JOURNAL OF Materials CHEMISTRY

Metallomesogens: synthesis and properties

Emerson Meyer, César Zucco and Hugo Gallardo*

Department of Chemistry, Universidade Federal de Santa Catarina, Cep 8800.040–900 Florianópolis, SC Brazil

The synthesis, characterization and mesogenic behaviour of the copper(II) and oxovanadium(IV) complexes derived from phenyltetrazole and benzothiazole and their corresponding ligands are reported. The ligands did not exhibit mesomorphism, whereas the complexes form monotropic smectic A and smectic C mesophases. The mesophases were identified according to their textures by optical microscopy.

Introduction

Liquid crystals have been known for more than 100 years, but the number of structural types and classes of chemical compounds capable of exhibiting mesomorphic properties has increased significantly only during the last 15–20 years, for example, metal-containing liquid crystals, which are termed 'metallomesogens', that combine the variety and range of metal-based coordination chemistry with the extraordinary physical characteristics of liquid crystals.[1,2]

Coordination compounds, usually complexes of mesogenic ligands, salts of organic acids, and certain organometallic and organoelement compounds with representative metals of s-, p-, d- and even f-block elements, have been made, and fall into two broad classes: the calamitic, where the metal atoms are bound to long thin ligands, giving complexes which are long, thin, and rod-like, and the discotic, where the metal is generally coordinated in the center of a flat disc-like organic ligand system. The ligands play a key role in determining the mesomorphic behavior, since they usually compose the periphery of the molecule, and hence play a role in controlling the shape.

Schiff bases derived from substituted salicyladehyde (**I**) are very versatile ligands which form (N–O) chelates with many metals.[3] Due to the diversity of substituents that can be introduced, a great variety of these mesogenic complexes has been reported.[4,5]

In this work we study the potentiality of tetrazole (**II**) and benzothiazole (**III**) derivatives in the generation of mesomorphic behavior. The design of these materials is based on the similarity of these ligands with Schiff's base imines derived from salicylaldehyde (Fig. 1).

In order to verify whether the structural correlation approach is suitable in the case of the heterocyclic ligands tetrazole and benzothiazole, we have studied their complexation behaviour and investigated the thermal behaviour of both ligands and complexes, with the general structure shown in Fig. 2.

Synthesis

The synthetic route used to prepare the tetrazole ligands and the copper(II) complexes is shown in Scheme 1. The heterocyclic ring was synthesized in several steps, starting from commercial 2,4-dihydroxybenzaldehyde **1**, aldoxime formation **2** and dehydration with acetic anhydride forming the 2,4-diacetoxybenzaldehyde **3**. The 2,4-dihydroxyphenyltetrazole **4** was obtained by treating **3** with sodium azide. Alkylation reaction with the appropriate alkyl halide furnished the 5-(2-hydroxy-4-alkoxyphenyl)-2-alkyltetrazoles **5**. Treatment of **5** with copper(II) acetate in ethanol gives the corresponding copper complexes.

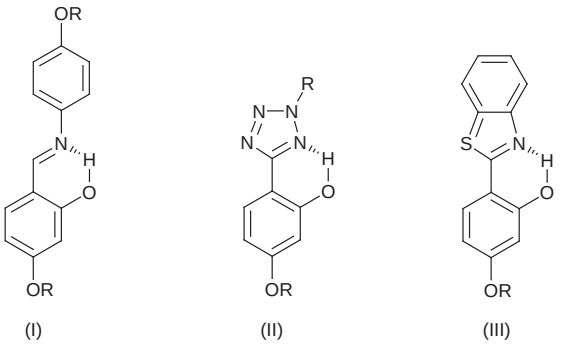
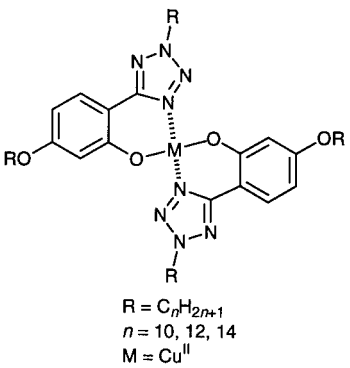


