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Chiral one-dimensional hydrogen bonded, antiferromagnetic chloro-bridged dinuclear copper(II) complex with tridentate Schiff base ligand

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ABSTRACT

Chiral one-dimensional hydrogen bonded copper(II) complex $[Cu(HL1)Cl]_2{\cdot}H_2O$ (**1**) (HL1 = *N*-(2-hydroxyethyl)-5-nitrosalicylaldimine) has been synthesized and characterized by elemental analysis, crystal structure analysis and magnetic susceptibility. X-ray diffraction studies show that **1** is a binuclear copper(II) complex with a pair of chlorine atoms bridging the copper atoms in a central Cu_2Cl_2 core. Each copper(II) atom is five-coordinated in a square-pyramidal environment. Variable-temperature magnetic susceptibility measurements on the a binuclear complex **1** in the range 2–300 K indicate a weak antiferromagnetic coupling between the binuclear copper(II) centers, with $J = -0.274$ cm^{-1} and the magneto-structural correlations are discussed in detail.

1. Introduction

Binuclear copper(II) complexes are an active research subject since quite a long time, as the dates for the references clarify. Many of these complexes have been of great interest mainly due to their structural and magnetic properties [1] and also important as models for copper proteins [2]. Several theoretical analyses have been carried out to clarify the structures and magnetic properties of chloro-bridged Cu(II) dimers, and different magnetic behavior ranging from ferro- to antiferromagnetic interactions has been found in these systems [3]. However, it is difficult to establish simple magnetostructural relationship between the strength of the magnetic exchange coupling constant *J* and the Cu–Cl–Cu bridging angle, Cu–Cl bridging bonds or Cu···Cu distances. This may be due to a large variation in structural features observed, together with the fact that chloride possesses both p and d orbitals which may participate in creating an exchange pathway [3d,4,5].

Recently, our research group has reported relation between magnetic and structural properties of binuclear copper(II) complexes [6]. In view of the importance of copper(II) compounds and our interest in magnetostructural relationship of transition metal complexes, we report here the synthesis, crystal structure and magnetic properties of a novel chiral one-dimensional copper(II) complex **1** linked by double chloro-bridge and hydrogen bonds, and provide some comparison to literature data using correlations previously developed for other chloride bridge Cu(II) dimers. It is interesting to note that although some structural and magnetic analyses of chloride bridge Cu(II) complexes have been reported [7], to the best of our knowledge, complex **1** represents the second example of exchange coupled chiral one-dimensional Cu(II) complex containing both chloride and hydrogen-bonds [8].

2. Experimental

2.1. Materials and physical measurements

All chemical reagents and solvents were purchased from Merck or Aldrich and used without further purification. Elemental (C, H, N) analyses were carried out by standard methods with a LECO, CHNS-932 analyzer. The temperature dependence of the magnetic susceptibility of polycrystalline samples was measured between 3 and 300 K at a field of 1.0 T using a Quantum Design model MPMS computer-controlled SQUID magnetometer. The effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828\ (\chi_m T)^{1/2}$ [1a], where χ_m, the molar magnetic susceptibility, was set equal to [1a] M_m/H. The synthetic route of the ligand and complex are outlined in Scheme 1.

2.2. Synthesis of the complex $[Cu(HL1)Cl]_2{\cdot}H_2O$ (**1**)

The tridentate Schiff base ligand, **HL1**, was prepared by reaction of ethanolamine (1 mmol) with 2-hydroxy-5-nitrobenzdehyde (1 mmol) in hot ethanol (100 mL). The solution obtained was stirred at 50 °C for 5 min. The yellow compound was precipitated from

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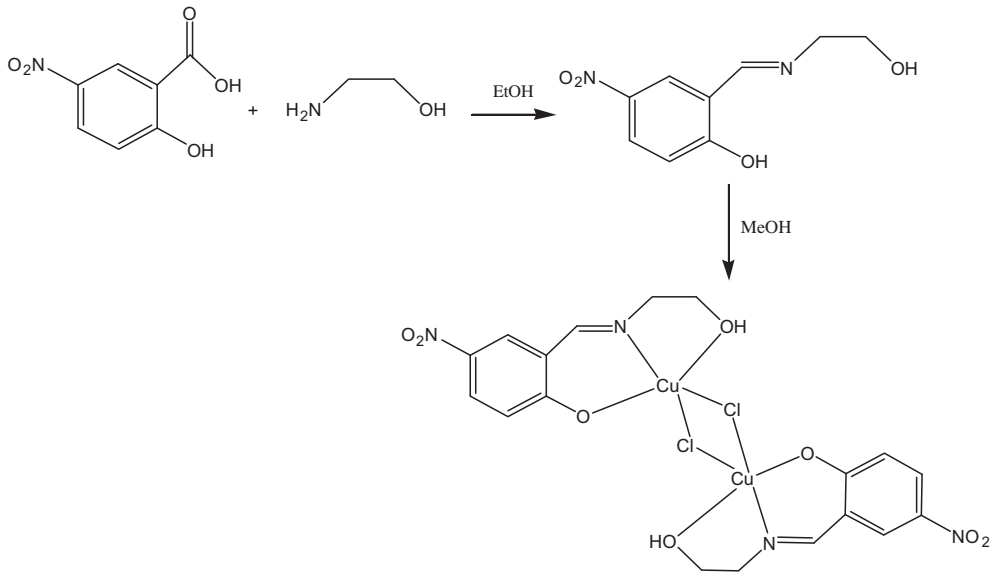

