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Magneto structural correlations of a 'stepped-wise' discrete tetranuclear unit of copper(II), $[Cu_4(\mu_2\text{-}OH)_2((\mu_3\text{-}OH)_2(2,2'\text{-}bipy)_4Cl_2]Cl_2 \cdot 6H_2O$

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Abstract

A tetranuclear 'stepped wise' copper(II) complex, $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-}bipy)_4Cl_2]Cl_2 \cdot 6H_2O$ has been synthesized and the crystal structure of the complex redetermined. The magnetic behavior has been investigated in the temperature range 300–4.2 K based on its novel binding modes of the OH^-, i.e. OH^- anions bridge the copper(II) centers in a bidentate (μ-2) as well as tridentate (μ-3) fashion and this shows ferromagnetic interactions. The fit of the experimental data was made by the irreducible tensor operator formalism (ITO) using the CLUMAG program based on the Hamiltonian; $H = -J_1(S_1S_2+S_3S_4)-J_2(S_1S_4)-J_3(S_1S_3+S_2S_4)$ and the best fit parameters, assuming the g factors are identical and $J_2 = J_3$, leads to $J_1 = 22.71$ cm^{-1}; $J_2 = J_3 = 0.34$ cm^{-1} and $g = 2.10$. The magnetic results are interpreted with structural parameters.

Keywords: Copper(II) complexes; Tetranuclear complexes; Magnetic properties and ferromagnetic interactions

1. Introduction

Binuclear and two linked binuclear, i.e. tetranuclear copper(II) complexes with monoatomic bridging ligands have been intensively studied over the last three decades both from a structural and a magnetic point of view. The copper(II) complexes containing μ-OH with $[Cu(\mu\text{-}OH)_2Cu]_n$ core structure are abundant and similar from a structural point of view and the structural homogeneity has allowed the establishment of a well-behaved magneto-structural correlations [1–5]. The replacement of the OH by OR ligands produces structural distortions yielding complexes with different type of geometries [6]. On the other hand the replacement of OH or OR bridging ligands by Cl with a $[Cu(\mu\text{-}Cl)_2Cu]_n$ motif displays a wealth of different structures with variety of bond distances (Cu–Cl) and angles (Cu–Cl–Cu) [7–10]. The most important motifs, i.e. (I) stepped-wise or ladder/chair-like, (II) cubane-like, and (III) double-open cubane-like of tetranuclear copper(II) complexes with O as bridging ligand are illustratrated in Scheme 1. The cubane-like and 'double-open-cubane' (Scheme 1II and III) are abundant and their magnetic properties are known and easy to interpret [5,6]. By contrast, the 'stepped-wise' or 'ladder/chair-like' Cu_4O_4 tetramers (Scheme 1I) are scant and their magnetic properties have been postulated without an easily applicable formula or without magnetic study [11]. Interestingly, these tetranuclear structures reveal a wide variety of bond distances (Cu–O) and angles (Cu–O–Cu) depending on the coordinating ligands and also on the counterions [11].

Here we present the magneto-structural correlations of a tetranuclear (binuclear of binuclear) 'stepped-wise' copper(II) complex, $[Cu_4(\mu_2\text{-}OH)_2((\mu_3\text{-}OH)_2(2,2'\text{-}bipy)_4Cl_2)Cl_2 \cdot 6H_2O$ formed by two Cu_2O_2 dinuclear

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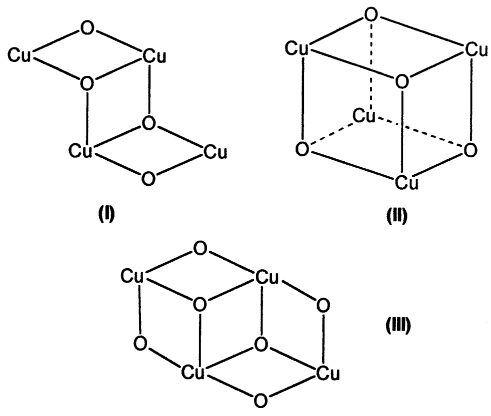


Scheme 1.

entities linked by two Cu–O bonds (Scheme 1I). The crystal structure of the title complex was reported by Zheng et al. [12] without magneto-structural correlations and after that Carbolla et al. [13] reported the same compound adopting the different synthetic procedure. The 2,2′-bipy ligand used in this study is well known for their stabilization due to π back bonding from the metal ion and the π–π interaction between the ring imparts the stabilization and overall conformation of the structure. The low temperature magnetic measurement of the complex shows three different ferromagnetic pathways with the parameters, $J_1 = 22.71$ cm^{-1}; $J_2 = J_3 = 0.34$ cm^{-1}, with identical g values, $g = 2.10$ and the magnetic results are interpreted with structural parameters.