Fig. 1 Schematic of the similarity between the coordination sites of salicylaldehydes and five-membered heterocyclic rings containing nitrogen



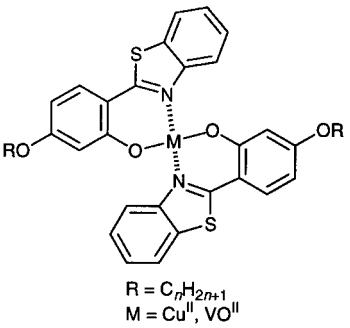
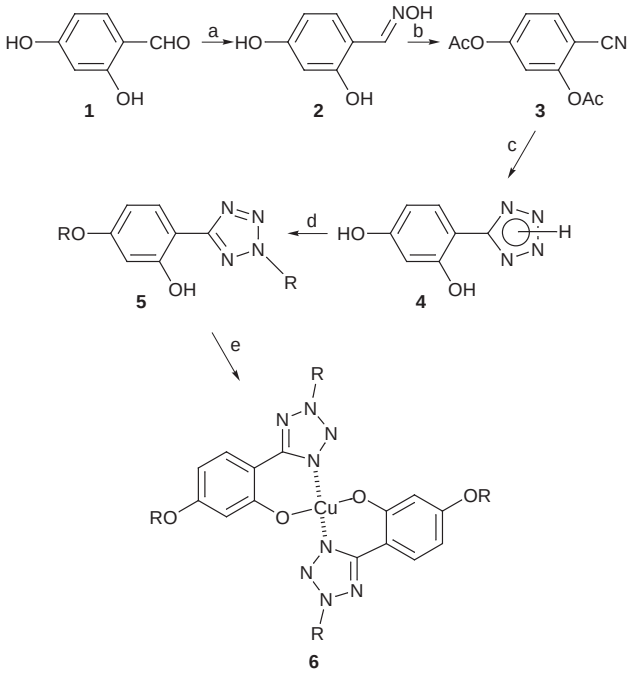
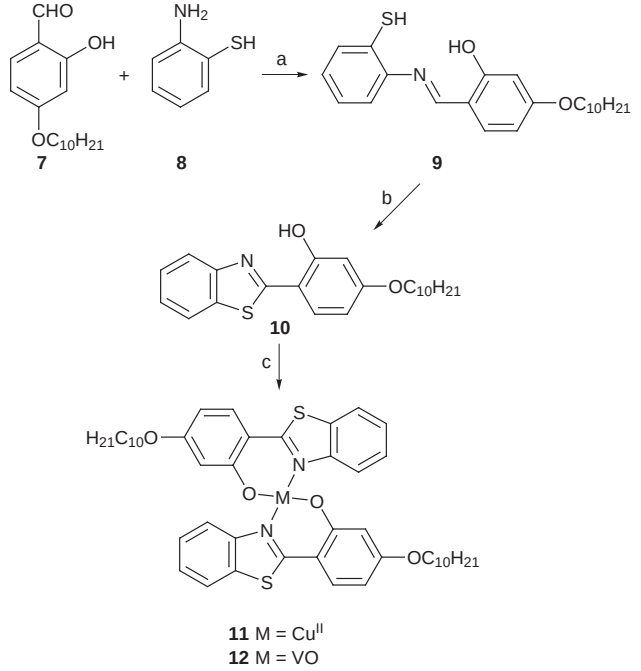


Fig. 2 Representation of the metal complexes of tetrazole and benzothioazole derivatives

The 5-(2-hydroxy-4-alkoxyphenyl)-2-alkyltetrazole **5** was prepared by O-alkylation and N-alkylations in one-pot synthesis from 5-(2,4-dihydroxyphenyl)tetrazole **4**. The tetrazolate anion is an ambidentate system in which alkylation reactions can occur at the N-1 or N-2 positions, the relative proportions



