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Synthesis and Characterization of Nickel (II) Metallomesogen for Liquid Crystal Sensing Application

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ABSTRACT

A new liquid crystalline ligand with octadecyloxy alkyl chain, and its nickel (II) complex have been synthesized. The ligand and complex are characterized by elemental analyses, Fourier transform infrared (FT-IR), 1H nuclear magnetic resonance (NMR) and ultraviolet (UV) -visible spectroscopy. The liquid crystalline properties of these compounds are investigated by polarizing optical microscopy (POM) studies. The complex shows enantiotropic phase with long temperature range and found suitable for liquid crystal sensing applications.

KEYWORDS: *Metallomesogens, liquid crystal, polarizing optical microscopy; calamitic phase, DFT*

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1. INTRODUCTION

Aroylhydrazone moiety is quiet prone towards liquid crystalline properties. Investigations on the mesomorphic properties of 4-alkoxy aroylhydrazones with ester substituted benzylidene moiety without lateral hydroxyl group [1] and with lateral hydroxyl group [2-4] and their Ni (II) and Cu (II) complexes were reported by Singh et al [5a]. On the basis of these mesomorphic investigations on aroylhydrazone based liquid crystals and few previous investigations on this topic [1--5], it is found that all these reports are based on condensation of simple alkoxy aroylhydrazides with different carbonyl compounds. No report on mesomorphic properties and structure-property relationship of long chain substituted aroylhydrazone and its metal complex are found till date. The present work briefs our results of synthesis, characterisation and mesomorphic properties of octadecyloxybenzyloxyaroylhydrazones derived from formaldehyde and their nickel (II) complex. The influence of complexation on mesomorphic properties in terms of the relationship between molecular structure and the thermal stability of the mesophases is also discussed.

2. Experimental

2.1. Materials

Ethyl 4-hydroxybenzoate, ethyl benzoate, 4-hydroxybenzoic acid, benzoic acid, 4- hydroxy benzaldehyde, formalin solution (37-41%, w/v), alkyl aldehydes, bromoalkanes, $LiAlH_4$, hydrazine monohydrate, thionyl chloride, potassium iodide, anhydrous K_2CO_3, nickel (II) acetate tetrahydrate purchased from Aldrich Chemicals, USA were used as received. All other solvents and reagents were purchased from Merck, India. The solvents used were purified and dried using the procedures described in the literature [1-5] and also briefly outlined here. Dichloromethane was first washed with 5% sodium bicarbonate solution, then with water and dried over anhydrous calcium chloride. It was fractionally distilled (b.p. 40-41^{o}C). Ethanol was refluxed over calcium oxide for ~ 6 h and was allowed to stand overnight. It was then fractionally distilled, b.p. 78-

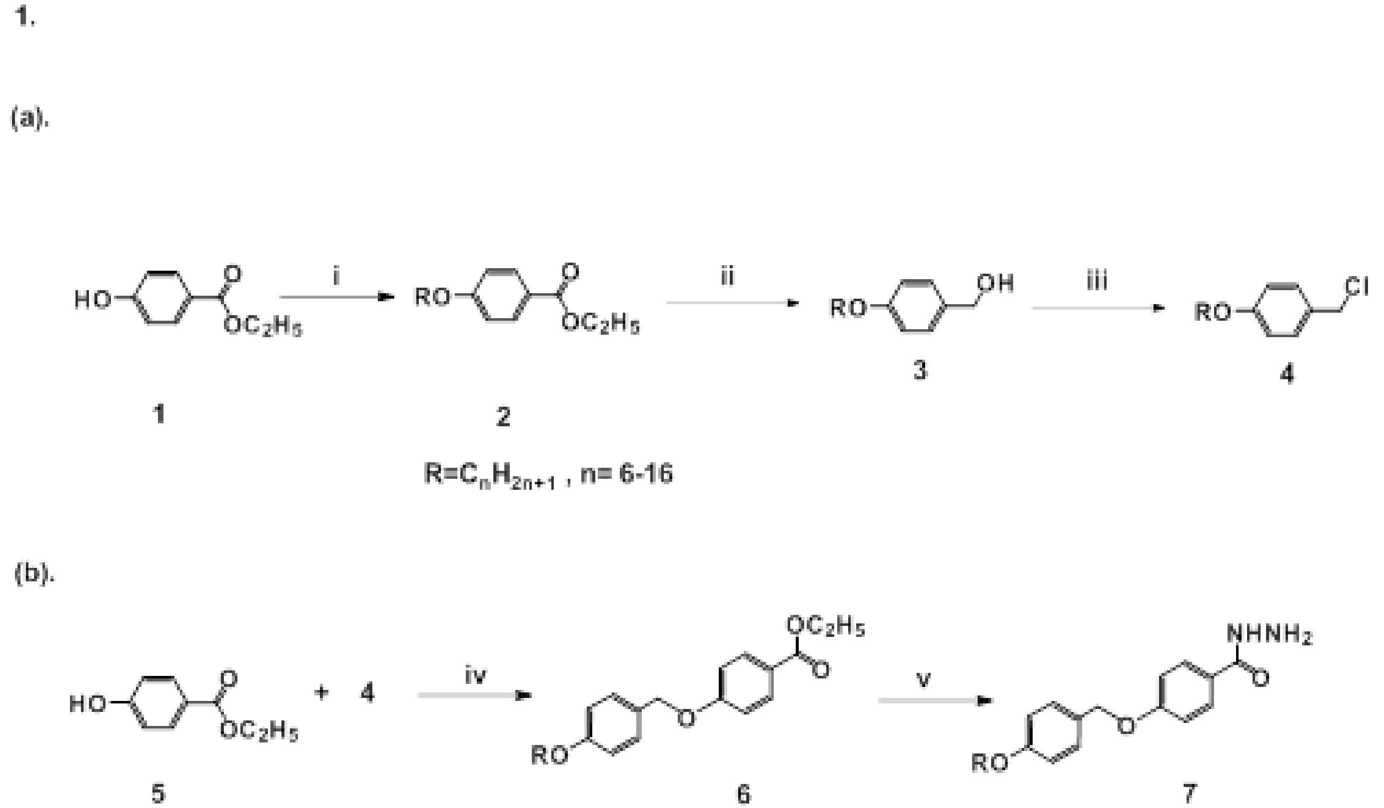
80^0C. Further it was dried on sodium wire and fractionally distilled. Methanol was purified by following the same procedure as used for ethanol. Acetone was kept on anhydrous potassium carbonate for 3 days and was fractionally distilled (b.p. 55-57°C). Chloroform was washed five to six times with about half its volume of water, then dried over calcium chloride for 24 h and distilled (b.p. 60-63°C).