2. Experimental

2.1. Reagents

High purity (99%) 2,2′-bipyridine was purchased from Aldrich Chemical Company Inc and all other chemicals were of AR grade.

2.2. Physical techniques

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. Magnetic measurements were carried out on the polycrystalline samples (30–40 mg) with a pendulum type magnetometer–susceptometer (MANICS DSM. 8) equipped with an Oxford helium continuous flow cryostat, working in the 300–4.2 K range, and a Drusch EAF 16UE electromagnet. The magnetic field was 0.5 T. The diamagnetic corrections were evaluated from Pascal's constants. EPR spectra were recorded on powder samples at X-band frequency with a BRUKER 300E automatic spectrometer, varying the temperature between 300 and 4 K.

2.3. Synthesis

A methanolic solution (10 cm^3) of 2,2′-bipyridine (1 mmol) was added to a well stirred methanolic solution of copper chloride dihydrate (1 mmol) in a round bottom flask and the resulting reaction mixture was stirred for 30 min. Then aqeous solution of disodium adipate (1 mmol) was added dropwise and the resulting solution was allowed to reflux for 24 h. Then it was filtered and the filtrate was allowed to stand in an open atmosphere. After a week plate like transparent bluish-green single crystals suitable for X-ray determination were obtained. These were filtered off followed by washing thoroughly with isopropanol and kept in vacuo. The yield is about 70%.

3. Results and discussion

3.1. Synthesis

Very recently the synthesis of the title complex has been reported independently by Zheng et al. [12] and Carbolla et al. [13] adopting different synthetic procedure. Zheng et al. [12] reported the role of adipic acid as effective promoting agent for the crystal growth while synthesizing the title complex. We also thought alike vide supra.

3.2. Salient features of the structure

The crystal structure of the title complex was redetermined and reveals the same structure reported by Zheng et. al. [12]. The ball and stick diagram of the title complex is shown in Fig. 1. The unit cell has one tetramer, $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-bipy})_4Cl_2]Cl_2 \cdot 6H_2O$ with six solvent water molecules and two uncoordinated chloride ions. It is worth mentioning that some salient features of this novel molecule were not reported by Zheng et. al. [12]. These were given below.

The 'stepped-wise' Cu_4O_4 core is outlined by the three four-membered ring (1) Cu(1)–O(2)–Cu(2)–O(1), (2) Cu(1)–O(1)–Cu(1)*–O(1)* and (3) Cu(1)*–O(2)*–Cu(2)*–O(1)*. The non-planar rings (1 and 3) are related by center of symmetry ($* = 1-x,\ 1-y,\ 1-z$) located at the centroid of the planar ring (2). The dihedral angle between central ring (2) and outer ring (1 or 3) is 73.4(1)°, and is similar to the corresponding value of 70.6° in the copper(II) oxo complex $[Cu_4L_2((\text{bipy})_4(\mu_3\text{-}OH)_2)[ClO_4]_4$ (HL = 5-hydroxy-6-methylpyridine-3,4-dimethanol) [11]. This value for the copper(I) bromo [14] and iodo [15] complexes $[\{CuX(PPh_3)\}_4]$ is 107.8° and 115.06°, respectively. The increase has been attributed to the steric factors [15]. Thus, it may be concluded that irrespective of the metal oxidation state and nature of the co-ligand, a systematic decrease in