Scheme 1 a, $NH_2OH \cdot HCl$, H_2O; b, Ac_2O; c, NaN_3, NH_4Cl, DMF; d, RBr, K_2CO_3, cyclohexanone; e, $Cu(OAc)_2$, EtOH



Scheme 2 a, Pyridine; b, $FeCl_3 \cdot 6H_2O$, ethanol; c, $Cu(OAc)_2 \cdot H_2O$ or $VOSO_4 \cdot 5H_2O$, ethanol

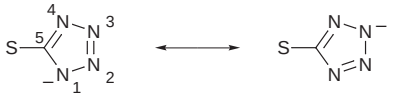


Fig. 3 Schematic diagram of canonical tetrazolate anions

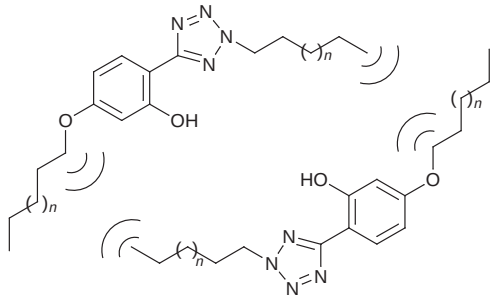


Fig. 4 Schematic diagram of the steric hindrance between rotamers of the tetrazole ligands ($n = 0,1,2,3\ldots$)

of which depend upon the conditions of the alkylation and the influence of the 5-substituent (Fig. 3).

However, in our case, spectroscopic evidence suggests that the N-2 anion in the tetrazole ring is the nucleophile in the alkylation step. The alkyl substituents at the 1- and 2-positions can be readily distinguished by the ^1H and ^{13}C chemical shifts of the the N-alkyl group. Alkyl groups bonded to N-1 are more shielded by *ca.* 0.15–0.35 ppm in the ^1H spectra and by *ca.* 2–6 ppm in the ^{13}C spectra to their corresponding N-2 isomers.[6] The regioselectivity in the alkylation was corroborated by the analysis of the ^{13}C NMR chemical shifts of the carbon atom C5, 164.8 ppm, in accordance with Butler and Garvin,[7] that in similar systems there is a perfect distinction between the isomeric forms N-1 and N-2, in view of the sensitive difference in the position of such peaks in the spectrum. This regioselectivity is due to the large steric hindrance at the N-1 position considering the bulky and large alkylating agents used.

The O-alkylation is also regioselective at the 4-hydroxyl group, because of the existence of strong intramolecular hydrogen bonding between the 2-hydroxyl group and the N-4 position of the tetrazole ring. This hydrogen bond was clearly observed both in the solid state by an X-ray crystallographic study of 5-(2,4-dihydroxyphenyl)tetrazole[8,9] **4** and in solution by ^1H and IR spectroscopy of **4** and its alkylated products **5**.

Complexation was carried out with copper(II) diacetate yielding the mesogenic structures **6**.

Rotamer complexes are considered forbidden, *a priori*, because of steric hindrance of the aliphatic groups which would impede the ligand bonding (Fig. 4).

The tetrazole ligands and the intermediate compounds were investigated by a variety of techniques, including IR, ^1H NMR, ^{13}C NMR, X-ray crystallography and elemental analyses. The analyses showed that the structures of all of the materials were consistent with those expected.

The general reaction pathway used to the target ligand 2-(4-decyloxy-2-hydroxyphenyl)benzothiazole and its complexes is shown in Scheme 2.

The ligand was synthesized using well known literature methods in two steps: first, reaction of 2-hydroxy-4-decyloxybenzaldehyde **7** with 2-aminothiophenol **8**: secondly, cyclization of the obtained Schiff base **9** with $FeCl_3 \cdot 6H_2O$. The chelates **11** were prepared by treatment of 2-(4-decyloxy-2-hydroxyphenyl)benzothiazole **10** with Cu^{II} and VO^{II} salts. The elemental and spectral analyses of the complexes and the intermediates were consistent with their proposed structures.