Scheme 1. The synthetic route of the ligand **HL1** and complex **1** evaluated in this study.

solution on cooling. Complex **1** was prepared by addition of $CuCl_2$ (1 mmol, 0.134 g) in 20 mL of hot methanol to the ligand (1 mmol, 0.277 g) in 30 mL of hot methanol. This solution has been warmed to 50 °C and stirred for 15 min. The resulting solution has been filtered rapidly and then allowed to stand at room temperature. Several weeks of standing have been led to the growth of green crystals of the title compound suitable for X-ray analysis.

2.2.1. HL1

Yellow crystals, yield 70%. *Anal*. Calc. for C, 51.43; H, 4.80; N, 13.33. Found: C, 51.39; H, 4.82; N, 13.31%. ^{1}H NMR (DMSO, δ ppm): 3.83–3.93 (–NCH_2CH_2OH, 4H), 5.15 (–NCH_2CH_2O*H*, 1H), 6.59 (–C*H*=CHOH–, 1H), 8 (–$CHNO_2$=C*H*–), 8.4 (–CH(NO2)–CH=C*H*–, 1H), 8.6 (–C*H*=N–, 1H). ^{13}C NMR (DMSO, δ ppm): 54.85 (–N–CH_2–), 59.73 (–HOCH_2–), 113.79 (–C*H*=CHOH–), 123.40 (–CH=CH–COH), 139.79 (C*H*=CH–COH), 133.30 (–C*H*=CNO_2–), 133.89 (–CH=CNO_2–), 168.22 (–C=COH–), 178.74 (–C=N–). IR (KBr) cm^{-1}: 3131, 3102, 2838, 2742, 1658, 1602, 1319, 1292, 1244, 1175. UV–Vis: λ_{max}(DMSO)/nm 335, 407.

*2.2.2. Complex **1***

Green crystals, yield 70%. *Anal*. Calc. for C, 34.08; H, 3.18; N, 8.83. Found: C, 34.12; H, 3.20; N, 8.79%. IR (KBr) cm^{-1}: 3131, 3105, 2971, 2918, 1596, 1312, 1244, 1190, 730, 651 λ_{max}(DMSO)/nm 242, 373.

2.3. X-ray structure determination

Diffraction measurements were made on a Bruker ApexII kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. The intensity data were integrated using the APEXII program [9]. Absorption corrections were applied based on equivalent reflections using SADABS [10]. The structures were solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXL [11]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.5 times the U_{equiv} of their attached carbon atoms for methyl hydrogens, and 1.2 times the U_{equiv} of their attached carbon atoms for all others. The H atoms of the water molecule were located in a difference Fourier map and refined isotropically. Distance restraints were also applied to the H atoms of the water molecules with a set value of 0.80 (1) Å. The absolute structure was determined on the basis of the Flack [12] parameter x = 0.005 (5). The Flack's parameter close to 0 is indicative of a non-centrosymmetric structure.

Powder X-ray measurements were performed using Cu Kα radiation (λ = 1.5418 Å) on a Bruker-AXS D8-Advance diffractometer equipped with a secondary monochromator. The data were collected in the range $5° < 2\theta < 50°$ in θ–θ mode with a step time of ns (5 s < n < 10 s) and step width of 0.03°. Powder patterns for bulk microcrystalline samples of each of **1** were consistent with the presence of no phase other than that identified in the single crystal experiment (Fig. S1).

3. Results and discussion

*3.1. Crystal structure description of **1***

The crystallographic data, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 1. A perspective ORTEP view with the atom-labeling scheme of complex **1** is presented in Fig. 1. Selected bond lengths and angles for the complex are given in Table 2. The complex crystallizes in chiral space group $P2_1$. The asymmetric unit of **1** consists of a $[Cu(HL1)Cl]_2$ dimeric unit with a lattice water molecule. The crystal structure determination shows that complex **1** is a dichloro-bridged dimer in which the copper ions are pentacoordinated as shown in Fig. 1. For the coordination polyhedron of the metal atom, the distortion of the coordination environment from a trigonal bipyramidal (TBP) to a square pyramidal (SP) can be evaluated by the Addison distortion index, τ defined as $\tau = (\alpha - \beta)/60$, where α and β are the two largest coordination angles. The coordination polyhedron of the metal atom is described as τ = 0 for perfect SP and 1 for ideal TBP [13]. In our case, the structural distortion indexes of **1** were found τ_{Cu1} = 0.008 and τ_{Cu2} = 0.009 respectively, indicate that Cu1 and Cu2 polyhedron are all close to square-pyramidal. The base of the pyramid of the copper atom (Cu1) is formed by the imine nitrogen atom (N1), the alkoxy and phenoxy oxygen atoms (O1 and O2) from the Schiff base ligand and a bridging chlorine atom (Cl1), while the apical position of the pyramid is occupied by the other bridging chlorine atom (Cl2). The Cu(2) atom