Synthesis of two New Dinuclear Copper(II) Complexes and ESR Studies ofCopper(II) – Copper(II) Interaction Through π System

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Abstract

Our main objective is a better understanding of spin– spin interaction of dinuclear copper(II) complexes through π system. The synthesis and characterization of two new dinuclear copper(II) complexes, based on the use of large, pyrole-containing macrocycles, the so called " expanded porphyrins" , $[Cu_2(macrocycle)]^{4+}$ is described. A chloroform solution spectrum of two complexes taken at room temperature and 130–135 K gave a classic electron spin resonance (ESR) pattern for both compounds. Both complexes show a triplet state(S = 1), with both ΔM = 1 and ΔM = 2 (half field) transition which is the characteristics of Cu(II)– Cu(II) dimer. The observation of ΔM = 2 band strongly suggests the spin– spin interaction occurs through π system. All compounds exhibit a typical ΔM = 1 transition with superhyperfine splitting due to the ^{14}N bound to copper.

Introduction

Many complexes are known to contain more than one transition metal cations, such compounds commonly named " polynuclear". Metal-metal interactions in these compouds have been subject of a large number of papers and reviews [1–6]. A variety of subclasses of compounds have been used to describe more conveniently the nature of metal-metal interactions. In some cases, one may be justified in speaking of a "direct" metal-metal bond; in others, the interaction occurs through the bridging ligands. Ligand has great influence on the metal-metal interaction, for example, $[Cu_2(HCO_2)_4(pyridine)_2]$

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has a magnetic moment of 1.1BM per copper atom at room temperature, while, $[Cu_2(CH_3–CO_2)_4\,(pyridine)_2]$ has a magnetic moment of 1.43 BM [7,8]. For more than four decades, we have known copper(II) which forms dinuclear complexes [9–16]. Complexes containing more than one copper(II) ion with one unpaired electron can generally be categorized according to their behavior into three main groups, depending on the strength of the metal-metal interaction. In the strong interacting type, formation of relatively strong metal-metal bonds occurs, and the molecule will display simple diamagnetic behavior. In the non-interacting type, the magnetic properties of the dimer (or polymer) are essentially unchanged from the paramagnetic monomer. In the weakly interacting type, there will be a weak coupling between the unpaired electron of the two metal ions, leads to a low-lying excited state of different spin multiplicity which can be populated at thermal energy at about 1000 cm^{-1} [17–21]. There have been many investigations on synthesis of dinuclear copper(II) complexes and the determination of there crystal structure, magnetic properties and stability constant [22–25]. Hatfield and his co-workers found a linear relationship between the bridging angle of Cu–O–Cu and 2J value (singlet-triplet) energy gap [26]. In this study, therefore, we have extended our earlier efforts in the synthesis and characterization of two new dinuclear copper(II) complexes.

Materials and Methods

All chemicals and reagents were of reagent grade quality, purchased from Merck Chemical Company, and used as received (no special purification or drying was required or used) Merck type 60 (230–400 mesh) silica gel was used for column chromatography. Electronic spectra on solution in quartz cells were obtained in the UV/Vis regions using a Beckman DU 7 spectrometer. Infrared spectra were performed in 4000–300 cm^{-1} as nujol mulls or KBr disks using FTIR Perkin–Elmer spectrometer. The spectra were calibrated using polystyrene bands at 3028, 1601 and 1208 cm^{-1}. ESR

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spectra were recorded on solutions of complexes both at ambient and liquid nitrogen temperatures using a IBM ER 300 spectrometer. Low resolution CI (chemical ionization) and FAB (fast atom bombardment) spectra were obtained using a Finnigan –MAT 70 instrument. 3–Nitrobenzyl alcohol or glycerol was used as the matrix for FAB mass spectra.

