

Mesomorphic and Magnetic Properties of a Copper(II) Complex Compared to an Oxovanadium(IV) Complex

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Abstract

A chiral complex, (S)-(+)-bis[N-*n*-heptyl(2-hydroxy-4-[4''-(2-methylbutyl)-4'-biphenyl-carboxyloxy]phenyl)methaniminato]copper(II) was synthesized and its mesomorphic and magnetic properties investigated, and compared to those of oxovanadium(IV) complex previously reported. Mesomorphically, the chiral complexes exhibited only a high temperature chiral nematic phase, while the corresponding ligand showed a variety of mesophases, including two blue phases. Magnetic susceptibilities and infrared absorption data of the complexes revealed a certain degree of intermolecular magnetic interaction in both complexes and dipole interactions in the oxovanadium(IV) complex. Temperature dependent molar effective magnetic moments of the complexes showed the possibility of molecular alignment in the applied magnetic field. Magnetically, compared with the previously reported chiral oxovanadium(IV) complex, the chiral copper(II) complex in this report was antiferromagnetic while the oxovanadium(IV) complex had been found to be ferromagnetic.

Keywords: Chiral metallomesogens, Copper(II) complex, Oxovanadium(IV) complex, Ferromagnetic, Antiferromagnetic.

1. Introduction

Liquid crystals, especially metal-containing liquid crystals, or metallomesogens, have attracted scientists' attention for many years. They show enormous potential for various applications, such as liquid crystal displays, ultramicroconductors and non-linear optics.

Magnetic properties of metallomesogens are recently of great interest, especially those of complexes of copper(II) and oxovanadium(IV) ions, with outer electronic structures of $3d^9$ and $3d^1$, respectively. Previously, the properties of the oxovanadium(IV) complex of the ligand, (S)-(+)-[N-*n*-heptyl(2-hydroxy-4-[4''-(2-methylbutyl)-4'-biphenyl-carboxyloxy]phenyl)methanimine, have been reported, where the possibility of magnetic alignment has been revealed[1]. In this paper, another complex with copper(II) ion as core ion is investigated. Oxovanadium(IV) complexes of various ligands show a hat-like shape at the core metal, while

copper(II) complexes have flat rectangular shapes. This difference in shapes of the metal cores may affect the properties of their complexes.

In this study, a copper(II) complex of the chiral ligand is synthesized and their properties investigated. The newly synthesized copper(II) complex is investigated using IR spectroscopy and the liquid crystal texture is observed under an optical polarizing microscope. Additionally, the chiral complex is continuously heated and cooled under a magnetic field, where changes in molar magnetic moment are measured by SQUID. The chiral structure of the ligand is chosen owing to the helical structure that might help boost the molecular orientation of the complexes. The molecular orientation of the complex molecules would lead to useful applications, especially in microclusters of molecules and in nanotechnology[2]. It has a potential for producing molecular wire for

connecting ultramicro circuits in electronic chips or self-assemble systems.

Mesomorphically, both the oxovanadium(IV) complex and the newly synthesized copper(II) complex are shown to be chiral nematic (**Photomicrograph 1**). From the results of the measurements of magnetic moments versus temperatures, the molecular orientation of oxovanadium(IV) complex is shown to be ferromagnetic while that of copper(II) complex is antiferromagnetic. Previously, a number of various metal complexes and metallomesogens, with a chiral center in the ligand molecule, have been reported to possess a certain degree of ferromagnetic and antiferromagnetic alignments [3]-[4], with some steric effects from chiral components in the ligands [5]-[6].

2. Results and Discussion

2.1 Syntheses and Characterisations

The syntheses of the intermediates are reported elsewhere [1]. The complex was synthesized using the method previously stated [7], with some slight modifications as shown in **Scheme 1**. Copper (II) acetate was used instead of the traditional copper(II) sulfate because the acetate ions in the solution act as a base, and thus help boost the complexation between the ligand **1** and the copper(II) ion, with no additional base needed.

The characterization of the copper complex, **2**, was performed using conventional methods, IR spectroscopy, elemental analysis, optical rotation and magnetic susceptibility at ambient temperature. The results were all satisfactory.

The optical properties of the copper complex, from optical polarizing microscopy, showed a right-handed helix, similar to that of the oxovanadium(IV) complex of the same ligand previously reported ($[\alpha]_D +2.9$ (24 °C, c 0.00407 in CHCl_3) [1], which might correspond to the S-configuration of the ligand.