2.2. Techniques

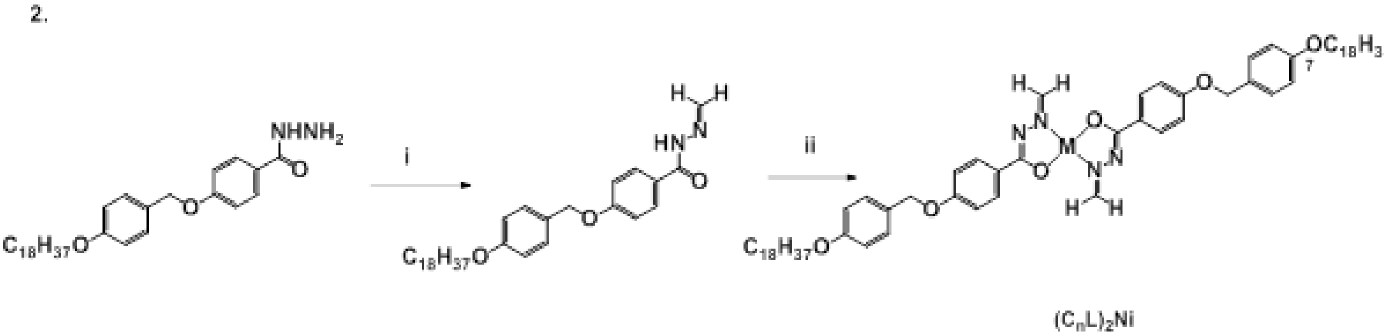
All the characterization techniques used for the samples were similar to those used in nickel (II) complex of similar metallomesogens [5]. Elemental analyses were performed on a CE-440 Exeter Analytical CHN analyser. IR spectra (4000–100 cm^{-1}) were recorded on a Varian 3100 FT-IR Excalibur series spectrophotometer. ^{1}H NMR spectra were obtained on a JEOL FT-NMR AL 300 MHz spectrometer using tetramethylsilane as the internal standard. UV-visible spectra were recorded on an (UV) -1700 Pharma Spec. Shimadzu UV–visible spectrophotometer. The mesophase type was identified by visual comparison with known phase standards using an Optica polarizing optical microscope fitted with a hot stage with temperature controlling accuracy of 0.1 K.

2.3. Synthesis

All the synthetic steps used for the work were performed based on the published reports [5,7,8]. The description of all the steps is given below for further understanding (Scheme-1 and 2)



Scheme 1 Reactions and reagents: (i) RBr (n equiv.), K_2CO_3 (4n equiv.), KI (catalyst), refluxing in 2-butanone, 24-72 h, 70-85%. (ii) LAH, stirring in dry THF at 0°C, 4 h, 88- 95% (iii) $SOCl_2$ (1.1 equiv.), refluxing in dry DCM, DMF (cat.), 20 min., 85-92% (iv) K_2CO_3 (3 equiv.), heating in DMF (1 equiv.) at 70°C, 6 h, 67-72% (v) NH_2NH_2 (1.5 equiv.), refluxing in absolute EtOH, 12 h, 85–90%.