Preparation of Ligands

Dialdehyde (4) was synthesized by the method of Cheeseman [27]. A 250 ml two-necked round bottom flask fitted with a thermometer, a magnetic stirring bar, and a reflux condenser attached to a nitrogen line. To the flask was added 50 ml CH_3OH, 50 ml $CHCl_3$, 1 mmol tetraamine (1), 2 mmol dialdehyde (4), and five drops of concentrated HCl for the preparation of $\mathbf{L_1}$. Ligand $\mathbf{L_2}$ was made by the addition of 50 ml CH_3OH, 50 ml $CHCl_3$, 1 mmol tetraamine (2), 4 mmol aldehyde (3) and five drops of concentrated HCl. After the addition, the content of the flask were allowed to reflux for 12 hours. The resulting solution was concentrated to dryness on a rotary evaporator. The residue was taken up in $CHCl_3$ or CH_3OH and eluted through a silica gel with 10 % CH_3OH / $CHCl_3$ as eluent.

Preparation of Complexes

A 250 two-necked round bottom flask fitted with a magnetic stirring bar, a thermometer, a reflux condenser, and a heating mantel. For the synthesis of $[Cu_2L_1]^{+4}$, 50 ml CH_3OH, 50 ml $CHCl_3$, 1 mmol ligand L_1 and 2 mmol of copper(II) acetate dihydrate was added to the flask. Complex $[Cu_2L_2]$ was made, by addition of 50 ml CH_3OH, 50 ml $CHCl_3$, 1 mmol ligand L_2 and 2 mmol copper(II) acetate dihydrate to the flask. Content of the flask was allowed to reflux for 24 hours. The solvent was removed by rotary evaporator and the rasidue was purified through a silica gel column with 10–20 % CH_3OH / $CHCl_3$ as eluent.

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Results and Discussion

The mechanism of exchange interactions in polynuclear metal complexes has occupied much experimental and theoretical work [28,29]. One major interest arises because the subject occupies a frontier area between coordination chemistry and solid state physics. For several decades, solid state physics have been interested in the magnetic properties of materials in which adjacent magnetic centers are strongly coupled to each other.The spin-spin interaction can be treated quantitatively using the approach outlined by Van Vleck [30]. The magnetic exchange between nearest neighbors may be represented by the spin Hamiltonian:

$$\mathbf{H_{ex} = -2\Sigma J_{ij} S_i S_j}$$

Where J_{ij} is an exchange integral between centers i and j. J_{ij} is negative for an antiferromagnetic and positive for ferromagnetic interaction. The study of copper(II) –copper(II) exchange interactions has received considerable attention in our group [31–42]. These complexes can be formulated as [$\mathbf{Cu_2L}$] and are of structural, optical and magnetic interest.

In this paper we present two new complexes and their optical and magnetic properties are investigated. The absorption spectra of free ligands show a broad band at UV region, which can be attributed to n→π* or π→π*[43–48]. All metaloporphyrins show the following characteristic UV- Vis spectra: (1) Q-band: Two visible bands in the range of 500 – 600nm. The lower-energy band (sometimes called α) is the electronic origin Q(0,0) of the lowest-energy excited singlet state. The higher-energy band (sometimes called β) includes one mode of vibrational excitation and is noted Q(1,0).
(2) B-bands: An exceedingly intense band (sometimes called Soret band) appears in the range of 380 – 420nm. It is origin B(0,0) of the second excited singlet state. All these bands are interpreted as n→π* or π→π* in origin [49]. The absorption spectra of of free ligand L_1 and its complex $[\mathbf{Cu_2L_1}]^{4+}$ has a Soret band at 527nm and two weak Q-bands at 651, and 568nm. The free ligand exhibits a band at 354nm. The spectrum of [$\mathbf{Cu_2L_2}$]

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shows an intense Soret-like band at 527nm. The Q-type bands occur at 564 and 634nm. The free ligand shows an absorption maximum at 378nm. Low resolution mass spectroscopic data provide initial support for the dinuclear nature of complexes, which are collected in Table 1. A strong absorption band at 500 cm^{-1} and lower regions, may be attributed to the symmetric infrared active Cu–O or Cu–N bond [50]. The most important difference between the spectra of the ligand $\mathbf{L_2}$ and its copper(II) complex can be found in the 3500–3300 cm^{-1} region. When going from free ligand $\mathbf{L_2}$ to its complex, the stretching vibration ν_{OH} disappears, pointing out that the OH group of the $\mathbf{L_2}$ has been deprotonated on the coordination to the copper ion. The observed ESR parameter for the complexes are independent of the nature of the solvent. The X–band spectra of the solution complexes at room temperature and 130 K shows typical triplet state feature with $\Delta M = 1$ transition. The spectroscopic splitting factor ($g_{av.}$) for all complexes are presented in Table 1.