2.2 Mesomorphic properties

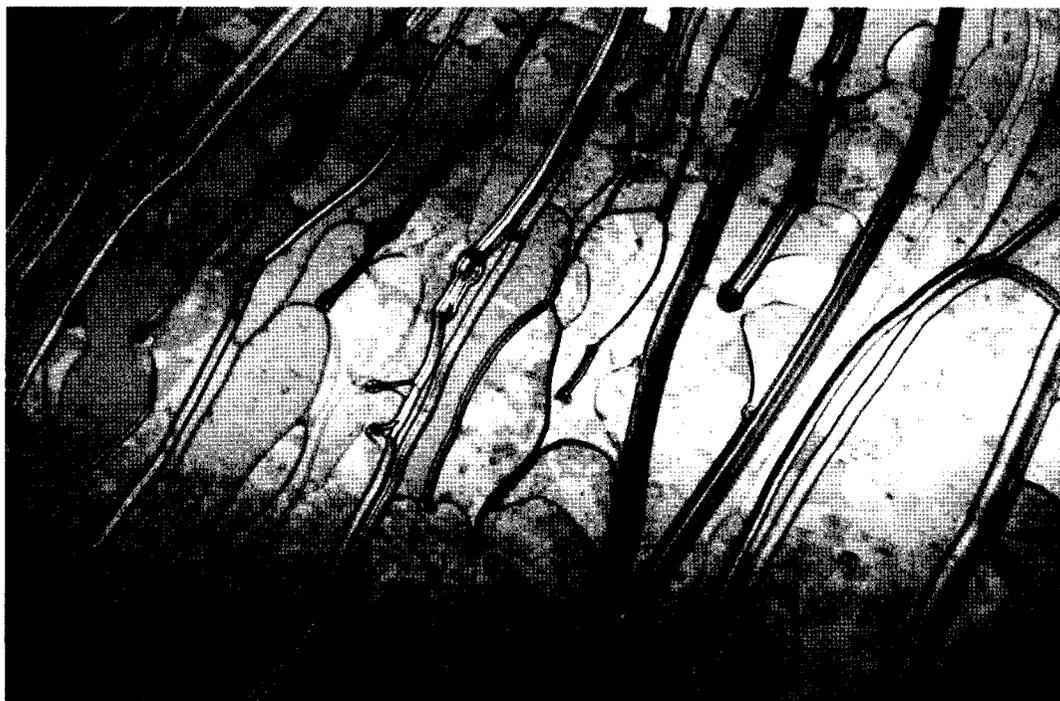
The copper (II) complex shows only high temperature chiral nematic phase, similar to that of the oxovanadium(IV) complex. However, the transition temperatures of the copper(II) complex are approximately 10 degrees higher than those of the oxovanadium(IV) complex. This may be due to the shape of the molecules,

where the oxovanadium(IV) complex molecule has a group of oxovanadium, or vanadyl, $\text{V}=\text{O}$, right up in the center of the molecule, but the copper(II) complex molecule is somewhat flat. The flat molecules can be packed together a little more closely than the others, thus raising the transition temperatures. The enthalpy changes from DSC measurements, in square brackets, kJ mol^{-1} , also show agreeable outcomes (VO(IV) complex: K 172 [29.0] N* 263.9 [2.0] Iso) [1], (Cu(II) complex, K 182 [33.0] N* 273 [3.2] Iso)

2.3 Magnetic properties

In this report, the magnetic properties are reported in terms of molar effective magnetic moment, μ_{eff} , in μ_B units. The effective magnetic moment of the copper(II) complex at solid state, $\mu_{\text{eff}}/\mu_B = 1.01$, shows a certain amount of antiferromagnetic interaction. A normal magnetic behaviour of a compound in solid state of an ion with single electron, $3d^1$ as in VO(IV) and $3d^9$ as in Cu(II), would give the value of around $1.8 \mu_B$ [8]. The effective magnetic moments versus temperatures of both complexes are shown in **Figure 1**. The moments of the oxovanadium(IV) complex show clearly a ferromagnetic behaviour [1], where the moments are higher than the average value of $1.8 \mu_B$, while those of copper(II) complex are antiferromagnetic, where the moments are lower than the average value of $1.8 \mu_B$. The possibility of the ferromagnetic and antiferromagnetic couplings of several metallomesogens of copper(II) and oxovanadium(IV) and a number of compounds have also been previously reported [9]-[12].

The oxovanadium(IV) complex in the previous report has shown a certain degree of ferromagnetic molecular alignment in a magnetic field, **Figure 1(a)** [1], as the moments increase during the processes. On the first heating process, namely, VO Heat 1, there is a discontinuity of the effective magnetic moment at melting and an increase of the value after becoming isotropic. And on the first cooling, the moments keep rising and become somewhat stable below crystallization. On the second heating process, VO Heat 2, the value reversely follows that of the first cooling step and above the isotropic point, 573 K (264 °C), the value increases once more.



Photomicrograph 1. Cholesteric phase of copper(II) complex **2** at 473 K (200 °C), x 100.

