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Mesomorphic and Magnetic Properties of Oxovanadium(IV) Complexes of (S)-(+)-N-*n*-Heptyl (2-hydroxy-4-[4”-(2-methylbutyl)-4’-biphenylcarboxyloxy]phenyl)-methanimine:Magnetic-induced Molecular Orientation

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Abstract

A Chiral complex, (2S)-(+)-bis[N-*n*-heptyl(2-hydroxy-4-[4”-(2-methylbutyl)-4’-biphenylcarboxyloxy]phenyl) methaniminato]oxovanadium(IV), was synthesised and its mesomorphic and magnetic properties were investigated. Mesomorphically, the complex exhibited only a high temperature chiral nematic phase, while the corresponding ligand showed a variety of mesophases, including a blue phase. Magnetic susceptibility and infrared absorption data of the complex revealed a certain degree of intermolecular magnetic and dipole interactions. Temperature dependent molar magnetic moment showed the possibility of molecular alignment in the applied magnetic field.

Introduction

Metallomesogens, or metal-containing liquid crystals, are of great interest due to their distinct thermodynamic, optical and electromagnetical properties. They show enormous potential for applications in many fields, such as non-linear optics, superconductors, ultramicroconductors, or even conventional liquid crystal displays [1-3].

Magnetic properties of metallomesogens have recently been becoming interesting, especially those of complexes of copper (II) and oxovanadium(IV) ions. Both ions possess a single electron which gives rise to the paramagnetic properties of the complexes. However, not many examples of magnetic investigations were reported [4-8]. Previously some complexes of Cu and VO with Schiff's bases were investigated by means of EPR and magnetic susceptibility measurements at various temperatures. A change in effective magnetic moment was reported when a complex was heated from crystal phase to mesophases, but there is no difference in the value for the crystal and isotropic phases [8].

In this investigation, we aim to study molecular alignment under a magnetic field of a chiral oxovanadium(IV) complex. A chiral structure was chosen owing to the helical structure of the chiral complex which may help to boost molecular orientation and hence the magnetically orientated complex molecules can be easily observed. Oxovanadium(IV) complex of structure 5 has been synthesised and mesomorphic properties investigated, using DSC measurement and the liquid crystal texture is observed under an optical polarising microscope. Furthermore, the complex is continuously heated and cooled under a magnetic field, where the change in molar magnetic moments is measured.

Results and Discussion

Syntheses and Characterisations

The compounds were synthesised following the procedure described elsewhere, Scheme 1 [9]. Acid hydrolysis of chiral cyanobiphenyl 1 was carried out using concentrated nitric and sulfuric acids, with glacial acetic acid as a solvent. An addition of a small amount of water helped shift the equilibrium of the reaction to the right, thus giving a satisfactory yield. Then, condensation of the chiral biphenyl acid 2 with 2,4-dihydroxybenzaldehyde to give compound 3 was performed at room temperature with 1,3-dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine (4-PPY). The esterification occurred mainly at the 4-OH group of the benzaldehyde as a result of hydrogen bonding between the hydrogen of the 2-OH group and the carbonyl moiety.

The ligand 4 was also obtained from condensation reaction of compound 3 and *n*-heptylamine. The water by-product was removed from the reaction using molecular sieve 4A in order to shift the reaction equilibrium to the right. In case of complexation reaction between the ligand 4 and oxovanadium(IV) sulfate, aqueous salt solution was added to the hot ethanolic solution of the ligand, followed by a weak acid solution in order to prevent the competition reactions between the acid and the oxovanadium(IV) ions and the acid and the ligand, which considerably lower the yield.

The oxovanadium(IV) complex was characterised by the typical infrared absorption peak at 980 cm^{-1}. This value shows a certain intermolecular dipole interaction as the typical value of a free V=O bond has been reported to be 997 cm^{-1} [10]. The lower the value, the higher the intermolecular dipole interaction.

Optical properties of the compounds are shown in Table 1. The complex exhibits highest molar optical rotation, more than twice that of the ligand. This may be due to the electron density of the oxovanadium(IV) ion which enhances the optical rotational power of the chiral centre. Absolute configurations also agreeably correspond to the helix direction, the S-configuration corresponds to a right-handed helix.