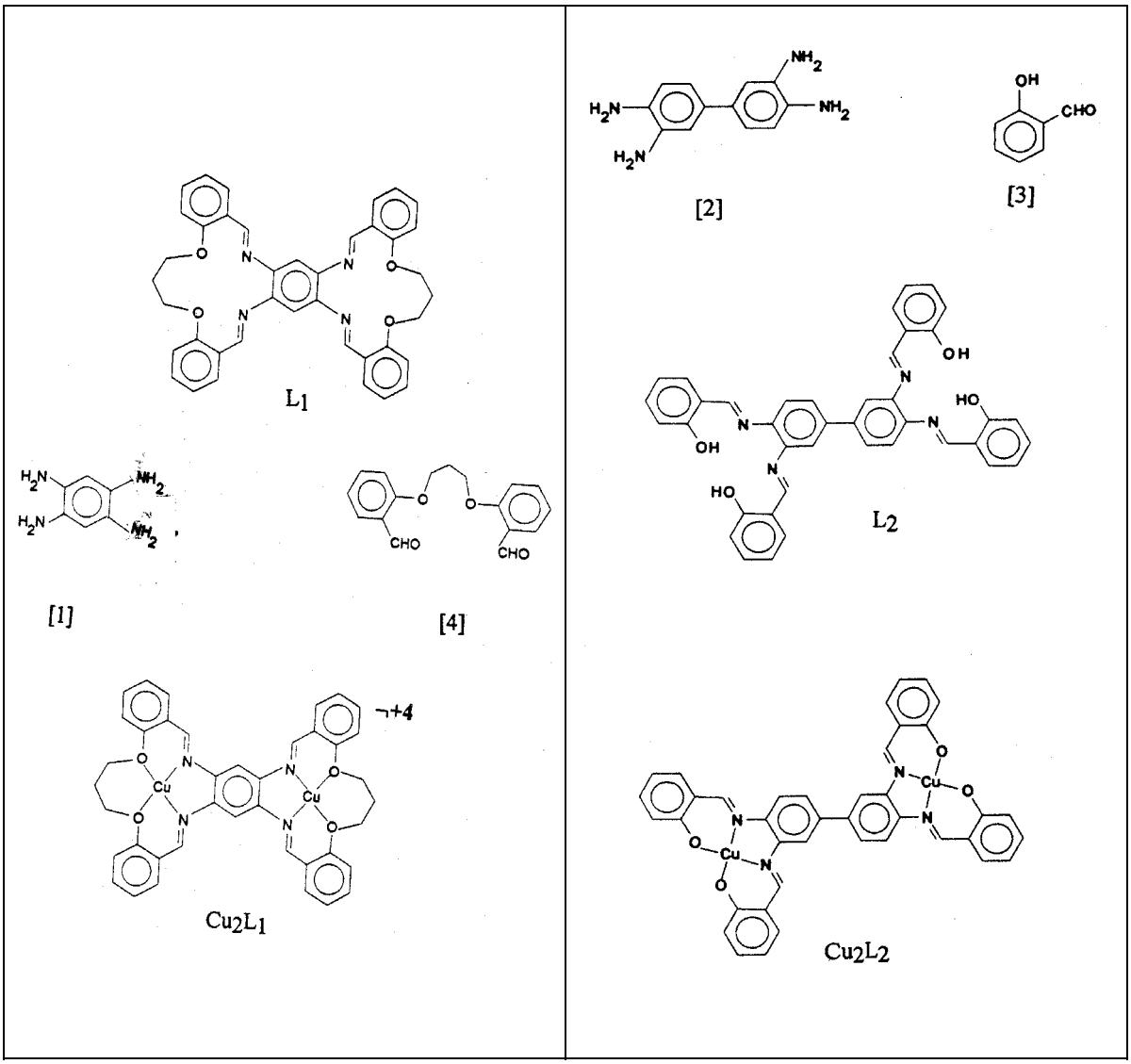
Table 1. Spectroscopic data for the ligands and complexes.

