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Dinuclear Copper(II) Complex, Super-exchange Interactions, Antiferromagnetic Coupling

Preparation and magnetic properties of a 3,5-dimethylpyrazolate bridged binuclear copper(II) complex \([Cu_2(L)(3,5-pyz)] (L = \text{1,3-Bis(2-Hydroxy-5-Chlorosalicylideneamino)propan-2-ol})\) is reported. The crystal structure determined by X-ray diffraction methods, \((C_2_2H_8N_4O_3Cl_2Cu_2)\), triclinic, space group \(P\overline{1}\), \(a = 9.622(3), \beta = 10.921(2), \gamma = 11.420(3) \text{Å}\), \(\alpha = 100.73(2), \beta = 94.04(2), \gamma = 108.08(2)^\circ\), \(V = 1110.2(5) \text{ Å}^3\), \(Z = 2\). Two copper(II) ions in a square-planar coordination are bridged via alkoxide oxygen and 3,5-dimethyl pyrozolate nitrogen atoms to form a dinuclear unit. The metal coordination sphere is four-coordinate, planar with an \(\text{N}_2\text{O}_2\) donor set. The dihedral angle between the two coordination planes is 166.83°. There are significant intermolecular interactions between neighbouring binuclear entities. The shortest intermolecular \(\text{Cu}(1)\ldots\text{Cu}(1)^\prime\) distance is \(2.666(3) \text{ Å} (i = 1-x, -y, 1-z)\). The variable-temperature magnetic susceptibility measurement for a powdered sample of the complex was carried out in the temperature range 5 - 350 K and analysed to obtain values of the parameter \(J\) in the exchange Hamiltonian \(\hat{H} = -2J\text{Sc}_\text{Cu}^\prime\text{Sc}_\text{Cu}\); \(2J = -164 \text{ cm}^{-1}\). The magnetic moment at 300 K is about 2.42 \(\mu_B\), and 0.22 \(\mu_B\) at 5 K. The weak antiferromagnetism of the present complex is reasonably explained in terms of the orbital countercomplementary effect based on Hoffmann’s theory for super-exchange interaction.

Introduction

There is continuing interest among inorganic chemists in studying the structures and magnetic properties of dinuclear multibridged copper(II) complexes [1 - 5]. Their investigations are carried out as attempts to understand the structure-magnetism relationships and the structural characteristics. Both single atom and multiatom bridges are known to propagate antiferromagnetic exchange with the magnitude of the exchange interaction being dependent upon the bridge identity, the dihedral angle between the two coordination planes, the planarity of the bonds around the bridging oxygen atom, the length of the copper-oxygen bridging bond, the Cu-O-Cu bridging angle and the metal ion stereochemistry. According to Hatfield and Hadgson [6 - 8], the antiferromagnetic interaction becomes stronger with increasing Cu-O-Cu angle, in bis(μ-hydrox) and bis(μ-alkoxo)-bridged copper(II) complexes. McKee and Smith [9] have observed an increase in the strength of antiferromagnetic exchange of binuclear complex in which two copper(II) ions were bridged by a single alkoxide oxygen with a larger Cu-O-Cu angle (135.3°). This was also supported by the work on the mono-μ-hydroxo-dicopper(II) complexes with large Cu-O-Cu angle [10, 11]. Recently the magneto-structural properties of binuclear copper(II) complexes which contain second bridging ligands such as pyrazolate or acetate ions have also received considerable attention. Nishida et al. [12] reported the preparation and structural characterisation of binuclear copper(II) complexes in which the copper ions are linked by alkoxide oxygen and pyrazolate nitrogen atoms. In these complexes, Cu-O-Cu bridge angle does not affect the strength of the exchange interaction by itself. This result seemed to be inconsistent with Hodgson’s rule. The strength of the exchange interaction can be either enhanced or attenuated depending on the...
presence of a second bridging ligand [13, 14]. This behaviour explained by using theories developed by Hoffmann et al. [15].

In this study, we have synthesized a \(\mu\)-pyrazolato-N,N'-bridged dicopper(II) complex of \(1,3\)-bis(2-hydroxy-5-chlorosalicylideneamino)propan-2-ol, and determined its crystal structure by X-ray diffraction methods. We have measured magnetic susceptibilities in the temperature range 5 - 350 K using the SQUID magnetometer to investigate the relationship between the magnetic properties and the molecular structure.

Experimental

Preparation

Caution: Perchlorate salts of the metal complexes with organic ligands are potentially explosive. Only a small amount of materials should be handled with caution.

