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Structures and magnetic properties of one-dimensional copper(II) complexes bridged with diazaaromatic rings

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Abstract

Seven kinds of polynuclear complexes of $[Cu(hfac)_2]$ (Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) with diazaaromatic rings have been prepared. The crystal structures of $[\{Cu(hfac)_2(\mu\text{-}L)\}_n]$ (L = 2,5- and 2,6-dimethylpyrazines, propylpyrazine (prpyz), quinoxaline, phenazine, 4,6-dimethylpyrimidine, and 1,6-naphthyridine) have been determined. These complexes consist of a one-dimensional chain structure, and the geometry around the copper ion is approximately an octahedral structure. The relations between the magnetic properties and coordination structure were discussed from the magnetic measurements. In the μ-prpyz complex, one nitrogen atom is coordinated to a copper ion at an axial position, and at the same time the other coordinated at an equatorial site of a neighboring copper ion. This complex showed antiferromagnetic interaction with $J/k_B = -0.086(3)$ K estimated from the Bonner–Fisher model. Weak magnetic interaction is caused by the somewhat long Cu–N distances due to the steric effect from the bridging ligands.
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1. Introduction

Many X-ray investigations have been reported on the polynuclear complexes of $[Cu(hfac)_2]$ (Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) with diazaaromatic rings [1–7]. Some of them revealed the relations between magnetic properties and coordination structures [3–6]. For example, we have reported the polynuclear complexes $[\{Cu(hfac)_2(\mu\text{-}4\text{-pym})\}_n]$ (4-pym = 4-methylpyrimidine) and $[\{Cu(hfac)_2(\mu\text{-}5\text{-pym})\}_n]$ (5-pym = 5-methylpyrimidine) showing ferromagnetic interactions [5]. The relationship between magnetic properties and coordination structures of μ-pyrimidine copper (II) complexes has been studied extensively [5,7], while μ-pyrazine complexes have not been studied systematically [5,8]. There have been a few papers on two kinds of μ-pyrazine (pyz) complexes, polynuclear $[\{Cu(hfac)_2(\mu\text{-pyz})\}_n]$ and dinuclear $[\{Cu-$
$(hfac)_2\}_2(\mu\text{-pyz})]$ [1,5,7]. Furthermore, infinite chain structures attract much attention from the viewpoint of supramolecular chemistry and low-dimensional physical properties. The investigation is now extended to one-dimensionally polymeric coordination of pyrazines and related diazaaromatic rings to $[Cu(hfac)_2]$. The introduction of bulky substituents would give rise to modification of the geometry around the Cu–N bond and accordingly the Cu–L–Cu superexchange magnetic coupling. For convenient discussion, the coordination geometry of the six-coordinated copper ion in $[\{Cu(hfac)_2(\mu\text{-}L)\}_n]$ (L = diazaaromatic rings) is classified as follows (Chart 1). These types of octahedral (Oh) structures have been reported previously [1–9].

Here we report the products from the reactions of $[Cu(hfac)_2]$ with diazaaromatic rings. The crystal structures of $[\{Cu(hfac)_2(\mu\text{-}L)\}_n]$ (L = 2,5-dimethlpyrazine (2,5-pyz), 2,6-dimethlpyrazine (2,6-pyz), propylpyrazine (prpyz), quinoxaline (qxln), phenazine (pnzn), 4,6-dimethylpyrimidine (4,6-pym), and 1,6-naphthyridine (1,6-nprn)) have been determined; the complexes are abbreviated hereafter as

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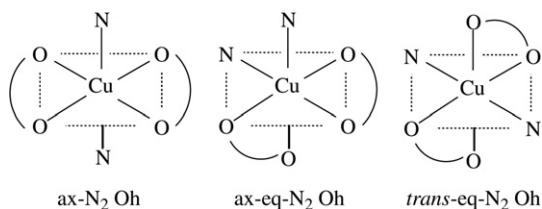
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Chart 1. Coordination geometry of a six-coordinated copper ion in polynuclear complexes.

1–**7**, respectively. These polymeric complexes are characterized to be one-dimensional polynuclear compounds and their magnetic properties are investigated on a SQUID magnetometer.

2. Results and discussion

2.1. Preparation and characterization

The products of reaction of [Cu(hfac)$_2$] with diazaaromatic rings are listed in Table 1. All of the products were characterized by means of spectroscopic methods, and the elemental analysis satisfied the 1/1 molar ratio of the Cu/L contents. Molecular structures with the atomic numbering and polymeric molecular arrangement in the crystals of (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**, and (g) **7** are shown in Figs. 1 and 2. Selected crystallographic data of the complexes are listed in Table 1 and the Cu–X (X = O, N) bond lengths in Table 2.

2.2. Crystal structures of ax-N$_2$ Oh type

Complexes **1**, **2**, **4**, **5**, and **6** are polynuclear and the geometry about the copper ion is approximately an Oh structure. The axial positions of the copper ion are occupied by nitrogen atoms of two diazaaromatic rings, and the four equatorial positions are occupied by oxygen atoms from the bidentate hfac ligands (Fig. 1). The coordination geometry of the copper ion belongs to the ax-N$_2$ Oh type.