Complex	λ_{max}	M/z	$g_{av.}$ (R. T.)	$G_{av.}$ (half–field)	$g_{av.}$ (130 K)
[L_1]	354	635	-------	-------	------
[L_2]	378	630	-------	-------	------
[Cu_2L_1]	651, 568, 527	761	2.0438	4.0770	2.0447
[Cu_2L_2]	634, 564, 527	753	2.0496	-------	2.0468

The spectra of both complexes at high field (3000 gauss) are similar. They exhibit typical superhyperfine splitting due to the ^{14}N bounded to copper(II). As seen in Fig. (**1**–**5**), the main hyperfine is splitted in five lines for each copper atom. The spacing between these lines are nearly the same and about 10 gauss which can be attributed to the interaction with the two ^{14}N nuclei [51–53]. A much weaker $\Delta M=2$ transition for

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[Cu_2L_1], confirming the occurrence of a copper(II) –copper(II) magnetic exchange interaction at half–field. The observation of this band strongly suggests that the hyperfine structure arises from spin–spin interaction through π system.



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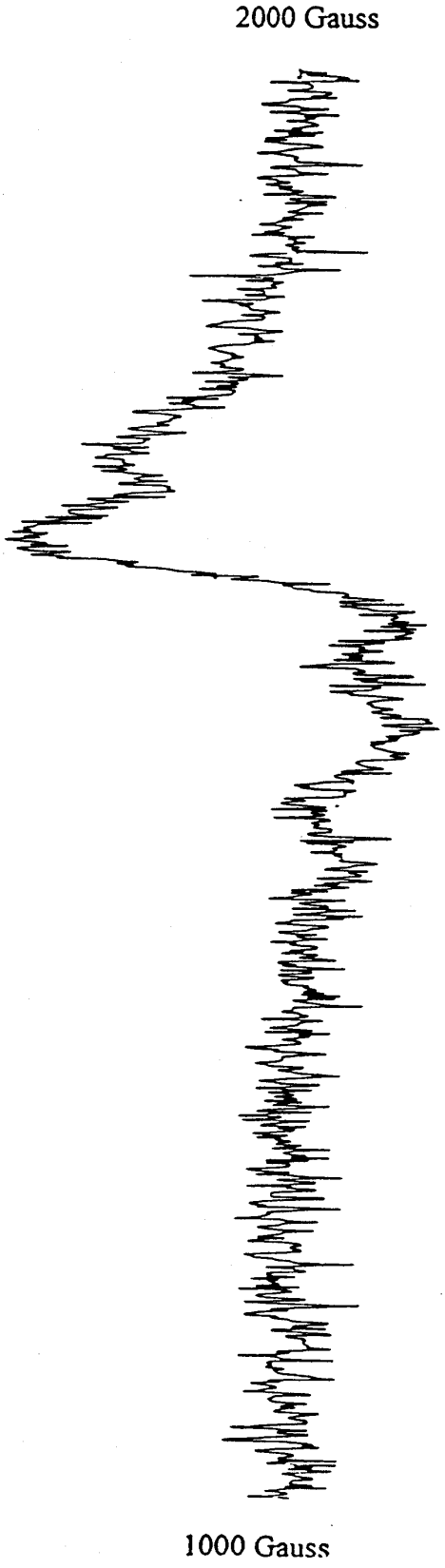


Figure 1: ESR spectra of complex $[Cu_2L_1]$ at 135 K. The field set was 1500 gauss, and the scan range was 1000 gauss.