Scheme 1

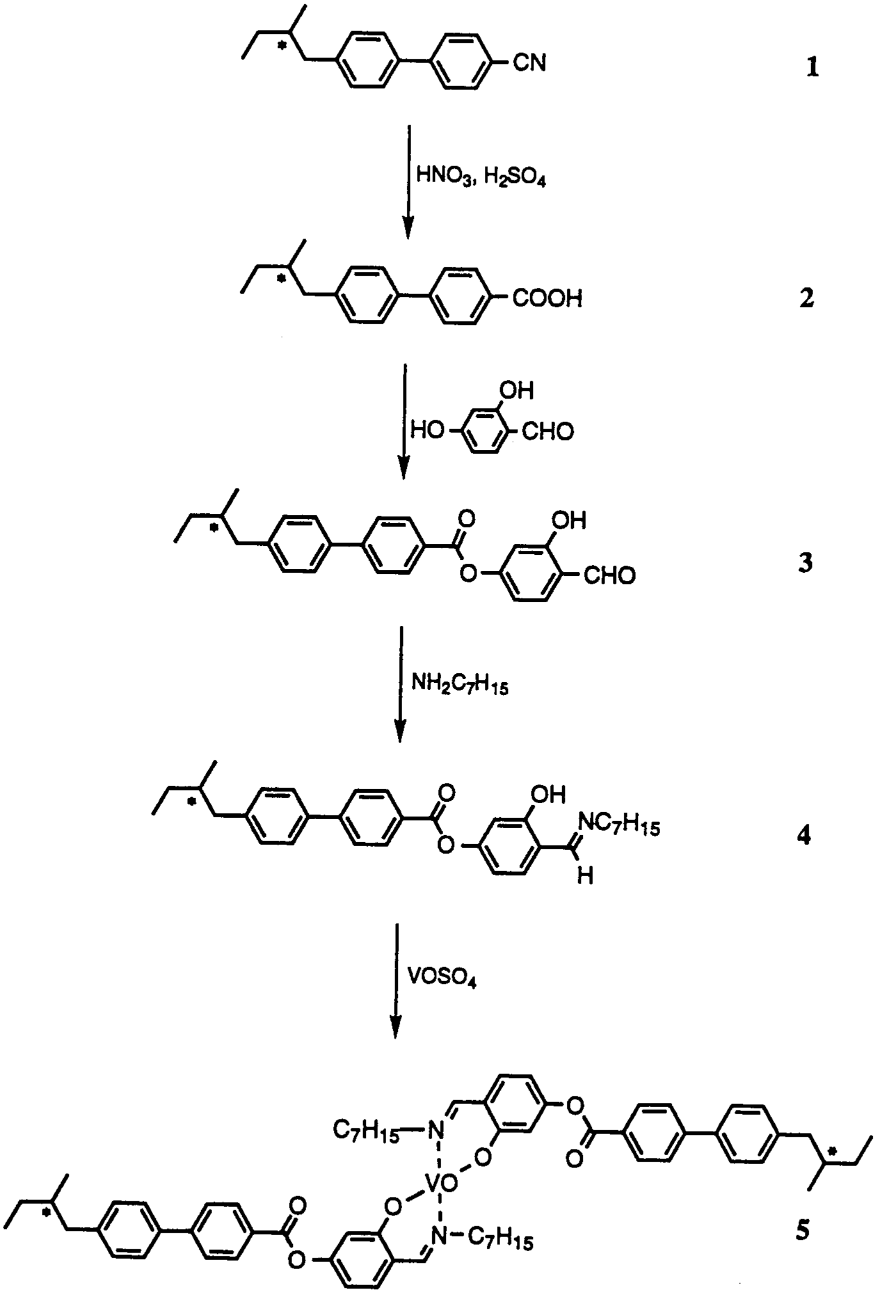

CN
1
HNO3, H2SO4
COOH
2
OH
HO
CHO
O
OH
O
CHO
3
NH2C7H15
O
OH
NC7H15
O
H
4
VOSO4
C7H15
N
O
O
O
O
VO
O
N
C7H15
O
O
5

Table 1 Absolute configuration C, optical rotations $[\alpha]_D$, molar optical rotations $^M[\alpha]_D$, mesomorphism and helix directions (for mesogens) of all the chiral compounds.