The copper(II) complex, on the other hand, shows a certain degree of antiferromagnetic molecular alignment in a magnetic field, **Figure 1(b)**, as the moments decrease during the processes. During the first heating cycle, Cu Heat 1, the effective magnetic moments remain almost constant up to the melting point, around 460 K (180 °C). At melting, the moments discontinue and move up slightly. This may be due to the relaxation of the complex molecules after transforming from solid to the liquid state. However, the moments stay almost at the same value up to the clearing point, 540 K (267 °C).

At the clearing point, around 540 K (267 °C), the moments drastically decrease. This obviously shows a certain degree of antiferromagnetic interactions in its isotropic liquid state. In the chiral nematic phase, as shown in **Photomicrograph 1**, the molecules are forced to stay in cholesteric helical arrangement which restrict the orientation on the molecules, thus the moments stay almost at the same value below clearing. However, when molecules are able to move freely in their

isotropic phase, an alignment in magnetic field is unleashed and they align better, thus raise the magnetic moments. Then, on the first cooling process, the moments become more stable after cooling down below the clearing point, where the sample is now back to mesomorphism and a solid phase once again.

When the sample is brought back to the starting temperature, the second heating cycle starts, Cu Heat 2. This time the moments are almost similar on both heating and cooling cycles, and similar to those of the first cooling cycle. This shows a nearly complete antiferromagnetic alignment of the sample molecules during the first cooling process, so the second heating and cooling processes yield similar values of effective magnetic moments as the first cooling process. In contrast, the oxovanadium(IV) complex molecules are unable to fully align during the first heating process, and the alignment continues during the second heating cycle.

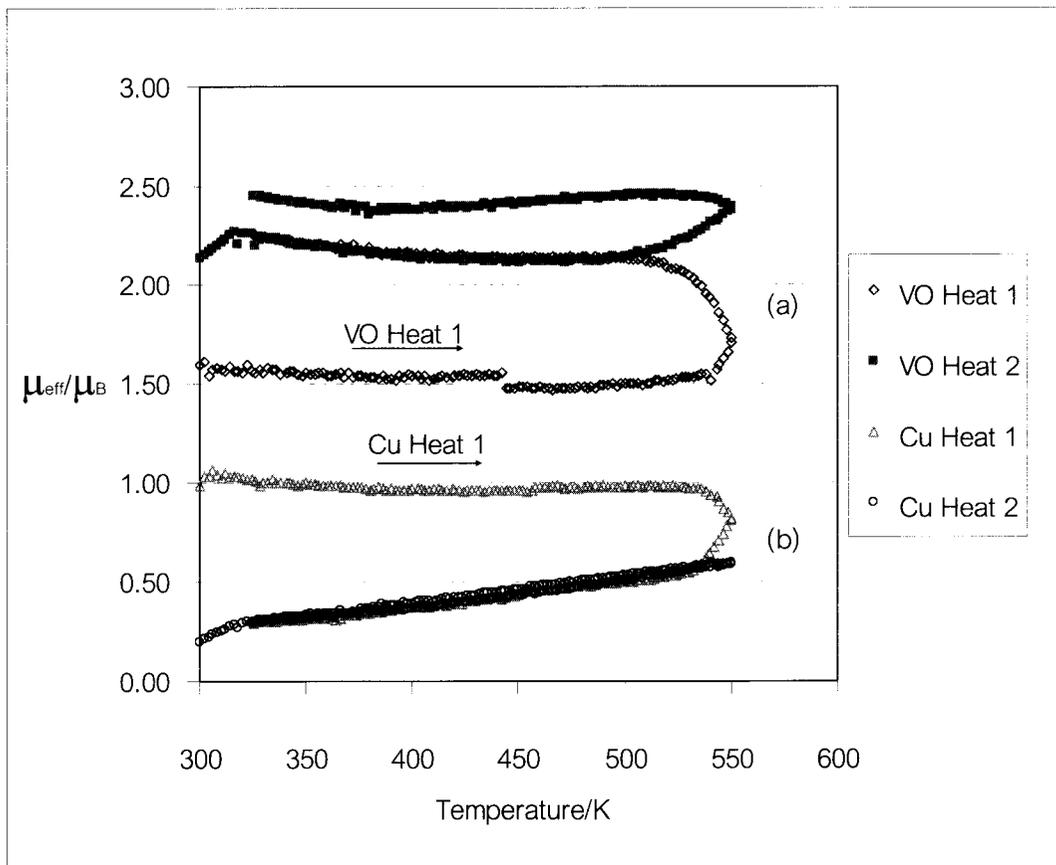


Figure. 1 Temperature dependent molar effective magnetic moments, μ_{eff} , of VO and Cu complexes, (a) and (b), respectively. For each complex, the sample was heated and cooled twice, Heat 1 and Heat 2, continuously. The values show a certain degree of magnetic interactions.