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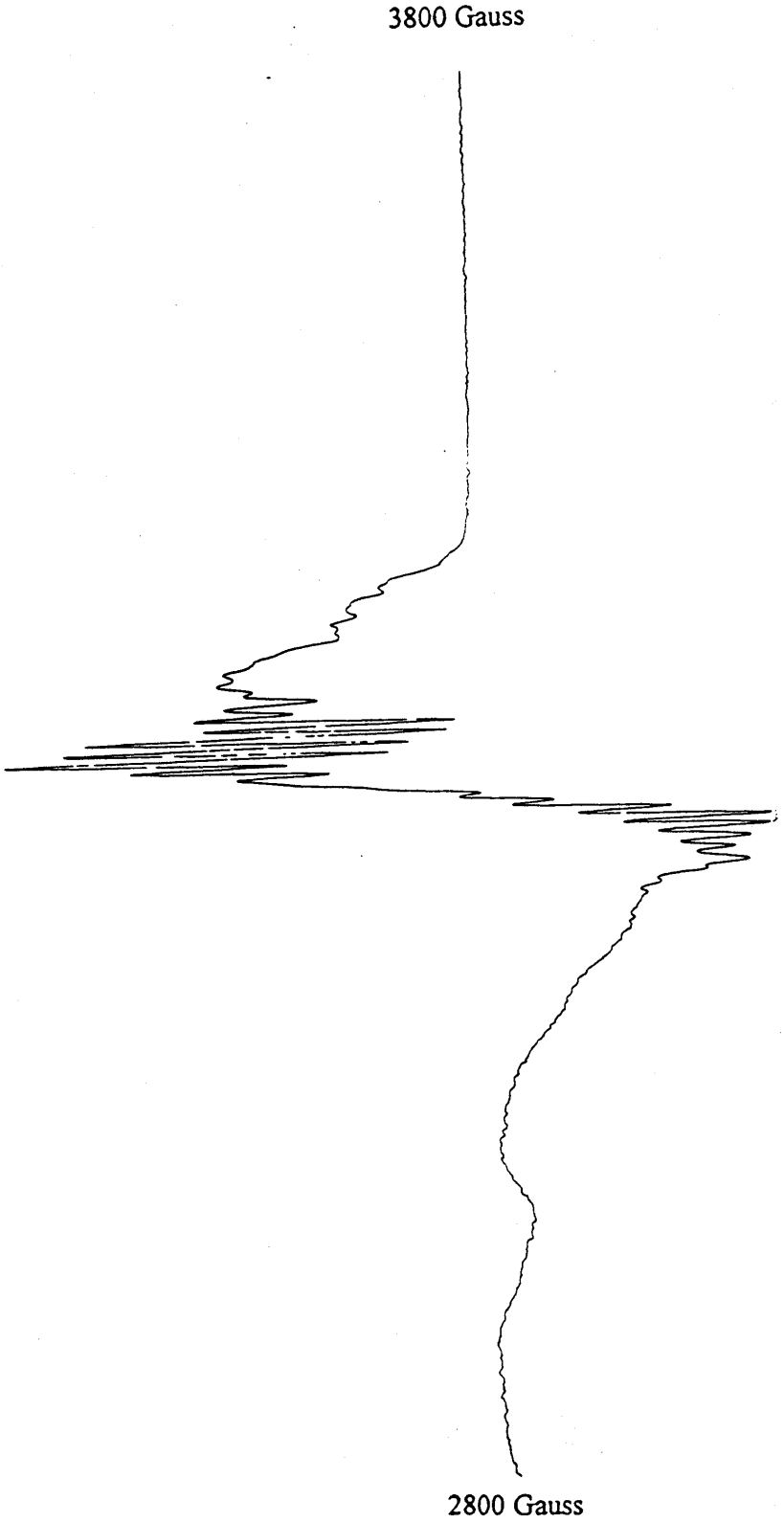


Figure 2: ESR spectra of complex [Cu_2L_1] at 130 K. The field set was 3300 gauss, and the scan range was 1000 gauss.