Scheme 2 Reagents and conditions: (i) Formadehyde, acetic acid (cat.), refluxing in EtOH, 12 h, 74–87%. (ii) Ni $(OAc)_2.4H_2O$ (1.1 equiv.), refluxing in absolute C_2H_5OH, 2 h, 66–70%.

3. Results and Discussions

3.1. Synthesis and characterisation

The synthesis of the ligands was carried out by a convergent strategy outlined in Schemes 1 and 2. Starting from ethyl 4-hydroxybenzoate ester, the alkylation with appropriate alkyl bromide in the presence of mild base in 2-butanone allowed us to obtain a reasonable yield of ethyl-4-alkoxybenzoate esters. Reduction of ethyl-4-alkoxybenzoate esters by stirring in LAH at ice temperature leads to formation of 4-alkoxybenzylalchohol. 4-alkoxybenzylalchohols, on further treatment with thionylchloride in dry DCM at ice temperature leads to formation of 4-alkoxybenzylchlorides. Ethyl 4-[4′-(alkoxy) benzyloxy) benzoates derivatives were prepared by the reactions of 4- alkoxybenzylchlorides with key compound ethyl-4-hydroxybenzoate esters in the presence of pyridine in dry THF. Reactions of 4-alkoxybenzyloxy esters derivatives with hydrazine hydrate in refluxing absolute ethanol yielded 4-alkoxybenzyloxy benzoylhydrazines. The Schiff's bases were obtained by the condensation of these hydrazine derivatives with formaldehydes in refluxing ethanol. The square planar nickel (II) complex of methylidene derivatives were prepared by refluxing mixture of 4-alkoxybenzyloxy benzoylhydrazines, formaldehyde (37%, w/v solution) and metal acetates together. Square planar nickel (II) complexes were prepared by the reaction of ligands with metal acetates in refluxing ethanol. The nickel complexes were then isolated as orange crystals by recrystallisation from absolute ethanol in good yields (66%). All the intermediates and final products were thoroughly purified and fully characterized, and satisfactory analysis data were obtained.

The octadecyloxy chain length compound showed IR absorption peaks at 3280 vs (N-H), 2918, 2851 (aliphatic C-H), 1642 (amide-I, C=O), 1576 (amide-II), 1600, 1518 (Ph), 1344, 1254 (OPh) and 1032 (N-N) cm^{-1}. The nickel (II) complex of this compound, exhibited absorption bands at 2923, 2858 (aliphatic C-H), 1608, 1515 (Ph), 1367, 1255 (O-Ph), 1045 (N-N) cm^{-1}. The absence of amidic proton and shift in ν (N-N) from 1033 cm^{-1} to 1045 cm^{-1} indicate enolization of ligand resulting in bonding of oxygen and azomethine nitrogen to the metal ion. The ^{1}H NMR spectra of ligand and nickel (II) complex exhibited peaks at 9.75 (s, 1H, NH), 8.21 (s, 1H,-CH=N), 7.92- 6.87 (m,-C_6H_4), 5.02 (s, 2H, Ar-CH_2-O-Ar), 3.94 (m, 4H,-$[OCH_2]_2$), 1.94 (m,-$[OCH_2CH_2]_2$), 1.75-1.27 (m,-$[CH_2]_{14}$), 0.86 (t,-$[CH3]_2$) and 8.32-7.25 (m,-C_6H_4), 7.11 (s, 2H,-CH=N), 6.95-6.88 (m,-C_6H_4), 5.01 (s, Ar-CH_2-O-Ar), 3.96 (m,-$[OCH_2]_4$), 1.81 (m,-$[OCH_2CH_2]_4$), 1.53-1.25 (m,-$[CH_2]_{28}$), 0.84 (t,-$[CH_3]_4$) respectively.

Absence of the amidic proton of [-C (=O) NH-N=C<] moiety and shifts in the position of the –CH=N signal in the complex (7.14 ppm) as compared to ligand (8.16 ppm), suggests coordination of ligand through the azomethine nitrogen and enolisation of ligand resulting in bonding of oxygen. The absorption bands at 411, 325, 296, 275 and 233 nm and 516, 413, 345, 316 and 280 nm for Ni (II) complex, respectively indicate square planar geometry of the complexes.

