Journal of Molecular Structure 1002 (2011) 135–144

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and properties of copper (II), oxovanadium (IV) and gadolinium (III) complexes derived from polar Schiff's bases

Lopamudra Chakraborty, Nirmalangshu Chakraborty, Atiqur Rahman Laskar, Manoj Kumar Paul, Nandiraju V.S. Rao *

Chemistry Department, Assam University, Silchar 788 011, Assam, India

ARTICLE INFO

Article history:
Received 1 April 2011
Received in revised form 5 July 2011
Accepted 5 July 2011
Available online 10 August 2011

Keywords:
Metallomesogens
Liquid crystals
Smectic phase
Polar compounds
Schiff's bases

ABSTRACT

The synthesis, liquid crystalline and optical properties of copper (II), oxovanadium (IV) and gadolinium (III) complexes derived from polar Schiff's bases viz., N-(4-n-hexadecyloxysalicylidene)-4′-substituted anilines with methoxy, fluoro and chloro substituents in the 4-position of N-aryl moiety are presented. All the ligands exhibited smectic A phase except methoxy homolog which exhibited nematic phase. Majority of the complexes exhibited smectic A phase with some of them exhibiting smectic E phases. The UV–Visible and photo-luminescent properties of the ligands and complexes are also discussed.

1. Introduction

Metal containing liquid crystals called as metallomesogens have received a lot of attention in the last three decades due to its importance in the basic liquid crystals research as well as its potential utility in industrial, chemical, medical, and sensor applications [1–13]. The nature of metal plays an important role to influence the mesomorphic properties of the organic ligand to which it coordinates. The importance of Schiff bases viz., N-(4-n-alkoxysalicylidene)-4′-n-alkyl(oxy)anilines lies in their rich mesomorphism at ambient temperatures and as well as their suitability for extension with many functional groups [14–16]. Extensive studies are carried out on metallomesogens of d-block elements coordinated to N-(4-n-alkoxysalicylidene)-4′-n-alkyl(oxy)anilines because of the ease of synthesis, stability of the complexes and rich variety of mesophases [10–13]. The incorporation of metal ion with unpaired electrons in these Schiff base ligands can lead to the formation of paramagnetic liquid crystalline (LC) materials. The alignment of paramagnetic LCs possessing large magnetic anisotropy can be realized by small magnetic field strengths. Hence the coordination of paramagnetic lanthanide ions with N-(4-n-alkoxysalicylidene)-4′-n-alkyl(oxy)anilines can generate low molar mass magnetic liquid crystals which possess large magnetic anisotropy. However related studies of the f-block lanthanide ion complexes are relatively limited to N-(4-n-alkoxysalicylidene)-n-alkylamines, **L1-L4** coordinated to lanthanide ions, as shown in Fig. 1 [14–17] apart from few examples of rare-earth containing metallomesogens with other ligands. The first calamitic bidentate salicylideneimine nO(OH)m_{ali}, possessing N-aliphatic moiety based lanthanide complexes was reported in 1991 [14] and a new nomenclature of lanthanidomesogens had been proposed [18–21]. However the efforts in different laboratories [17] to coordinate f-block metals with the salicylideneimine based ligands with an aryl moiety [14–17] on nitrogen atom of the central bridging imine group have been unsuccessful. The difference in basicity of the nitrogens of N-alkyl and N-aryl imines of the ligand to form a zwitter ion led to the coordination of the zwitter ionic N-alkyl imines only to form the lanthanide complexes, while it is not realized with aromatic imines.

N, N′-aromatic donors shown in Fig. 2 [22] viz., 4,7-disubstituted phenanthroline (**L5** and **L6**), or 4,4′-dimethoxy-2,2′-bipyridine (**L7**) coordination with the lanthanide ions was successful, while diethyl-2,2′-bipyridine-4,4′-dicarboxylate (**L8**) did not participate in coordination. Hence it has been accounted for an electronic destabilization of the ester groups on the aromatic bipyridine core, which is associated with a more flexible conformation with respect to the phenanthroline to make this ligand not compatible for chelation with a lanthanide ion of any size. In fact the influence of the substituents on the basicity and the coordination ability of the N, N′-aromatic ligands, viz., 4,4′-dimethoxy-2,2′-bipyridine, (**L3**) the bipyridine bearing a methoxy group in 4,4′-position, produced high yields of the complexes reflecting the dramatically enhanced activation towards coordination.