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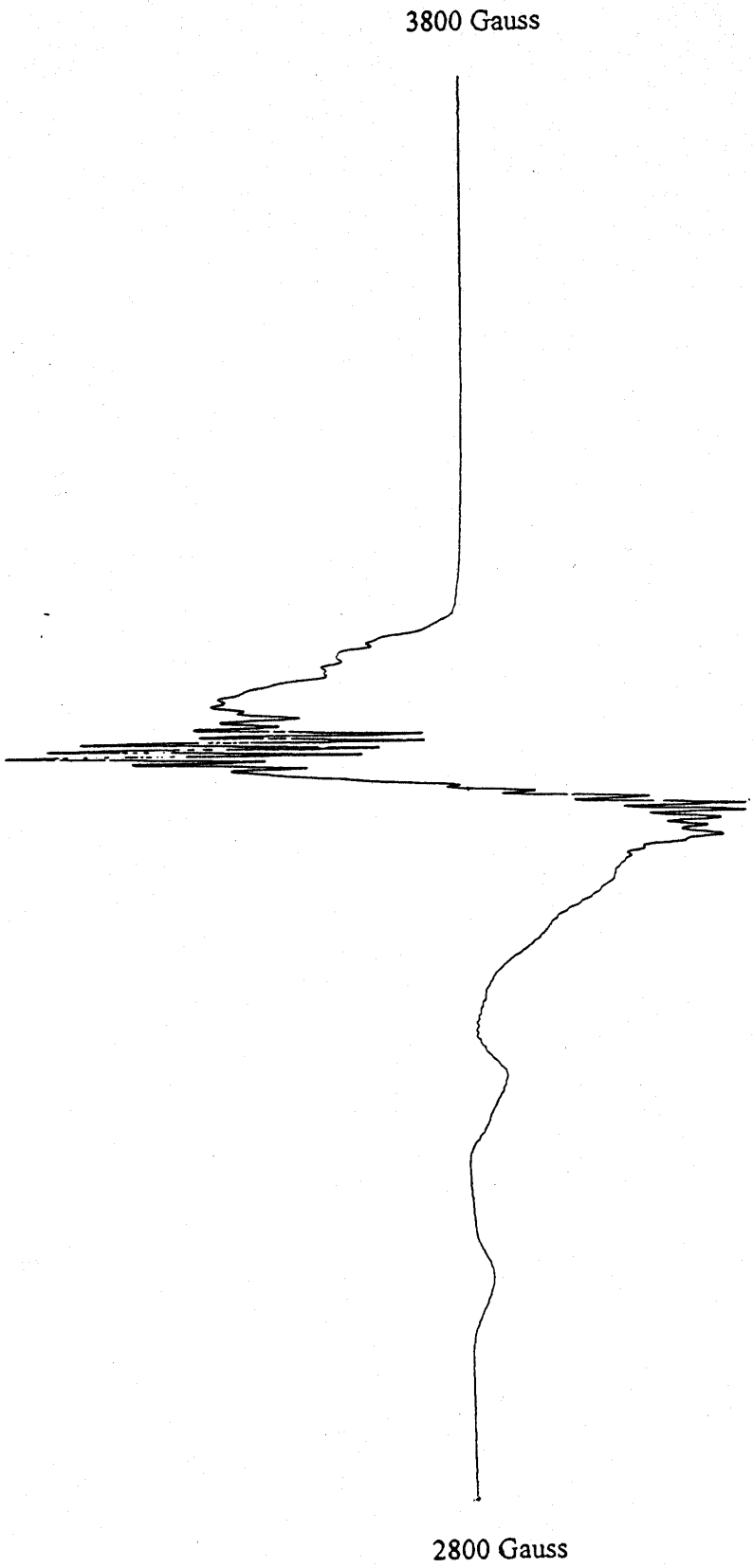


Figure 3: ESR spectra of complex $[Cu_2L_1]$ at room temperature. The field set was 3300 gauss, and the scan range was 1000 gauss.