Compound No.	C^a	$[\alpha]_D{}^b$	$^M[\alpha]_D{}^c$	Mesomorphism	Helix direction^d
2	S	+8.2	+93.4	N*	RH
3	S	+7.4	+148.6	none	none
4	S	+6.5	+289.8	(S_C*),N*,BPII	RH
5	S	+2.9	+737.5	N*	RH

a = configuration of the chiral centres.
b = (10^{-1} deg cm^2 g^{-1})
c = (10^{-1} deg cm^{-1} dm^3 mol^{-1})
d RH = right-handed.
N* = chiral nematic, S_C* = chiral smectic C, BPII = bule phase of type II

The preliminary powder x-ray diffraction result revealed that the complex might be in the point group P_1, as a result of the chiral moiety of the molecule. Full results of the x-ray investigation will be discussed in a separate report.

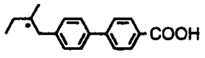
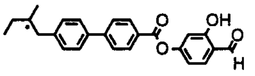
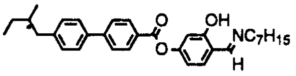
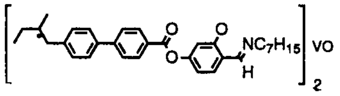
Mesomorphic properties

Mesomorphic properties of all the compounds are reported in Table 2. The acid **2** has been reported to exhibit a chiral nematic phase in the temperature range 224-247 °C, while the cyanobiphenyl parent compound is liquid at room temperature [11-12].

The compound containing substitutent 2,4-dihydroxybenzaldehyde, 3, is surprisingly nonmesogenic. This may be due to the bulky rigid core but short flexible side chain, which, as a result, is unable to stabilise a mesophases. On the other hand, the imine 4, exhibits a series of chiral mesophases. This observation stresses the significance of the flexible side chain to the mesomorphic properties.

The oxovanadium(IV) complex, 5, disappointingly shows only a high temperature chiral nematic phase. This observation may be explained by the huge proportion of the complex molecules. As the molecule is quite large, MW = 1034, most of the inter- and intramoleular interactions combine or cancel each other and only major interactions survive, so that only primary transitions can be observed.

Table 2 Mesomorphic properties of all the compounds above room temperature. Enthalpy changes, ΔH/kJ mol^{-1}, are shown below the corresponding transition temperatures.

2		K 221 N* 246.8 Iso 49.8 6.7
3		mp = 128 °C
4		K 95 (S$_C$* 52.2) N* 154.0 BPII 154.4 Isc 29.0 unobserv. 0.5 0.05
5		K 172 N* 263.9 Iso 29.0 2.0

K = crystal phase, N* = chiral nematic phase, Iso = isotropic phase, S$_C$* = chiral smectic C phase, BPII = blue phase II, and mp = melting point

Magnetic properties

The oxovanadium(IV) complex, 5, showed paramagnetic properties, with an effective paramagnetic moment of 1.74 μB due to the unpaired electron of the VO^{2+}ion. A typical value of the effective paramagnetic moment at 20°C of an oxovanadium(IV) complex is in the range 1.7-1.9 μB. [10].

Temperature-dependent molar magnetic moments at high temperature are shown in Figure 1. Discontinuities of molar magnetic moments can be observed around the transition temperatures. When the complex was heated for the first time, the value gradually decreased to around 170°C where the value jumped down 0.7 unit. When the temperature almost reached the clearing point, above 250°C, the value became stable. Shortly after the complex was fully isotropic, above 265°C, the value started to increase and became steady in the cooling process, with a higher value than that of the heating. The discontinuity at 170°C corresponds to the melting temperature at 172° C where the complex melts from crystal to chiral nematic phase. This shows a certain degree of magnetic-enhanced molecular alignment.

