu-enriched compound of 1 has been used for this purpose.

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