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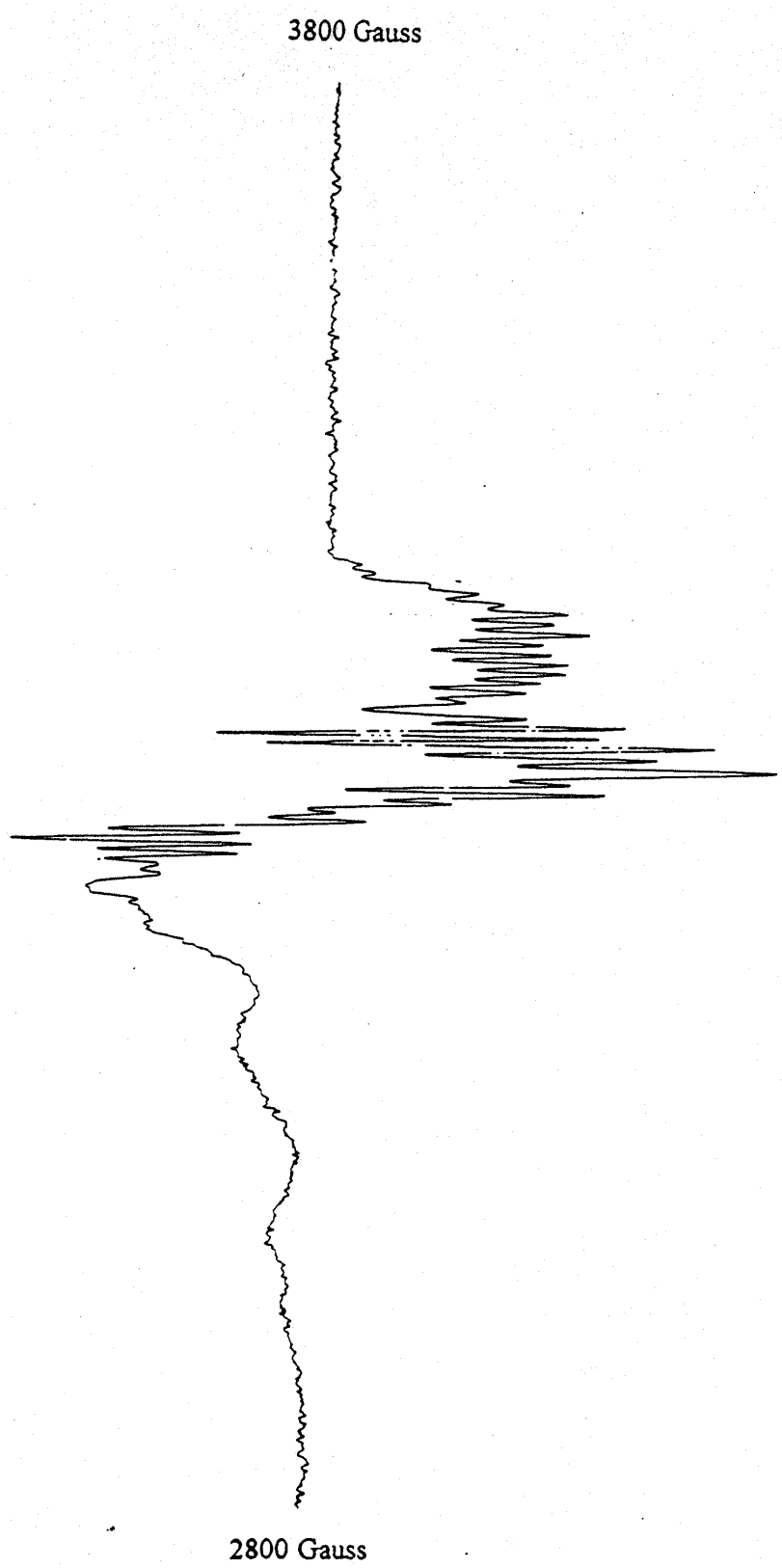


Figure 4: ESR spectra of complex $[Cu_2L_2]$ at 130 K. The field set was 3300 gauss, and the scan range was 1000 gauss.