Complex **1**. The Cu(1)–N(1) bond (2.543(3) Å) is longer than that of [{Cu(hfac)$_2$(μ-pyz)}$_n$] (2.529(9) Å) [1]. Furthermore, the Cu(1)–N(1)–C(2) bond angle (130.7(2)) is larger than that of Cu(1)–N(1)–C(1) (111.9(2)). Similar bond angles are observed in [{Cu(hfac)$_2$}$_3$(μ-2,3,5-pyz)$_2$] (2,3,5-pyz = 2,3,5-trimethylpyrazine) [2b]. Thus, the neighboring methyl group of the nitrogen atom hinders the approach of the copper ion to the nitrogen atom.

Complex **2**. The Cu(1)–N(1) bond (2.606(2) Å) is longer than the Cu(1)–N(2′) bond (2.408(2) Å). The longer Cu–N bond arises from the steric hindrance of neighboring methyl groups of the 1-nitrogen atom. On the other hand, the 2,6-pyz molecules in **2** are arranged in a head-to-tail fashion. This fashion may result from a mutual repulsion between the hfac ligands coordinated to Cu(1) and the neighboring methyl groups of the 1-nitrogen atom.

Although 2,3,5- and 2,6-pyz molecules have a sterically crowded 2,6-dimethylpyridine-type nitrogen atom [10], the former gave trinuclear complex [{Cu(hfac)$_2$}$_3$(μ-2,3, 5-pyz)$_2$] [2b], but the latter gave polynuclear **2**. In [{Cu(hfac)$_2$}$_3$(μ-2,3,5-pyz)$_2$], the geometry about Cu(2) is approximately a trigonal bipyramid with the nitrogen atom N(2) from 2,3,5-pyz molecule at the equatorial position. The Cu(2)–N(2) bond length is 2.030(9) Å. Generally, the coordinating ability of the ligand is affected by steric factors in addition to the electronic effect [11]. In this case, the coordinating ability of the 1-nitrogen atom in 2,6-pyz seems to be weaker than that of the 4-nitrogen atom in 2,3,5-pyz.

Complex **4**. The Cu(2)–N(2) and Cu(2)–N(3) bonds (2.615(7) and 2.657(8) Å, respectively) are somewhat longer than those of [{Cu(hfac)$_2$(μ-pyz)}$_n$] and **1** (Table 2). In addition, the bond angles Cu–N–C are not equal. For example, the Cu(1)–N(1)–C(1) and Cu(1)–N(1)–C(8) bond angles are 116.5(5) and 127.5(5)°, respectively. The peri-hydrogen atoms attached to the qxln ring hinder the approach of the chelated copper ion (Fig. 1(d)) [10].

Complex **5**. To our knowledge, the Cu(1)–N(1) bond (2.856(4) Å) is one of the longest Cu–N bonds of [{Cu(hfac)$_2$(μ-L)}$_n$] ever reported [1–7]. On the other hand, Cu(1)–O(1) and Cu(1)–O(2) bonds (1.915(3) and 1.923(3) Å, respectively) are notably shorter than those of [{Cu(hfac)$_2$(μ-L)}$_n$] (Table 2). The bond angles O(1)–Cu(1)–N(1) and O(2)–Cu(1)–N(1) are equal (90.0°), and Cu(1)–N(1)–C(1) and Cu(1)–N(1)–C(1′) are also equal (122.1(2)). Thus the coordination geometry of the copper ion belongs to the extremely elongated ax-N$_2$ Oh type. It should be noted that the Cu–N distance of 2.856(4) Å is shorter by ca. 0.1 Å than the sum of the van der Waals radii of Cu (1.40 Å) and N (1.55 Å) [12]. Although the Cu–N bond is quite long in **5**, the interaction between the Cu and N atoms seems to be attracting, from the nitrogen atoms located just above the copper center despite of the steric hindrance. The bonding character is also supported by the spectroscopic methods (see the UV–Vis study section).

The steric hindrance of the peri-hydrogen atoms attached to the phenazine ring is much larger than that of quinoxaline, which is unhindered on one side of the nitrogen atom described above. Similar steric hindrance of peri-hydrogen atoms is observed in the [Cu(acac)$_2$]–acridine complex (Hacac = pentane-2,4-dione) in the ESR measurements [10].

Complex **6**. The Cu(1)–N(2′) bond (2.628(4) Å) is considerably longer than that of **1** (2.543(3) Å), while Cu(1)–N(1) bond (2.505(3) Å) is somewhat shorter. The coordination geometry of Cu(1) belongs to the ax-N$_2$ Oh type owing to the steric reason. Its structure is rather different from those of [{Cu(hfac)$_2$(μ-pym)}$_n$] (pym = pyrimidine) and [{Cu(hfac)$_2$(μ-4-pym)}$_n$], which have the ax–eq-N$_2$ Oh structure [5,7].

2.3. Crystal structures of ax-N$_2$ and trans–eq-N$_2$ Oh type

Complex **3**. The geometry about Cu(1), Cu(2) and Cu(3) forms approximately an Oh structure. The coordination