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Research Article

Preparation and Study Some Properties for Liquid Crystalline Material

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Keywords

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Abstract

One ligands have been synthesized from benzidine derivatives. This ligand has been mixed with metal ions such as (Ni^{II} and Zn^{II}) to synthesis liquid crystalline complexes with reactants ratio (2:1). These prepared molecules have liquid crystalline behavior according to characterization by optical Polarizing Optical Microscope (POM). different physical chemical techniques such as spectroscopic (UV-Visible, FT-IR, X-ray powder diffraction (XRD)), and molar conductivity have beenexamine. The results are showing enantiotropy nematic phase (marble and schleiren textures through heating and cooling respectively) for all compounds, and have polycrystalline structure.

1. Introduction

Liquid Crystals (LCs) are intermediate state between solid and liquid state. It is often called a mesomorphic state which is state of matter in which the degree of molecular order is intermediate between the perfect threedimensional, long-range positional and orientational order found in solid crystals and the absence of long-range order found in isotropic liquids, gases, and amorphous solids it is also called as meso intermediate [1].

Materials that exhibit liquid crystal mesophases typically have molecular structures that can be classified as spherical, rod-like, disc-like, or even any regular geometrical shape, with combinations of the two producing phasmidic liquid crystals[2], depending on the physical chemical parameters responsible for the phase transitions to thermotropic and lyotropic [3]. Thermotropic liquid crystal phases are formed by pure mesogens in a certain temperature range and hence the prefix (thermo) referring to phase transitions in which heat is generated or consumed[4]While lyotropic liquid crystal, the transition is induced by the influence of solvents[5]under appropriate conditions of concentration and temperature[6].
LCs are finding numerous applications because of their ability to change orientation of molecules in response to very weak physical and chemical cues, such as electromagnetic fields, surface modifications and pressure gradients[7]

In the last decades, the introduction of a metal ion leads to a new class of liquid crystals: metallomesogens. The metal complexes which contain organic mesogens as ligands may retain these properties. Also, the introduction of a metal ion in an organic compound which does not exhibit liquid crystal properties lead to a new complex with liquid crystal properties[8]

In this paper,one ligandshas been synthesized which are [Di-Cinnamylidene Benzidine] with symbol (A_1), and its complexes with (Ni^{II}, Zn^{II})take symbols (M_1A_1, M_2A_1) respectively. These compounds are characterized by POM, UV-VIS, FT-IR,XRD, and molar conductivity.

2. Theoretical part:

The assignment of the mesophases is based on different experimental techniques. Phase transitions are usually detected not only by calorimetry but also by polarizing optical microscopy. Textural features obtained by polarizing microscopy give first hints about the mesophase type [9]. Powder X-ray Diffraction (XRD) is one of the primary techniques used by mineralogists andsolid state chemists to examine the physico-chemical make-up of unknown materials. Diffraction pattern gives information on translational symmetry - size and shape of the unit cell from Peak Positions and information on electron density inside the unit cell, namely where the atoms are located from peak Intensities [10], a crystalline size (average grain size) has been calculated using Debye-Scherrer formula [10,11].

$$G_s = \frac{0.94\,\lambda}{\beta\,\cos\theta} \quad \ldots (1)$$

Layer spacing(d) values were obtained from the inner meridional arc by using Bragg equation [12]:

$$n\lambda = 2d\,\sin\theta \quad \ldots (2)$$

Where: (λ) is wave length of X-ray (0.15405 nm), (β) is FWHM (full width at half maximum in rad.), (θ) is the diffraction angle, (G_s) is crystalline size, (n) is integer that indicates the order of the reflection, and (d) is layer spacing.

3. Experimental Part:

3.1. Physical Measurements:

Liquid crystalline properties were investigated by Polarizing Optical Microscopy (POM) using a Leitz Laborlux 12 pols attached to a Linkam with hot stage and digital camera. Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for (1×10^{-3}) M solutions in absolute ethanol at 25°C using a Shimadzu 1800 spectrophotometer matched quartz cell. FT-IR data were acquired on Shimadzu-FTIR spectrophotometer in the frequency range of (4000-400) cm^{-1} with samples embedded in (KBr) discs. Structural characterization of compounds and their metal complexes are well documented by X-ray diffraction patterns.

Conductivity measurements were made with dimethyl formamide (DMF) using a (DDS-307W) digital conductivity meter at room temperature. Melting points (m.p.) were obtained on a Stuart SMP-30 capillary melting point apparatus.

3.2.Procedures of Synthesis:

3.2.1. Synthesis of Di-Cinnamylidene Benzidine (A_1):

The benzidine (1.84 g; 0.01 mol) dissolved with cinnamaldehyde (2.64 g; 0.02 mol) in ethanol (20 mL), three drops of glacial acetic acidadd to the solution and the mixture was refluxed for (2 hours). The Schiff base compound was isolated after the volume of the mixture was reduced to half using rotary evaporation and the obtained yellow solid product was collected by filtration, washed several times with ethanol and recrystallization from absolute ethanol [13].