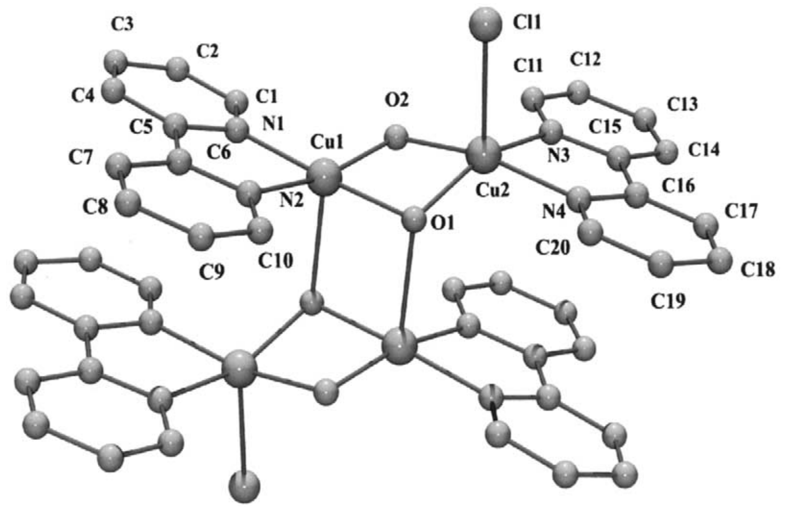


Fig. 1. Ball and stick diagram of the cation, $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-bipy})_4Cl_2]^{2+}$.

dihedral angle with decrease in size of the bridging atom is observed. The coordination geometry around the each copper(II) is distorted square pyramidal. The two μ_3-OH ions play a crucial role in bridging the four coppers together to build the 'stepped-wise' structure. Although the Cu_4O_4 moiety shows 'stepped-wise' structure, it is interesting to note that the four copper atoms are coplanar with the separation distances being Cu(1)–Cu(2) 2.934(1), Cu(1)–Cu(1)* 3.170(1), Cu(1)–Cu(2)* 3.599(1), Cu(2)–Cu(2)* 5.751 Å. Thus the copper atoms are arranged in a rhombic Cu_4 structure with two oxygen-capped edge sharing copper triangles. Although tetrahedral [16] and the square/rectangular [17] Cu_4 are reported in the literature, only two examples of rhombic [18] Cu_4 are reported till date. This complex represents one of the rare examples of rhombic Cu_4 compounds.

The angles at copper(II) centers and bridging oxygen atoms within the three rings show deviations from 90°, as expected for an ideal cubane-like structure. In the Cu_4O_4 moiety, the ranges of angles at copper atoms are 81.1(1)°–85.2(1)° and at bridging oxygen atoms are 94.8(1)°–112.8(1)° showing that at the metal atoms, all angles are $< 90°$ whereas at oxygen atoms all angles are $> 90°$. The bipy ligands are nearly planar [largest deviation of atoms from the mean planes is 0.043(4) Å] and the dihedral angle between the mean planes of the four pyridyl rings is 2.0(3)° (mean value). The intra-ring C–N and C–C bonds are 1.347(8) Å (mean value) and 1.378(6) Å (mean value) as expected. (The angles subtended by the bipy ligands at Cu(1) and Cu(2) are 80.9(1)° and 80.5(1)°, respectively.

Every tetrameric unit is linked to the four neighboring tetrameric moieties by the presence of weak hydrogen bonding interactions between aryl C–H and terminal chloride ligand (Cl1). Interactions involving π–π stacking between pyridine ligands (separation 3.631(2)–3.788(3) Å, dihedral angles 1.6°–5.5°) together with the hydrogen bonding lead to a sheet like polymeric structure in *xz* plane. When these sheets stack, channels are generated parallel to the *z* direction in which hydrogen bonded solvent water and chloride ions are located which contribute to stabilize the overall structure.

3.3. Magnetic study

The magnetic properties of the title complex in the form of $\chi_M T$ versus T plot are shown in Fig. 2, being the magnetic susceptibility per four copper(II) ions. The value of $\chi_M T$ at room temperature is 1.69 $cm^3\ mol^{-1}$ K which corresponds to four spin doublets. The $\chi_M T$ values increase monotonically until 4 K, attaining a value of 2.27 $cm^3\ mol^{-1}$ K. This feature is characteristic