Results and Discussion

Tetrazole system

The optical and thermal data of the ligands and complexes are gathered in Table 1.

Ligands. All the free ligands synthesized were not mesomorphic. This fact is due in part to a loss of linearity in the molecule due to the presence of the tetrazole ring, which is unable to make co-linear disubstitution bondings. Another contribution to the loss of liquid crystallinity is the strong intermolecular dipolar repulsions brought about by the presence of the lateral hydroxide groups.

Table 1 Optical and thermal data (in °C) of the tetrazolic ligands and complexes of Cu^{II}

ligand	mp	complex	Cryst		SmA		SmC		Iso
$n=10$	40–42	$n=10$	·	117.0	·	(106.7)	·	(67.4)	·
$n=12$	50–52	$n=12$		110.0	·	(103.4)	—	—	·
$n=14$	60–62	$n=14$	·	116.0	·	(92.7)	—	—	·

Complexes. The C=N stretching vibration of the ligands is located in the 1630–1634 cm^{-1} region and is shifted to lower wavenumbers (aproximately 20 cm^{-1}) upon chelation, indicating that the tetrazolic N atom is involved in metal–nitrogen bond formation.

As can be observed, all the complexes exhibit mesogenic behavior. The mesophases were identified according to their textures which were observed by optical microscopy.[10–12]

All the complexes $n=10$–14 show monotropic SmA mesophases. Complex $n=10$, in addition, gives a monotropic SmC phase. On cooling the isotropic liquid, the SmA phase appears, *via batônnets*, forming a focal-conic textures.

The different mesomorphic behaviour when compared to the Schiff bases complexes is unsurprising, given that one would expect them to be not effectively isostructural, but in the coordination geometry only small differences in metal–ligand bond lengths and angles can be expected.

The difference in mesomorphic behavior compared to the Schiff bases is not surprising considering the very different electronic and steric character of the tetrazole heteroaromatic system.

The low thermal stability of the mesophases can be interpreted as being due to the reduced anisotropy of the complexes because of the deviation from linearity of the aliphatic chains caused by the heterocyclic ring (Fig. 5).

Benzothiazole system

The thermal data of the ligand and complexes are gathered in Table 2.

The IR spectra show a shift of the ligand C=N stretching band (1632 cm^{-1}) to lower wavenumbers (1608 cm^{-1}, copper(II) complex; 1605 cm^{-1}, oxovanadium(IV) complex), which indicates that the N atom of benzothiazole participates in the formation of the complex. For the oxovanadium(IV) complex the stretching band characteristic of the V=O group was observed at 976 cm^{-1}.

While in classic organic structures, the basic question is, frequently, to increase intermolecular contact to induce mesomorphism, in coordination compounds the problem is to avoid intermolecular contacts (whenever a coordination site is accessible), and strong dipolar interactions (associated with the high polarizability of transition metals), sufficiently strong to cause three dimensional order and consequently the absence of a mesophase.

The addition of a long aliphatic chain to the rigid nucleus furnishes both the anisotropy and irregular packing needed to promote mesomorphism.

Based on these considerations the absence of mesomorphic behavior in the free ligand **10** and the complexes **11** and **12** can be attributed to the small number of aliphatic substituents permitting interactions that favor only three dimensional order.