3.2.2.General Synthesis of Complexes:

The prepared Schiff base (0.002 mol) in (10 mL)ethanolhave been mixed withNi^{II}(0.41g; 0.001mol) and Zn^{II}(0.13g; 0.001mol) of chlorinated salts respectively and refluxed for (1 hour). The resulted complexes were collected by filteration and then washedseveral times with ethanol, dried and stored.As in following Table, where: X is coordinated molecules of water[14]

Table (1) Molar conductance and m.p. of ligand and its complexes.

No.	Compounds formula	Compounds symbol	Compounds color	m.p. °C	$\Lambda\times10^{-3}$ $\Omega^{-1}mol^{-1}cm^{2}$
1	$C_{30}H_{24}N_2$	A_1	Yellow	270.3	—
2	$[Ni(C_{30}H_{24}N_2)]\ Cl_2.X$	M_1A_1	Dark yellow	230.4	135
3	$[Zn(C_{30}H_{24}N_2)]\ Cl_2.X$	M_2A_1	Orang	189.1	144

4. Results and Discussion:

4.1. Mesomorphic Properties:

The compounds are examined by using (POM), showed by heating nematic phase taking marble form, while by cooling from isotropic liquid exhibit schleiren texture by separation of distinct droplets growing to form a large colored flooring when continued cooling, this is distinguishes nematic phase. Figure (1) shows a photograph showing nematic phase of (A_1) compound at heating and cooling. Reason of exhibited nematic phase in heating and cooling attributable in (A_1) ligand and their complexes to presence of four aromatic rings in the molecular structure [15].

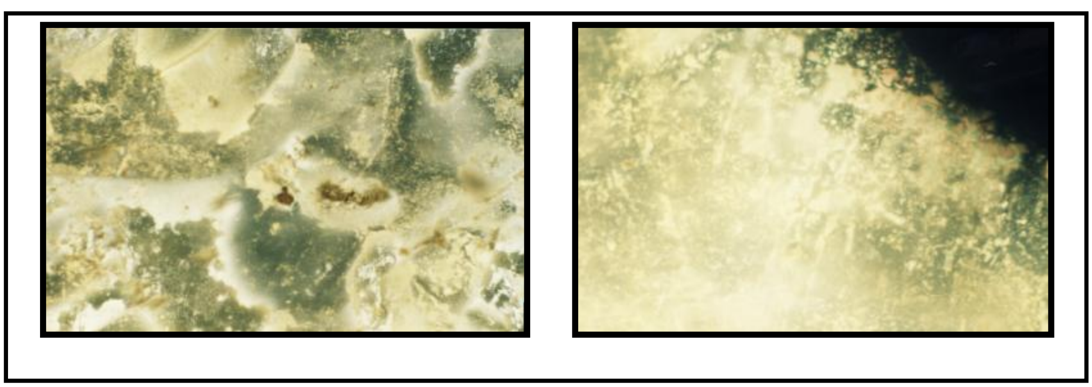

Figure (1) Nematic phase of ligand (A_1).

4. 2. UV-VIS spectroscopic:

The UV-Vis spectra of ligands show two bands at (270) nm assigned to ($\sigma \rightarrow \sigma^*$) and ($\pi \rightarrow \pi^*$) and (420-560) nm assigned to ($n \rightarrow \pi^*$).While the UV-Visible spectra for the prepared complexes showed one broadband between (410-470) nmassigned to ($n \rightarrow \pi^*$)[16]. Figure (2) exhibits UV-VIS spectra of (A_1)and their complexes**.**