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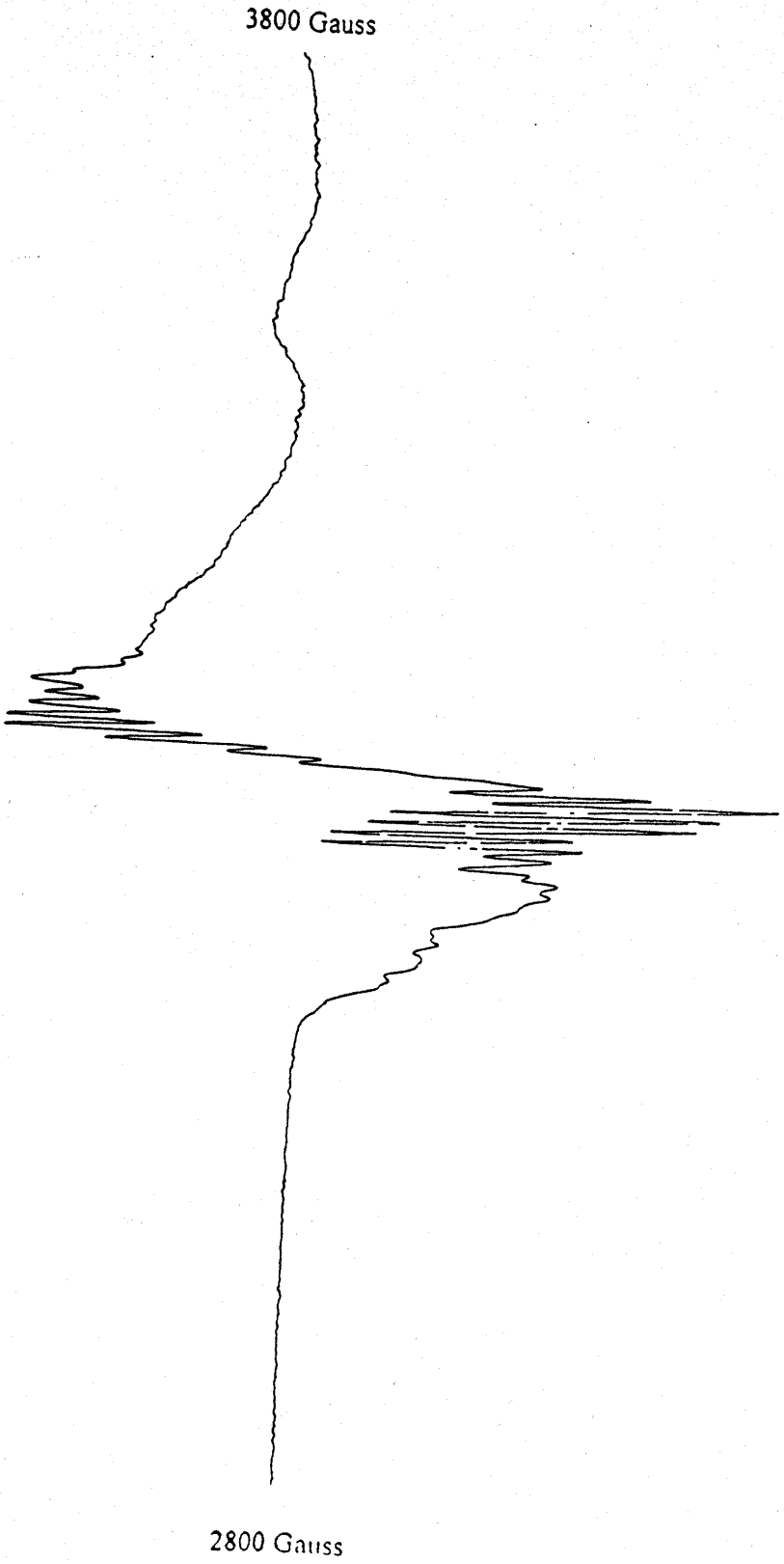


Figure 5: ESR spectra of complex [Cu2L2] at room temperature. The field set was 3300 gauss, and the scan range was 1000 gauss.

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