---

* Corresponding author. Tel.: +91 9435522541; fax: +91 3842270806.
E-mail address: drnvsrao@gmail.com (N.V.S. Rao).

0022-2860/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2011.07.010

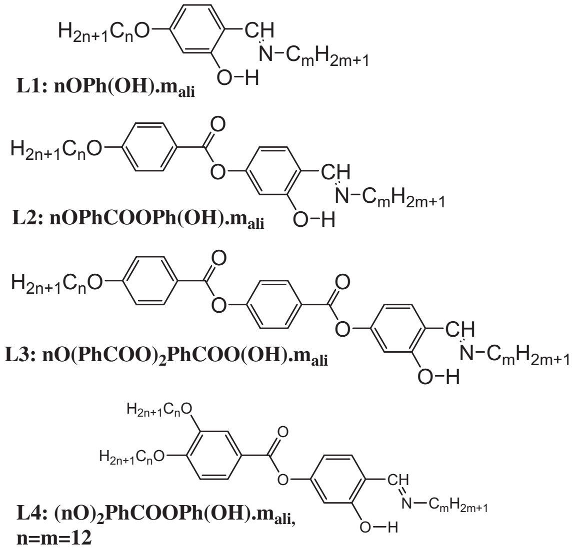

Fig. 1. Molecular structure of Schiff's base ligands studied extensively for complexation [14–17].

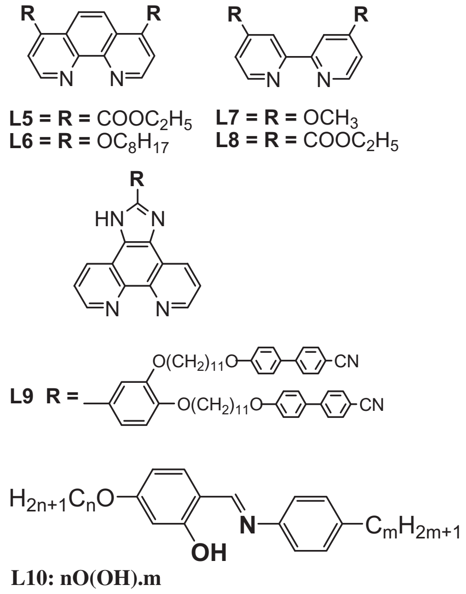

Fig. 2. Molecular structure of N, N′-aromatic donors for complexation.

However modification of the phenanthroline ligand (**L9**) in 5,6-positions fused with a substituted imidazo ring led the realization of nematic phase [23].

Hence the design and synthesis of lanthanide containing liquid crystals viz., salicylideneimine based promesogenic ligands, with a polar group substituted in an aryl moiety on nitrogen atom of the central bridging imine group, to coordinate with f-block metals presents a special experimental challenge. Our previous attempts were successful in reporting the complexation of different lanthanide ions with N-(4-n-alkoxysalicylidene)-4′-n-alkylanilines, **L10** [24,25]. The lanthanide complexes in general exhibited SmA phase but some of them exhibited columnar phases [25,26] depending on the aliphatic chains component in the ligand. In continuation of earlier work we report here the complexation of different lanthanide (III) ions with N-(4-n-hexadecyloxysalicylidene)-4′-substituted-anilines, the substituent being a polar group in N-aryl moiety, characterization of mesomorphism of the ligands as well as complexes and their spectroscopic characteristics. A comparison with complexes of d-block elements is also presented.