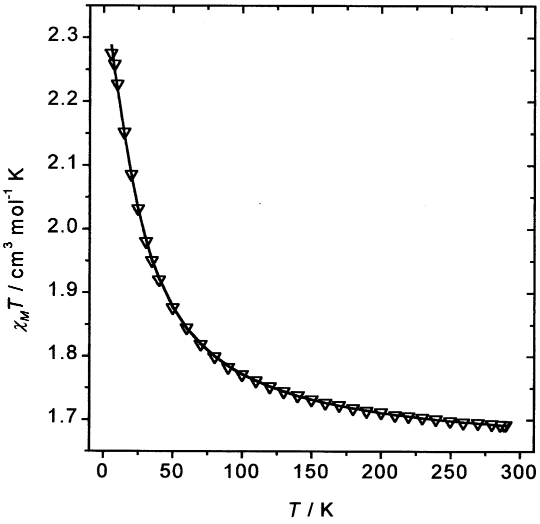


Fig. 2. $\chi_M T$ vs. T plot for $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-bipy})_4Cl_2]Cl_2\cdot 6H_2O$. The solid line corresponds to the best fit obtained.

of the presence of appreciable ferromagnetic interactions between the copper(II) ions.

In order to interpret the magnetic properties it is convenient to schematize this tetranuclear entity to see which are the exchange pathways and the possible Hamiltonian to use (Scheme 2).

Thus, in the light of the above structural discussion of the title complex, we interpret its magnetic behavior through a tetranuclear model with the following spin Hamiltonian (1)

$$H = -J_1(S_1S_2 + S_3S_4) - J_2(S_1S_4) - J_3(S_1S_3 + S_2S_4) \quad (1)$$

In which J_1, J_2 and J_3 are the exchange coupling constants across Cu(1)–Cu(2) and Cu(3)–Cu(4); Cu(1)–Cu(4), and Cu(1)–Cu(3) and Cu(2)–Cu(4), respectively. This Hamiltonian can not be solved by Kambe's method. Thus, the fit is made by the irreducible tensor operator formalism (ITO) using the CLUMAG program [19]. The fit of the magnetic data is made assuming that the g factors are identical and, as can be expected from the structure, assuming also $J_1 \gg J_2 = J_3$. An excellent fit was obtained with $J_1 = 22.71$ cm^{-1}, $J_2 = J_3 = 0.34$ cm^{-1}, $g = 2.10$ and $R = 1.3 \times 10^{-5}$. (R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{obs}]^2$). Taking into account that one J value (J_1) is very predominant we attempted to fit the magnetic data through a simple Bleaney–Bowers expression for a copper(II) dimer [20] the value of the computed J_1 being 21.74 cm^{-1} and $g = 2.10$; obviously the parameter R is worse (1×10^{-4}) because the fit is bad at low temperatures (Fig. 3). Introducing in the Bleaney–Bowers formula a new J' parameter, according to the theory of intermolecular interactions reported by Kahn [5a].

$$\chi_M = Ng^2\beta^2F(J, T)/(kT - zJ'F(J, T)) \quad (2)$$

with $F(J, T) = 2[3 + \exp(-J/kT)]^{-1}$, a quite good fit can be obtained with the following parameters: $J_1 = 22.79$ cm^{-1}; $J' = 0.24$ cm^{-1}, $g = 2.10$ and $R = 3.75 \times 10^{-6}$.

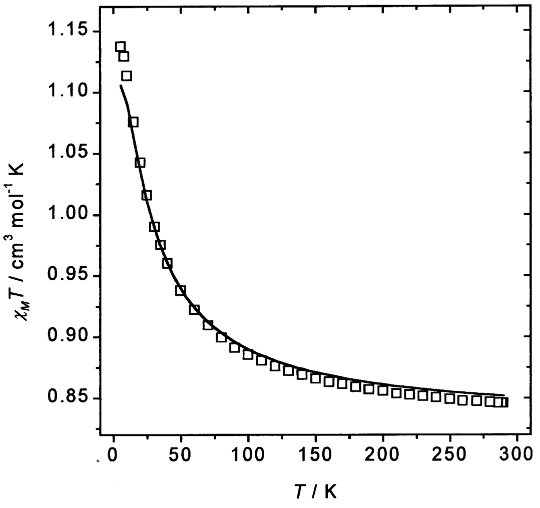
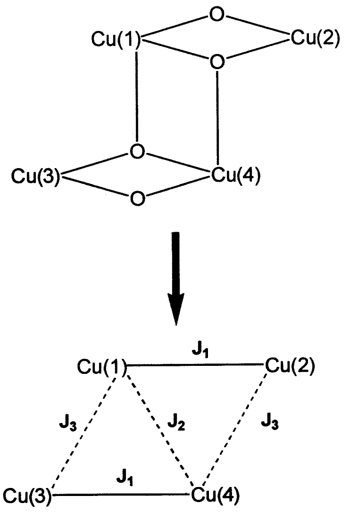