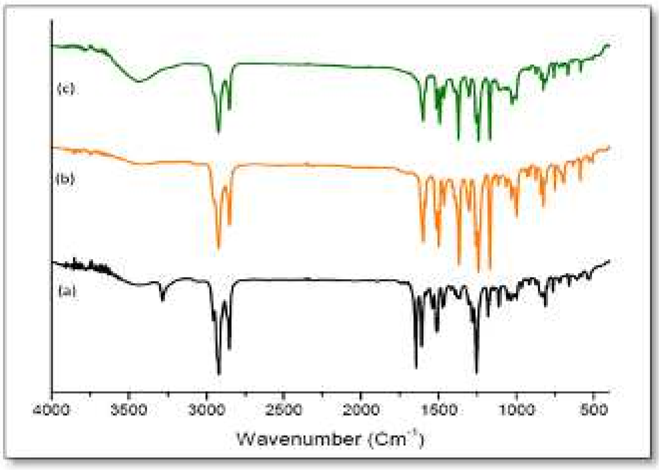


Figure 1 IR spectra of ligand and their nickel (II) and copper (II) complexes

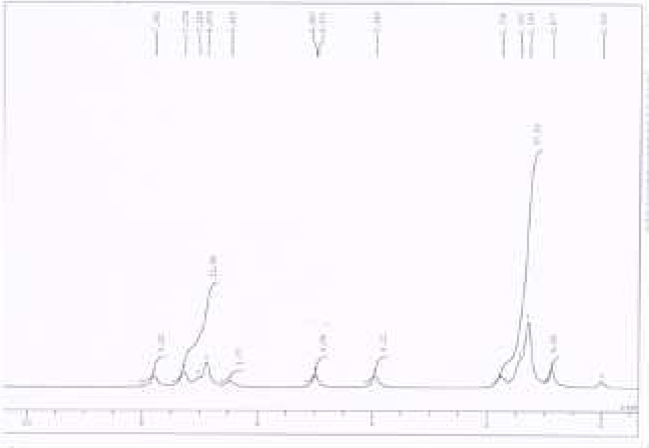


Figure 2 ^{1}H NMR of nickel (II) complex of octadecyloxy derivative

3.2. Mesomorphic behaviour of novel substituted aroylhydrazone compounds

The thermotropic behaviour of the aroylhydrazone ligands was studied by polarized optical microscopy (POM) as studied for metallomesogens [1-8].

TGA [2-5] measurement performed on nickel (II) complexes of methylidene derivatives proved their good thermal stability up to 260°C. The nickel (II) complexes of formaldehyde derivatives with octadecyloxy aliphatic chain length displayed two reversible transitions. They are close together in the first heating curve but become well separated on cooling with an important super cooling effect for the low temperature transitions. Above 143°C the compound becomes birefringent and a mesophase typical of a smectic C [6-8] phase with schlieren texture is observed (Figure 3) between cross polarizers. Above 168°C the compound appears fluid and isotropic between cross polarizers. Cooling from isotropic liquid, the compound shows similar texture to that of first heating cycle.

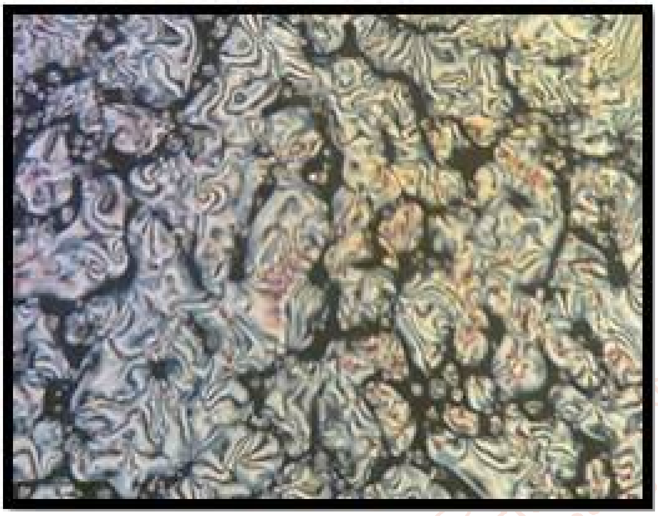


Figure 3 POM image of nickel (II) complex of octadecyloxy derivative at 143^{o}C

3.3. Conclusion

The present study describes a new family of octadecyloxy substituted liquid crystals based on aroylhydrazone core. The increased core size, as anticipated, has a very large effect on the properties of these new materials when compared with simple long-chain aroylhydrazone mesogens. In summary, the results indicated that metallomesogen, Nickel (II) complex with a methylidene substituted core display SmC phases depending on size of alkyl chain and nature of metal ions. Nickel (II) complexes show mesophase with clearing temperatures with very high stability hence must be useful for liquid crystal sensing applications.

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