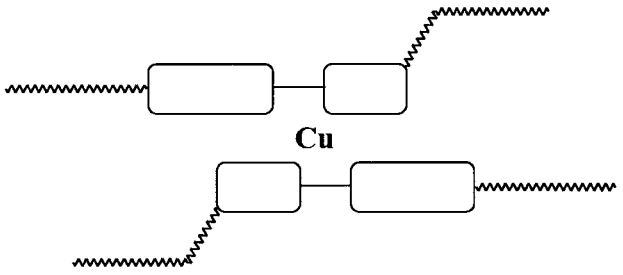


Fig. 5 Sketch of geometry of copper complexes

Table 2 Transition temperatures (°C)

structure	C		I
ligand	·	97	·
copper complex	·	216	·
oxovanadium complex	·	194	·

Experimental

The transition temperatures for all compounds were determined by optical microscopy using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP-52 heating stage. The purity of the compounds was evaluated by thin layer chromatography and elemental analysis. The IR spectra were recorded using the KBr disc method with a Perkin-Elmer model 283 spectrometer, and the ^{1}H NMR and ^{13}C NMR spectra were recorded at 80 MHz (Bruker WP-80) or 270 MHz (Bruker HX-270).

Materials

2,4-Dihydroxybenzaldehyde (Aldrich), 2-hydroxybenzaldehyde (Merck), hydroxylamine hydrochloride (Aldrich), sodium azide (Aldrich), 1-bromodecane (Aldrich), 1-bromododecane (Aldrich), 1-bromotetradecane (Aldrich), 2-aminothiophenol (Aldrich) and resorcinol (Aldrich) were used as received. Anhydrous sodium sulfate (Aldrich), potassium carbonate (Merck), copper acetate (Aldrich), iron(III) chloride hexahydrate (Merck) and vanadyl sulfate pentahydrate (Fluka) were used without purification. Acetic anhydride (Merck), *N*,*N*-dimethylformamide (Merck), ethanol (Merck), methanol (Merck), acetic acid (Merck), acetone (Aldrich), cyclohexanone (Carlo Erba) and pyridine (Merck) were purified by distillation prior to use.

2,4-Dihydroxybenzaldoxime 2. To a solution of hydroxylamine hydrochloride (0.05 mol) and sodium acetate (0.05 mol) in water (30 ml), at 40 °C, 2,4-dihydroxybenzaldehyde (0.05 mol) was added and the mixture was stirred for 10 min. The mixture was cooled and filtered. The solid was collected and recrystallized from water (92% yield). Mp 194–196 °C; IR (KBr): 3359, 1624, 1525 cm^{-1}.

2,4-Diacetoxybenzonitrile 3. 2,4-Dihydroxybenzaldoxime (0.05 mol) was added slowly to acetic anhydride (30 ml) at room temperature. After an additional 30 min at room temperature (rt) the reaction mixture was warmed slowly to 100 °C over a 2 h period. Removal of the solvent gave a solid which was recrystallized from methanol–water (3:1) (75% yield). Mp 72–73 °C; IR (KBr): 2229, 1780, 1186 cm^{-1}.

5-(2,4-Dihydroxyphenyl)tetrazole 4. A suspension of 2,4-diacetoxybenzonitrile (0.05 mol), sodium azide (0.15 mol) and ammonium chloride (0.15 mol) in dimethylformamide (50 ml) was heated to 150 °C over a 6 h period. The reaction mixture was allowed to come to rt with stirring over 1 h. The reaction mixture was poured into ice cold water (100 ml), and the resulting material was filtered and washed with cold water.

The crude product was recrystallized from ethanol–water (3:1) to give 5-(2,4-dihydroxyphenyl)tetrazole as colorless crystals (85% yield). Mp 304 °C; IR (KBr): 3348, 1612, 1490 cm^{-1}; Anal. Calc. for $C_7H_6N_4O_2$: C, 47.19; H, 3.37; N, 31.46. Found: C, 47.20; H, 3.20; N, 31.92.