Moreover, when the complex was heated above isotropic temperature, the molar magnetic moment rapidly increased which is an indication of molecular alignment in the applied magenetic field. The difference in molar magnetic moments on heating and cooling indicates the difference in molecular alignment of the complex. The higher value on cooling indicates the parallel orientation of the complex molecules along the applied magnetic field, or may be partly due to ferromagnetic orientation.

When the sample was continuously heated for the second time, no step-change in molar magnetic moment was observed. However, only a small change of the value between the second heating and first cooling steps was observed. An explanation could be that the complex molecules were aligned as a result of the applied field from the first heating step, thus there was no drastic change in molecular orientation, as at the molar magnetic moment.

When the sample was cooled down for the second time, the magnetic field helped align the molecules.. The higher molar magnetic moment of the second cooling compared with the first cooling revealed the higher ferromagnetic alignment after the second cooling step.

This observation raises the possibility of molecular alignment in an applied magnetic field, which may lead to various applications, *i.e.*, perfectly-aligned liquid crystal displays, molecular wire, superconductor fabrication, catalyst manufacturing, etc.. Further study should concentrate on mesomorphic alignment using an applied magnetic field, both ferromagnetic and antiferromagnetic, also a combination of electric and magnetic fields of a polar and paramagnetic compound.

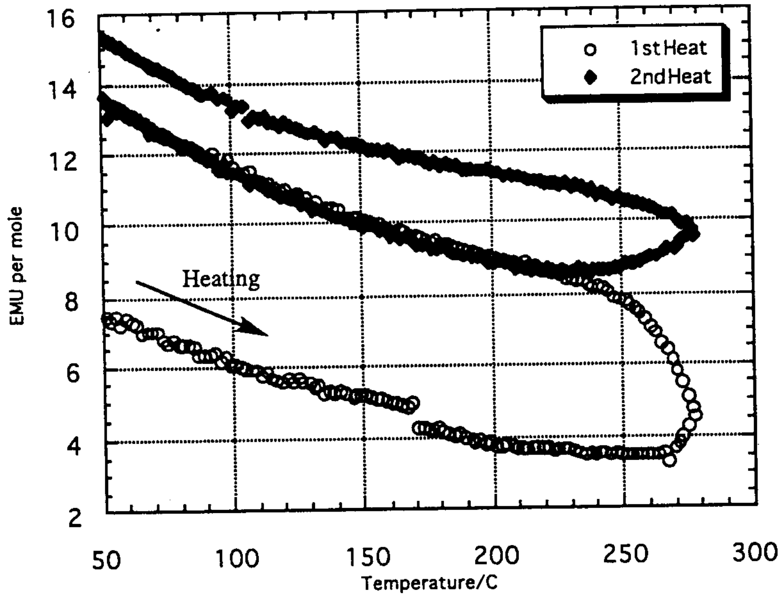


Figure 1 Temperature dependent molar magnetic moment of compound 5.

Experimental

The structure of all intermediates and final products were elucidated by a variety of analytical techniques. ^{1}H-NMR spectra were recorded on a JEOL JNM-GX 270 FT NMR spectrometer, infrared spectra were recorded on a Perkin-Elmer 783 IR spectrometer as either KBr disks or liquid films and mass spectra were recorded on a Finnigan Mat 1020 Automate GC/MS spectrometer. Satisfactory analyses were achieved in all instances. Elemental analyses were performed on a Carlo-Erba 1106 CHN analyser and Perkin-Elmer 2400 Series CHN analyser using cyclohexanone-2,4-dinitrophenylhydrazone as the reference standard.

Effective paramagnetic moments were recorded at 20°C on a Johnson Matthey Susceptibility Balance using mercury(II) cobalt(II) thiocyanate [$HgCo(NCS)_4$] as the reference standard [$\chi_g(20°C) = 20.64 \times 10^{-8}$ m^3 kg^{-1}] and the values were corrected for the diamagnetic contributions of the ligands. Temperature dependent magnetic moments were recorded on Quantum Design MPMS system 5. Optical rotation of all compounds were measured in chloroformic solution at ambient temperature and the $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

The mesomorphic phase sequence of each compound was determined by thermal optical microscopy using an Olympus BH-2 polarising microscope equipped with a Mettler FP52 hotstage and FP5 temperature controller. Optical results were confirmed by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7-PC equipped with an intracooler. Samples were encapsulated in standard aluminium pans and the mesophase ranges scanned at rates of 10°C min^{-1}. The accuracy of data derived from the DSC experiments was confirmed by measuring the enthalph of fusion and melting temperature of pure indium metal. The enthalpy of 29.8 J g^{-1} and melting temperature of 156.7°C compared well with the literature values of 28.5 j g^{-1} and 156.6°C, respectively.