The Schiff base ligand was prepared by reaction of \(1,3\)-diaminopropan-2-ol (0.1 mmol) with 5-chlorosalicylaldehyde (0.2 mmol) in a methanol (100 ml). The yellow Schiff base precipitated from solution on cooling. Binuclear complex was obtained when a sample of ligand (0.1 mmol) in methanol (50 ml) was added dropwise to a stirred mixture containing \(3,5\)-dimethylpyrazole (0.1 mmol) and copper(II) perchlorate hexahydrate (0.2 mmol) in methanol (25 ml). Triethylamine (0.3 mmol) was added to the solution. The mixture was stirred and thin green crystals collected and washed with methanol. Recrystallization from acetonitrile afforded single crystals suitable for X-ray structure determination. \(C_{20}H_{22}N_{4}O_{3}Cl_{2}Cu_{2}\) (586.42): calcd C 40.96, H 3.78; found: C 40.89, H 3.76.

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [16] using a single crystal with dimensions \(0.20 \times 0.30 \times 0.60\) mm with graphite monochromatized CuK\(_{\alpha}\) radiation (\(\lambda = 1.5418\) Å) by using \(\omega - 2\theta\) scan technique. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections (\(14^\circ \leq \theta \leq 28^\circ\)) carefully centered on the diffractometer. 5261 reflections were measured in the range \(0^\circ \leq \theta \leq 74.33^\circ\). A total of 3390 reflections were assumed as observed applying the condition \(I > 3\sigma(I)\). Three reflections were measured every 2 hour as orientation and intensity control, significant intensity decrease was not observed. The crystallographic data, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 1. Data reduction were achieved using the RC93 [17]. Data corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [16]. The structure was solved by SIR92 [18] and refined by CRYSTALS [19]. The H atom parameters were not refined. The final positional parameters are presented...
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$). Equivalent isotropic $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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in Tab. 2. A perspective drawing of the molecule is shown in Fig. 2 [20]. Selected bond lengths and angles are summarized in Table 3. Lists of atomic parameters as well as structure factor tables have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146876 [21].

Susceptibility measurements

Magnetic susceptibility measurements of the powdered sample were performed over the temperature range 5 - 350 K with a MPMS Quantum Design SQUID magnetometer. Details of the apparatus have already been described [22]. A magnetic field strength of 1kG was used during the data acquisition. A diamagnetic correction of the molar magnetic susceptibility of the compound was estimated from Pascal’s constants [23] and used to correct experimental susceptibility data, yielding molar susceptibilities of the compound. Magnetic moments were obtained from the relation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$.

Discussion

X-ray crystal structure

The complex consists of binuclear molecules in which each copper ion in a square planar coordination is surrounded by two O and two N atoms. The Cu-N and Cu-O bond lengths are comparable with the lengths which are in reported binuclear copper(II) complexes [24 - 27]. The distance between the two copper(II) ions is 3.355(1) Å and the Cu-O-Cu bridging angle is 124.67(2)° which is in the range of other reported similar binuclear copper(II) complexes [27 - 30]. The dihedral angle formed by the two coordination planes is 166.83°, thereby the whole molecule is nearly planar, as seen in Fig. 3. The sum of the bond angles around the bridging oxygen atom is 355.27°, indicating that the bonds around this oxygen atom are essentially planar.

![Fig. 3. View of the unit cell packing.](image-url)
Magnetic properties

The variable-temperature magnetic susceptibility measurements for a powdered sample of the complex were carried out in the temperature range 5 to 350 K. The magnetic susceptibilities of the complex are shown as a function of temperature in Fig. 4a, and the magnetic moments are shown as a function of temperature in Fig. 4b. The variable-temperature data was fitted to the modified the Bleaney-Bowers equation [31] (eq. 1).

\[
\chi = \frac{N g^2 \mu_B^2}{3k(T - \theta)} \left[ 1 + \frac{1}{3} \exp(-2J/KT) \right]^{-1} (1 - x_p) + \frac{Ng^2 \mu_B^2}{4kT} x_p + N_o
\]

using the isotropic (Heisenberg) exchange Hamiltonian

\[
\mathcal{H} = -2JS_1 \cdot S_2
\]

for two interacting S = 1/2 centers, where \(-2J\) is the energy difference between spin-singlet and -triplet states. \(N_o\) is the temperature-independent paramagnetism, \(x_p\) is the fraction of a monomeric impurity, \(\theta\) is a Weiss-like correction for intermolecular interactions. Least squares fitting of the data leads to \(2J = -164 \text{ cm}^{-1}\), \(g = 2.0\), \(x_p = 1.6\%\) and \(\theta = -56 \text{ K}\). The non-zero value of \(\theta\) may be due to the intermolecular interaction between the binuclear complex. Fig. 4a, shows a broad maximum at a temperature of ca. 175 K indicative of an antiferromagnetically coupled system. A small amount of monomeric impurity is responsible for the increases in susceptibility below 15 K. From Fig. 4b, it is clear that the observed and calculated magnetic moment \(\mu_{\text{eff}}\) decreases from a value of 2.42\(\mu_B\) at 300 K to 0.22\(\mu_B\) at 5 K.