General procedure for preparation of 5-(2-hydroxy-4-alkoxyphenyl)-2-alkyltetrazoles 5. To a suspension of 5-(2,4-dihydroxyphenyl)tetrazole (0.03 mol) and anhydrous potassium carbonate (0.06 mol), in cyclohexanone (50 ml), was added the appropriate alkyl halide (0.065 mol). The reaction mixture was stirred for 72 h at 150 °C. The mixture was then allowed to cool and filtered. The filtrate was poured into ice cold water (100 ml) and the residue formed was recrystallized from ethanol.

homologue	melting point/°C	yield (%)
$C_{10}H_{21}$	40–42	66
$C_{12}H_{25}$	50–52	70
$C_{14}H_{29}$	60–62	70

For the homologue $C_{14}H_{29}$: IR (KBr): 3314, 2954, 1634, 1472 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 9.81 (s, 1H), 7.90–6.57 (m, 3H), 4.64 (t, $J=7.1$ Hz, 2H), 3.98 (t, $J=6.5$ Hz, 2H), 2.05 (q, 2H), 1.79 (q, 2H), 1.44–1.19 (m, 44H), 0.87 (t, 6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 164.18, 162.50, 158.01, 128.31, 108.16, 104.18, 102.11, 68.21, 58.30, 31.95–14.15 ppm. Anal. Calc. for $C_{35}H_{62}N_4O_2$: C, 73.56; H, 10.86; N, 9.80. Found: C, 73.58; H, 11.05; N, 9.52.

General procedure for preparation of bis[5-(2-hydroxy-4-alkoxyphenyl)-2-alkyltetrazole]copper(II) 6. An ethanolic solution (10 ml) of the appropriate tetrazole (2 mmol) was added to a hot ethanolic solution (10 ml) of copper(II) acetate (1 mmol). The solution was refluxed for 20 min and then cooled. The precipitate was collected by filtration and recrystallized from chloroform–ethanol (1:3). The green copper complexes were characterized by IR spectroscopy and elemental analysis. The ^1H NMR spectra of the complexes exhibit large shifts relative to the free ligands, and all signals are broadened as a result of the paramagnetic metallic ion.

homologue	yield (%)
$C_{10}H_{21}$	62
$C_{12}H_{25}$	65
$C_{14}H_{29}$	60

For the homologue $C_{14}H_{29}$: IR (KBr): 2956, 1610, 1466 cm^{-1}. Anal. Calc. for $C_{70}H_{122}N_8O_4Cu$: C, 69.80; H, 10.14; N, 9.31. Found: C, 69.66; H, 10.18; N, 9.55.

2-Hydroxy-4-decyloxybenzaldehyde 7. To a suspension of 2,4-dihydroxybenzaldehyde (0.03 mol) and anhydrous potassium carbonate (0.03 mol) in acetone (50 ml) was added 1-bromodecane (0.035 mol). The reaction mixture was refluxed for 56 h. The mixture was then allowed to cool and filtered. The solvent was removed and the residue was distilled at reduced pressure giving the product as a clear liquid (63% yield): bp 185 °C (0.5 mm); IR (thin film): 3300, 2920, 1650 cm^{-1}.

2-(2-Hydroxy-4-decyloxyphenyl)benzothiazole 10. 2-Hydroxy-4-decyloxybenzaldehyde (0.02 mol) was dissolved in 10 ml of dry pyridine containing 2-aminothiophenol (0.02 mol) under an atmosphere of nitrogen and was stirred 5 h at room temperature. The pyridine was then removed by evaporation *in vacuo*, and the resulting residue was added to a hot ethanolic solution of $FeCl_3 \cdot 6H_2O$. The mixture was then allowed to cool and filtered. The solid was collected and recrystallized from ethanol (82% yield). Mp 97 °C; IR (KBr): 3400, 2919, 1632 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 12.71 (s, 1H), 7.96–6.52 (m, 7H), 4.02 (t, $J=6.4$ Hz, 2H), 1.82 (t, $J=6.75$ Hz, 2H), 1.30 (m, 14H), 0.90 (t, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 169.28, 163.03, 159.87, 151.87, 131.87, 129.51, 126.44, 124.89, 121.58, 121.32, 110.15, 108.05, 101.77, 68.23, 31.82–14.04 ppm. Anal. Calc. for $C_{23}H_{29}NO_2S$: C, 71.96; H, 7.56; N, 3.65. Found: C, 71.66; H, 7.55; N, 4.00.