(S)-(+)-4-[4'-(2-Methylbutyl)phenyl]benzoic acid (2)

S)-(+)-4-[4'-(2-Methylbutyl) cyanobiphenyl (25.0 g, 0.10 mol) was stirred and heated under reflux with concentrated sulfuric acid (40 cm^3), concentrated nitric acid (5 cm^3), water (40 cm^3) and glacial acetic acid (400 cm^3) (8 h) and stirred overnight at room temperature. The mixture was then stirred and heated under reflux (4 h). The hot clear solution was poured into ice-water mixture (1000 cm^3) with vigorous stirring. The white precipitate so formed was allowed to reach room temperature (2 h) before being filtered off and recrystallised from methanol.

Yield = 24.9 g (92 %).
Mesomorphism (°C); K 221 N* 246.8 Iso.
δ_H (270 MHz, $CDCl_3$, Me_4Si):0.90 (3H, d, *J* 7.0, -$CHCH_3$), 0.95 (3H, t, *J* 7.0, -CH_2CH_3), 1.25 (2H, m, CH_3CH_2-), 1.65 (1H, m, -CH_2CH-), 2.40 (1H, ABX, *J* 13.5 (gem), 8.1 (anti)), 2.65 (1H, ABX, *J* 13.5 (gem), 5.9 (syn)), 7.25 (2H, AA'BB', -C_6H_4-), 7.70 (4H, AA'BB', -C_6H_4- C_6H_4-), 8.05 (2H, AA'BB', -C_6H_4-), 12.80 (1H, s, -COOH). ν_{max} (KBr)/cm^{-1}:3000-2800 (CH str.), 2550 (broad, -OH), 1675 (broad, C=O str.). m/z:268 [M^+], 211 (100%), 165, 152, 57. $[\alpha]_D$+8.2(27°C, *c* 0.02354 in $CHCl_3$).

(S)-(+)-2-Hydroxy-4-[4"-(2-methylbutyl)-4'-biphenylcarboxyloxy]benzaldhyde (3)

A mixture of compound 2 (2.7 g, 10 mmol), 2,4-dihydroxybenzaldehyde (1.6 g, 11 mmol), N,N-dicyclohexylcarbodiimide (DCC) (4.5 g, 22 mmol) and 4-pyrrollidinopyridine (4-PPY) (0.3 g, 2 mmol) in dichloromethane (50 cm^3) was stirred at room temperature (24 h). The ester was purified by column chromatography (silicagel, 40-60 μm, dichloromethane) and after evaporation isolated as a pale yellow solid.

Yield = 2.3 g (59 %); m.p. 128°C.
δ_H (270 MHz, $CDCl_3$, Me_4Si):0.88 (3H, d, *J* 7.0, -$CHCH_3$), 0.93 (3H, t, *J* 7.0, -CH_2CH_3), 1.10-1.50 (2H, m, CH_3CH_2-), 1.68 (1H, m, -CH_2CH-), 2.42 (1H, ABX, *J* 13.5 (gem), 8.1 (anti)), 2.69 (1H, ABX, *J* 13.5 (gem), 5.9 (syn)), 6.93 (2H, m, aromatic 5-H and aromatic 3-H), 7.20-7.80 (7H, AA'BB', - C_6H_4- C_6H_4- and aromatic 6-H), 8.23 (2H, AA'BB', - C_6H_4-), 9.85 (1H, s, ArC*H*O). 11.30 (1H, s, ArO*H*). ν_{max} (KBr)/cm^{-1}:3000-2750 (CH str.), 1740 (ester, C=O str.), 1670 (aldehyde, C=O str.), 1145 (ester, C-O str.). m/z:388 [M^+], 359, 331, 251 (100%), 165. $[\alpha]_D$+7.4 (27°C, *c* 0.01932 in $CHCl_3$).