Some interesting general trends emerge some interesting results between structural and magnetic relationship from the data in Table 4.

The dihedral angle between the two coordination planes is considered to be a key factor in determine the spin-exchange interaction between the two copper ions. The larger the dihedral angle, the greater the strength of the exchange coupling. The dihedral angle decreases in the order \(\mathbf{a} > \mathbf{b} > \mathbf{f} > \mathbf{e} > \mathbf{c} > \mathbf{d}\) while \(-2J\) decreases in the order \(\mathbf{e} > \mathbf{d} > \mathbf{c} > \mathbf{b} > \mathbf{a} > \mathbf{f}\). This indicates that the dihedral angle of the coordination sphere of unsymmetric doubly bridged complexes may play only a minor role in determining the exchange interaction. The planarity of the bonds around the bridging oxygen has also been
considered as the determining factor for the antiferromagnetic interaction. In fact there is considerable variation in the planarity of the bonds around the bridging oxygens of the complexes under consideration. However, there could not be found any systematic correlation between the planarity of the molecule and the J value. For instance, in the case of a and c, although the sum of the three bond angles around the oxygen is nearly identical, the \(-2J\) values are quite different. Therefore, this factor also does not seem to be the main factor affecting the J value. Perhaps the most widely accepted criterion for correlating structure and magnetism is the Cu-O-Cu bridging angle [32 - 38]. According to Hatfield, the antiferromagnetic interaction becomes stronger with increasing Cu-O-Cu angle, in bis(\(\mu\)-hydroxo) and bis(\(\mu\)-alkoxy)-bridged copper(II) complexes [6]. Although the Cu-O-Cu angle of the title compound is almost identical with that of complex a, the antiferromagnetic super-exchange interaction is weaker. It is thus clear that the Cu-O-Cu bridge angle does not affect the strength of the exchange interaction by itself.

Clearly, the different approach must be employed in order to correlate the structural and magnetic properties. Atomic orbitals on the alkoxide and HOMO’s on pyrazolate ions are considered combined with magnetic \(d_{z^2}\) and \(d_{\alpha}\) orbitals on the metal centers, producing new molecular orbitals, designated \(d_{\alpha}'\) and \(d_{\sigma}'\), with energies \(\epsilon_1\) and \(\epsilon_2\). These magnetic orbitals should contribute effectively to the super-exchange interaction in the present system. According to Hoffmann et al. [15] the square of the difference in energy between these two new orbitals largely determines the magnitude of the antiferromagnetic exchange interactions. If both bridging ligands interact with the same combination of the magnetic orbitals, the super-exchange interaction through the two bridges work in a complementary fashion and the antiferromagnetic exchange interaction is enhanced. Contrary, if bridging ligands that attempt to stabilise different combinations of the magnetic orbitals, the super-exchange interaction through two bridges will work in a countercomplementary fashion and antiferromagnetic exchange interaction attenuated (Fig. 5).

Nishida et al. [12] have been calculated the HOMOs on pyrazolate ion and analysed the interaction between magnetic d orbitals and ligand HOMO’s to produce \(d_{\alpha}'\) and \(d_{\sigma}'\). Nishida et al., show that when \(\psi_\alpha\) is higher in energy a \(\psi_\alpha\) (empirically this is observed), the splitting between \(d_{\alpha}'\) and \(d_{\sigma}'\) is actually compressed. The energies of the interacting orbitals appear to cause the pyrazolate bridge to work in countercomplementary fashion with alkoxide bridge. However, if \(\psi_\alpha\) overlaps more effectively with \(d_{\alpha}\) than \(\psi_\sigma\) with \(d_{\sigma}\), the overlap integrals between interacting orbitals favor enhancement of antiferromagnetic exchange coupling. In other words,
overlap considerations may influence the pyrazolate bridge to act in a complementary fashion with the alkoxide bridge to increase $-2J$. In the case of f the 3,5 dimethyl pyrazolate bridge exerts a counter-complementary effect on the antiferromagnetic interaction caused by the alkoxide bridge. This effect may be ascribed as the main factor for the smaller $-2J$ value of this work compared with that of a, b, c, d, e.

As a result, in alkoxide bridged dicopper(II) complexes antiferromagnetic interaction through the alkoxide oxygen is large when the Cu-O-Cu angle is large, as seen in e complex (Table 3). When two copper ions are doubly bridged with alkoxide oxygen and $\mu$-pyrazolate nitrogens, as in the cases of a, b, c, d and f, $\mu$-pyrazolate bridge is to increase or decrease the energy separation between $d_a$ and $d_s$ depending on the relative degree of interaction between $d_a$ and $\psi_a$ and between $d_s$ and $\psi_b$.

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[21] Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC-146876.