Fig. 3. $\chi_M T$ vs. T plot for [$Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-bipy})_4Cl_2$]$Cl_2 \cdot 6H_2O$ using the Bleaney–Bowers equation. The solid line corresponds to the best fit obtained.

Finally, we can conclude that J_1 value is practically the same with the fit assuming four copper(II) or only two copper(II) ions. Actually, the structure is a tetranuclear but the J' ($J_2 = J_3$) parameter must be very low (see below). The calculated J' ($J_2 = J_3$) parameters are 0.34 cm^{-1} from the CLUMAG program and 0.24 cm^{-1} from the mean field approximation. The result with CLUMAG program is more chemical, because it takes into account the structure of the compound as a tetranuclear.

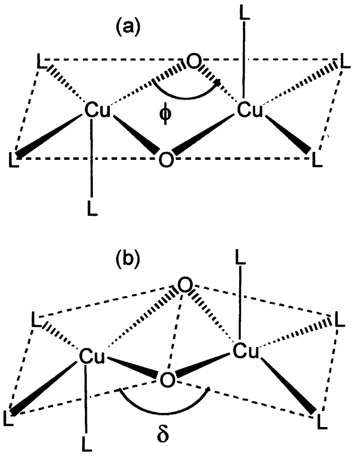


Scheme 2.

3.4. Magnetostructural correlations

Hatfield, Hodgson and co-workers first observed the linear relations between J and the Cu–O–Cu bridging angle in a series of bi-bridged copper(II) hydroxide complexes with Cu_2O_2 core and established magnetostructural correlation [21]. A remarkable linear relationship was found for a wide variety of compounds containing the planar $Cu_2(OH)_2$ core. According to these authors the interaction is ferromagnetic for angles less than 97.5°, with an increasing antiferromagnetic interaction as the angle increases. When the bridging hydroxide groups are replaced by alkoxide linkages (OR^-) the situation was not so clear. A considerable scatter was observed in the plot of J versus ϕ [22]. More recently, a study of the different factors, which affect this coupling in the μ-alkoxide complexes has been developed by Thompson and coworkers [23].

The influence of all these factors have been recently theoretically studied [24,25]: (a) the ferromagnetic character is favored when the Cu–O–Cu angle (Scheme 3a) diminishes; (b) the calculated J values seem to



Scheme 3.

indicate that the reduction of the Cu–O distance mainly affects the ferromagnetic term, diminishing the overall antiferromagnetic character of the complex; (c) the hinge distortion (Scheme 3b) reduces the antiferromagnetic coupling, reaching a ferromagnetic behavior for small values of Cu–O–Cu angles; (d) the asymmetry of the Cu_2O_2 core is less important. The calculated J parameters show values intermediate between those of the two related symmetric structures, close to the corresponding to a symmetric structure with an average angle; (e) with OH^- bridging groups, a good theoretical description of the magnetic behavior of these compounds cannot be achieved as the position of the hydrogen of the OH group is not taken into account. The inaccuracy in the location of the hydrogen atoms of the hydroxo bridges induces uncertainty in the calculated values of J. The ferromagnetic character is favored when the out-of-plane displacement of the hydrogen atom increases. Most of these correlations were already semi-quantitatively predicted by Kahn and coworkers long time ago [26]. These correlations agree with those reported by Willet et al. for similar Cl bridges where the dependence between J and the structural parameters is studied [27].

In the title complex the Cu–O–Cu angles are 99.1° and 96.36°, the hinge distortion angle is 12° and the Cu–O distances are short: from 1.98 to 1.925 Å. These three factors can explain the ferromagnetic coupling between the two copper(II) ions.