Bis[2-(2-hydroxy-4-decyloxyphenyl)benzothiazole] copper(II) 11. An ethanolic solution (10 ml) of 2-(2-hydroxy-4-decyloxyphenyl)benzothiazole (2 mmol) was added to a hot ethanolic solution (10 ml) of copper(II) acetate (1 mmol). The solution was refluxed for 20 min and then cooled. The precipitate was collected by filtration and recrystallized from cyclohexane–ethanol (1:3) (68% yield). The brown copper complex was characterized by IR spectroscopy and elemental analysis. The ^1H NMR spectrum of the complex exhibits large shifts relative to the free ligand, and all signals are broadened as a result of the paramagnetic metallic ion. Mp 216 °C; IR (KBr): 2922, 1608, 1468 cm^{-1}. Anal. Calc. for $C_{46}H_{56}N_2O_4S_2Cu$: C, 66.71; H, 6.76; N, 3.38. Found: C, 66.76; H, 6.67; N, 3.48.

Bis[2-(2-hydroxy-4-decyloxyphenyl)benzothiazole]oxovanadium(IV) 12. An ethanolic solution (10 ml) of 2-(2-hydroxy-4-decyloxyphenyl)benzothiazole (2 mmol) was added to a hot ethanolic solution (10 ml) of vanadyl sulfate pentahydrate (1 mmol). The solution was refluxed for 20 min and then cooled. The precipitate was collected by filtration and recrystallized from cyclohexane–ethanol (1:3) (65% yield). The green oxovanadium complex was characterized by IR spectroscopy and elemental analysis. The ^1H NMR spectrum of the complex exhibits large shifts relative to the free ligand, and all signals are broadened as a result of the paramagnetic metallic ion. Mp 194 °C; IR (KBr): 2920, 1605, 1469, 976 cm^{-1}. Anal. Calc. for $C_{46}H_{56}N_2O_5S_2V$: C, 66.44; H, 6.73; N, 3.37. Found: C, 66.43; H, 6.58; N, 3.44.

The authors gratefully acknowledge the financial support of CNPq, CAPES and PRONEX.

References

1 A. M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 375.
2 P. Espinet, M. A. Estruelas, L. A. Oro and J. L. Serrano, *Coord. Chem. Rev.*, 1992, **117**, 215.
3 S. A. Hudson and P. M. Maitlis, *Chem. Rev.*, 1993, **93**, 861.
4 M. J. Baena, J. Barberá, P. Espinet, A. Ezcurra, M. B. Ros and J. L. Serrano, *J. Am. Chem. Soc.*, 1994, **116**, 1899.
5 E. Campillos, M. Marcos and J. L. Serrano, *J. Mater. Chem.*, 1993, **3**, 1049.
6 R. N. Butler and V. C. Garvin, *J. Chem. Soc., Perkin Trans. 1*, 1981, 390.
7 R. N. Butler, T. M. Mcevoy, F. C. Scott and J. C. Tobin, *Can. J. Chem.*, 1977, **55**, 1564.
8 H. Gallardo, E. Meyer and I. Vencato, *Acta Crystallogr., Sect. C*, 1995, **51**, 2430.
9 H. Gallardo, I. M. Begnini and I. Vencato, *Acta Crystallogr., Sect. C*, 1997, **51**, 2430.
10 D. Demus and H. Zaschke, *Flússige Kristalle in Tabellen II*, Springer Verlag, Leipzig, 1984.
11 H. Sackmann and D. Demus, *Mol. Cryst. Liq. Cryst.*, 1966, **2**, 81.
12 G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals: Textures and Structure*, Heyden and Son Inc., 1984, pp. 47–48.

Paper 8/01159A; *Received* 9*th February*, 1998