Apart from those probable applications discussed in the previous report [1], results of this experiment may lead to the possibility of molecular alignment in magnetic fields, which is very important in many self-assemble systems, especially in one of the most popular themes nowadays, nanotechnology. On the application side, a nanosystem may be a magnetically preassembled in either a ferromagnetic or antiferromagnetic manner, and the system is made active. The active system may be chemical reactions, catalytic work, detection of trace species and any other magnetic interactions in molecular levels. Further study on the syntheses of other different systems may bring about fruitful applications in liquid crystal displays, molecular wires and ultramicroconductors.

3. Experimental

Characterizations of the copper complex were elucidated as followed: IR spectroscopy was recorded on a Perkin-Elmer 783 IR spectrometer with a KBr disc. Elemental analysis was performed on a Carlo-Erba 1106 CHN analyzer using cyclohexanone-2,4-dinitrophenylhydrazine as reference standard. The effective paramagnetic moment of the copper(II) complex crystals was recorded at 21 °C on a Johnson Matthey susceptibility balance using mercury(II) cobalt(II) thiocyanate ($\text{HgCo}(\text{NCS})_4$) as reference standard [$\chi_g(20\text{ °C}) = 20.64 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$] and the value was corrected for the diamagnetic contribution of the ligand.

Temperature dependent molar effective magnetic moments were recorded on a Quantum Design MPMS system 5 and the values were

corrected for the diamagnetic contribution of the ligand and the aluminum container. Optical rotation of the chiral complex was measured in chloroform solution at ambient temperature with the unit of $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. The mesomorphic sequence of the complex was determined by a thermal optical polarizing microscope (Olympus BH-2) equipped with Mettler FP83 Hotstage and FP5 Temperature Controller. Satisfactory analyses were achieved in all instances.

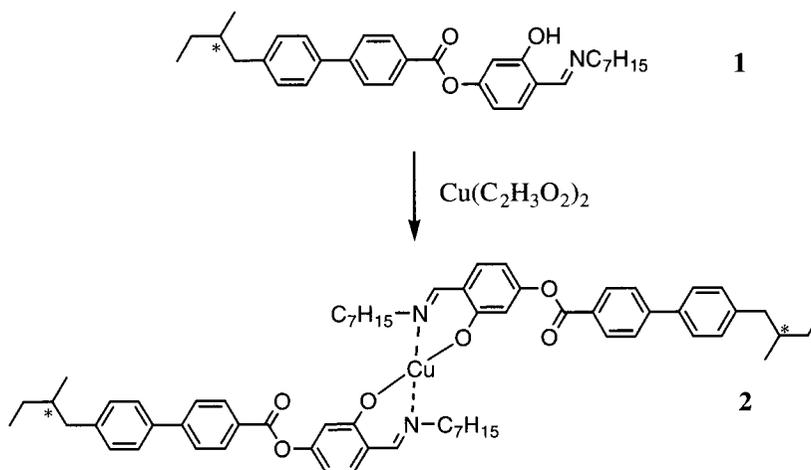
The ligand, **1**, (1.0 g, 2 mmol) was dissolved in ethanol (50 cm^3) and the mixture heated to reflux (20 min), where a clear yellow solution was formed. A solution of two-fold excess copper(II) acetate (0.4 g, 2 mmol) in 2:1 ethanol:water solvent (20 cm^3) was added to the yellow solution, with continuous stirring, but without further heating. The resulting mixture

was then brought back to reflux with gentle heating (1 hr). The mixture with deep green precipitate was allowed to cool back to room temperature and the precipitate was filtered off and washed with water ($2 \times 20 \text{ cm}^3$) and then with acetone ($2 \times 20 \text{ cm}^3$). The complex product, **2**, was finally purified by recrystallization from a solution of hot acetone and dichloromethane (1:1). The purified product was left to dry in vacuum at room temperature.

4. Acknowledgement

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Scheme 1



Yield = 0.6 g (55%); μ_{eff} (21 °C) / μ_{B} = 1.21.

Mesomorphism (optical polarizing microscope) / °C and Enthalpy Changes (DSC) [$\Delta H / (\text{kJ mol}^{-1})$];
K 182 [33.0] N* 273 [3.2] Iso.

IR, ν_{max} (KBr) / cm^{-1} : 3000-2800 (CH str.), 1725 (C=O str.), 1615 (imine, C=N), 1150 (ester, C-O).

Elemental analysis, found (cal.): %C 74.32(74.42), %H 7.35(7.42), %N 2.68(2.71).

$[\alpha]_{\text{D}}$ +3.8 (25 °C, c 0.00533 in CHCl_3).

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