(S)-(+)-N-*n*-Heptyl(2-hydroxy-4-[4"-(2-methylbutyl)-4'-biphenylcarboxyloxy]-phenyl)methanimine (4)

Compound 3 (2.0 g, 5 mmol) was dissolved in ethanol (60 cm^3) and heptylamine (0.6 g, 5 mmol) was added dropwise followed by 4 drops of glacial acetic acid and a small quantity of molecular sieves (4 Å). The molecular sieves were filtered off after 5 hours stirring and the solution heated under reflux. Half the solvent was removed *in vacuo* and the remaining solution stored at -20°C for three days. The resulting pale yellow plates were filtered off and washed with ethanol.

Yield = 2.1 g (87 %).
Mesomorphism (°C); K 9.5(S_C* 52.2) N* 154.0 BPII 154.4 Iso.
δ_H (270 MHz, $CDCl_3$, Me_4Si):0.85-0.97 (9H, m, $-CH_3$, $-CH_3$ and $-CH_3$), 1.12-1.52 (12H, m,-$(CH_2)_5$- and $-CH_3CH_2CH-$), 1.68 (1H, m, $-CH_2CH-$), 2.43 (1H, ABX, *J* 13.5 (gem), 8.1 (anti)), 2.69 (1H, ABX, *J* 13.5 (gem), 5.9 (syn)), 3.59 (2H, t, *J* 7.0,$=NCH_2-$), 6.75 (1H, q, *J* 8.9, 3.2, aromatic 5-H), 6.85 (1H, d, *J* 3.2, aromatic 3-H), 7.27 (3H, AA'BB', $-C_6H_4-$ and aromatic 6-H), 7.57 (2H, AA'BB' $-C_6H_4-$), 7.72 (2H, AA'BB' $-C_6H_4-$), 8.23 (2H, AA'BB', $-C_6H_4-$), 8.23 (1H, s, $-CH=N-$), 14.10 (1H, s, ArO*H*). ν_{max} (KBr)/cm^{-1}:3000-2800 (CH str.), 1630 (C=O str.), 1730 (imine, C=N), 1145 (C-O str). m/z:485 [M^+], 442, 251(100%), 194, 166. Elemental analysis, found (cal.) %C 79.40 (79.14), %H 8.01 (8.09), %N 3.03 (2.88). $[\alpha]_D$+6.5(25°C, *c* 0.01088 in $CHCl_3$).

(2S)-(+)-Bis[N-*n*-heptyl(2-hydroxy-4-[4"-(2-methylbutyl)-4'-biphenylcarboxyloxy]phenyl)methaniminato]oxovanadium(IV) (5)

Ligand (4) (1.0 g, 2 mmol) was dissolved in ethanol (75 cm^3) and the mixture heated to reflux. A solution of vanadyl sulfate pentahydrate (0.5 g, 2 mmol) in water (10 cm^3) was added to the clear yellow solution and continuousl stirred, without further heating. An aqueous solution of anhydrous sodium acetate (0.35 g, 4 mmol) in water (10 cm^3) was slowly added to the yellow-green solution and the mixture was heated under reflux (10 min.). The dark brown-green precipitate was filtered off and washed with water and then ethanol. The product was purified by recrystallisation from hot acetone.

Yield = 0.5 g (48 %); μ_{eff}(20°C)/μ_B = 1.74.
Mesomorphism (°C); K 178 N* 263.9 Iso.
ν_{max} (KBr)/cm^{-1}:3000-2800 (CH str.), 1730 (C=O str.), 1615 (imine, C=N), 1150 (ester, C-O), 980 (V=O str.) Elemental analysis, found (cal.): %C74.16 (74.18), %H 7.50 (7.39), %N 2.92 (2.70). $[\alpha]_D$+2.9 (24°C, *c* 0.00407 in $CHCl_3$).

Acknowledgement

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