The last point concerns the very weak ferromagnetic interaction between copper(II) ions through the di-μ-oxo axial skeleton in the title complex (J_2 and J_3 in the Scheme 2). The magnetic orbital on Cu(1) (or Cu(2)) is mainly located in the equatorial plane and the spin density on its axial position is expected to be very small. The distance Cu(1)–O(1) is 2.335(3) Å. Thus, the poor overlap between the magnetic orbitals centered on two parallel dinuclear entities suggests that only a weak magnetic coupling is to be expected, ferro- or antiferromagnetic in character. Experimentally these two couplings are positive, but very weak.

3.5. Epr spectra

The epr spectra of the title complex have been registered at different temperatures (from r.t. to 4 K) to confirm the ferromagnetic coupling between the two nearest copper(II) ions in the tetranuclear entity. From the CLUMAG program, it is possible to draw the energy diagram of the tetranuclear complex. This diagram is shown in Fig. 4. The $S=2$ and $S=1$ states have very similar energy. Taking into account that $S=2$ is due to the $J_2 \approx J_3$ couplings (positive but very small) we can assume that $S=1$ is actually the ground state. Thus, a simulation spectrum is made for a $S=1$ state, which is given in Fig. 5. This is the typical spectrum for an $S=1$ spin state [28]. The best simulation corresponds to the following parameters: $g_x = g_y = 2.128$; $g_z = 2.095$; $D = 149$ G (0.014 cm^{-1}); $E = 0$ G; $\Delta H_{x,y} = 60$ G, $\Delta H_z = 35$ G. In general there is a small variation with the temperature. Increasing the temperature the spectrum is very similar (indicating that the $S=1$ spin state is practically the only populated, as corresponding to a ferromagnetic dinuclear complex). Some possible hyperfine splittings are observed. Evidently these spectra are not those corresponding to each copper(II) ions but to the tetranuclear (dinuclear) entity whose ground state is $S=1$ (2) taking into account the ferromagnetic coupling.

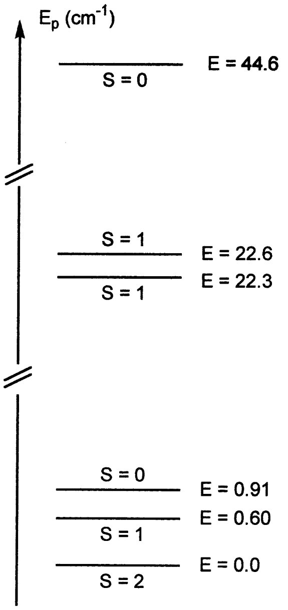


Fig. 4. Energy level diagram of the tetranuclear complex $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-bipy})_4Cl_2]Cl_2 \cdot 6H_2O$.

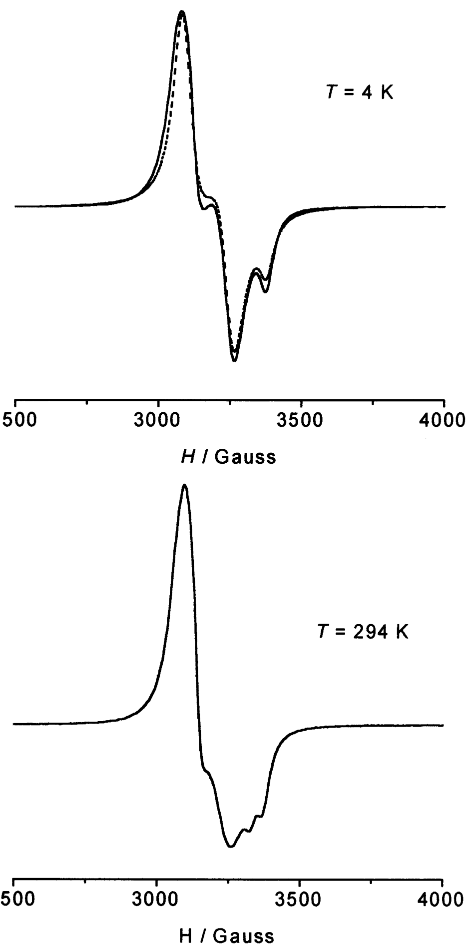


Fig. 5. EPR spectra of $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(2,2'\text{-bipy})_4Cl_2]Cl_2\cdot 6H_2O$ at 4 and 294 K.

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