2. Results and discussion

The synthesis of ligands viz., N-(4-n-decyloxysalicylidene)-4′-substituted-(methyloxy, chloro and fluoro)-anilines (hereafter abbreviated as 16O(OH)X where X = H, OMe, F, Cl) and their Cu (II) and VO (IV) (*d*-block) complexes and Gd (III) (f-block) complexes as detailed in Scheme 1, was carried out following the procedure described in experimental section. Sm(III) and Pr(III) complexes were also synthesized and characterized by IR, UV–Vis and fluorescence studies.

Elemental analysis of the ligands and copper (II) and oxovanadium (IV) complexes were consistent with their proposed molecular formulas (Table 1). Elemental analysis of lanthanide complexes revealed that the stoichiometry is $\{[\mathrm{Ln(LH)_2L}](\mathrm{NO_3})_2\}$, where Ln = Gd, and LH = **2, 3** and **4**. We investigated the ionic conductivity of solutions of the ligand **3** [16O(OH)F], $c = 1.0 \times 10^{-4}$ M and **3-Gd** (Gadolinium complex, $c = 1.0 \times 10^{-3}$ M) in double distilled and dried N,N′-dimethylformamide (DMF). The conductivity values (Table 2) inferred that the ligand is a non-electrolyte. However the **3-Gd**, (Gd complex) is a 2:1 electrolyte with the two nitrate ions participation from outer coordination sphere [27] confirming the elemental analysis data. The room temperature infrared spectra of the ligands **1, 2, 3** and **4** exhibited characteristic bands (ν(C=N)) at 1622–1627 cm^{-1}. The C=N stretching vibration is shifted to lower frequencies for the copper (II) (1608 cm^{-1}) and oxovanadium (IV) (1608–1610 cm^{-1}) complexes compared to that of free ligands. This reflects the azomethine N atom is involved in metal-nitrogen bond formation. The oxovanadium (IV) complexes exhibit a stretching band at around 966–987 cm^{-1} assigned to ν(V—O) suggesting that these complexes have a monomeric structure [28–31].

However the infrared spectra of lanthanide (III) complexes exhibited characteristic C=N stretching vibration (ν(C=N)) at ~1640 ± 5 cm^{-1} and 1616–1622 cm^{-1} (Table 1) for the complexes (Representative IR spectra of the complex **2-Gd** and **3-Gd** are shown in Fig. 3.), apart from the characteristic bands of aromatic ring (C=C), Ar(C—H), CH$_3$, and CH$_2$ vibrations. These two bands confirm two types of coordination one through the oxygen atom and another through the nitrogen atom. The band at ~1616–1622 cm^{-1} reflects the participation of azomethine N atom in metal-nitrogen bond formation in the case of toluidine (**2-Gd**) and chloro complexes (**4-Gd**). However the absence of C=N stretching vibration for fluoro complex **3-Gd** at ~1620 cm^{-1} reflects the absence of metal-nitrogen coordination bond formation. The weak O—H stretching vibration of the ligand at 2870–2850 cm^{-1}, is overlapped by the CH modes in the lanthanide complexes reflecting the N—H vibration of the protonated nitrogen atom in C=N$^+$H as well as the participation of hydrogen atom in the intramolecular hydrogen bonding with the phenolic oxygen atom as reported earlier [32]. This abnormal behavior may be due to coordination of the metal through O-atom of the ligand only, the proton of the O-atom migrate to the N-atom of the imine moiety which may -lead to formation of zwitter ion (C=N$^+$—H) of ligand. The observed vibrations of two bands at 1635–1645 cm^{-1} and ~1620 cm^{-1} for the complex $\mathrm{Gd[(L^4H)_2(L)]{\cdot}(NO_3)_2}$, are due to two types of CH=N stretching and compression vibrations. One of these is the elongated stretching viz., exactly opposite with an increase in the imine **C=N** stretching vibration of the complex (at 1635–1645 cm^{-1}) in the infrared spectra when compared to the stretching vibration in the free Schiff base ligand, while the other one is a compressed imine bond appearing at a lower value of 1620 cm^{-1}. The vibration at higher