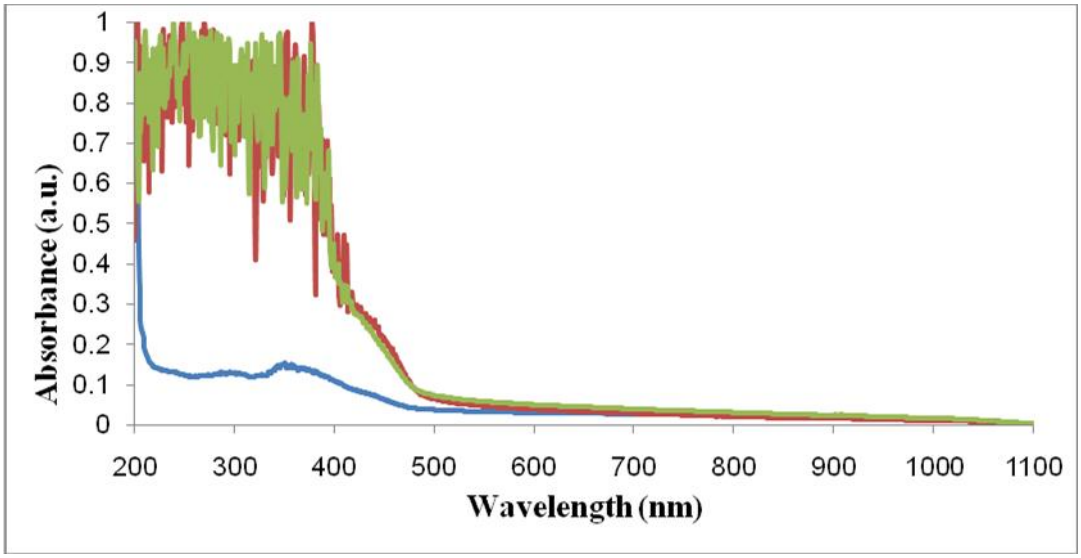

Figure 2. UV-VIS spectra of (A_1) and their complexes.

4.3. FT-IR Analysis:

The FT-IR data of the complexes were compared with respective of the free ligand in order to identify the coordination modes upon the chelation process. FT-IR of ligands (A_1) have vabiration band (1630) cm^{-1} for (C═C) aromatic, and (1605) cm^{-1} for azomethine groups (CH═N) this group is active [17], while these bands shift lower wave numbers upon complexation with the metal ions.The new bands appearing in the region (464-522) cm^{-1}probably due to the formation of (M-N). Figure (3) exhibits bandabsorption of (A_1)and their complexes**.**

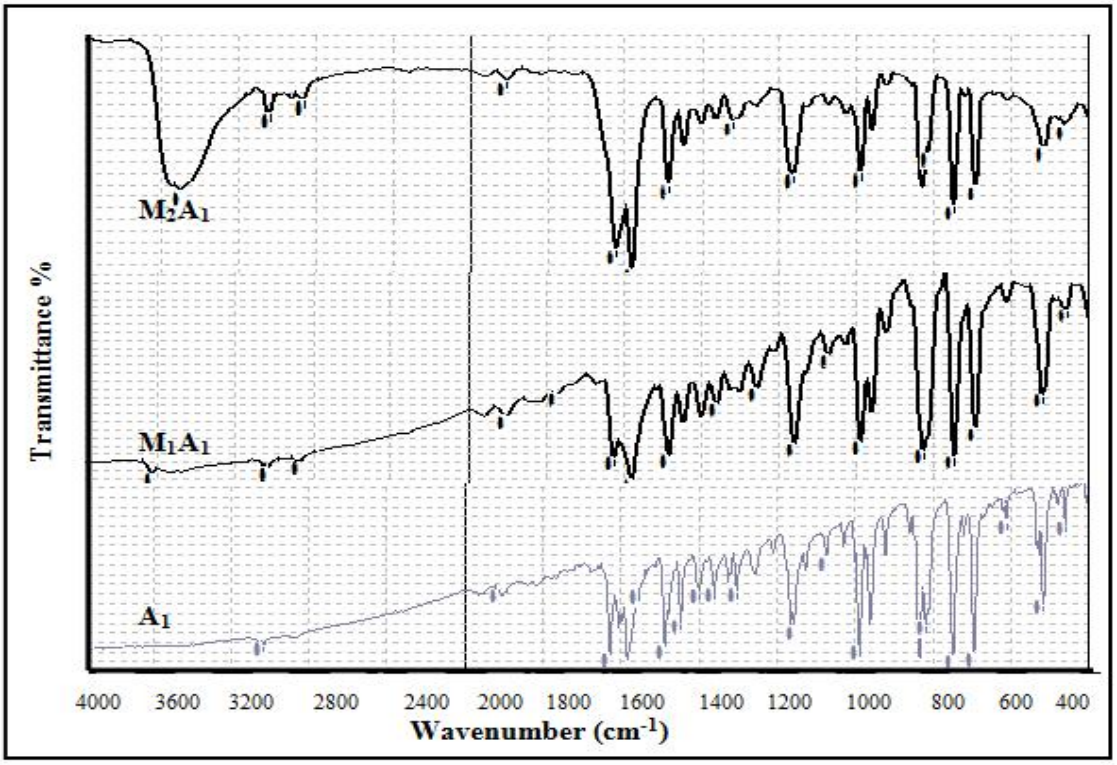

Figure (3)FT-IR spectra of ligand (A_1) and their complexes.

Table (2) FT-IR characteristic bands frequencies (cm^{-1}) of the ligands and its complexes.

No.	Compounds symbol	Stretchof (aromatic) C=C	Stretch of (C=N)	Stretch of (M–N)
1	A_1	1630	1605	—
2	M_1A_1	1620	1591	459
3	M_2A_1	1618	1589	464

4.4. Structural properties:

Liquid crystal compounds and its complexes examined by (XRD) to identifying the crystalline composition, the examination found that ligands (A_1)has polycrystalline structure and complexes (M_1A_1, and M_2A_1) have monoclinic structure[18]from this study, crystalline size (grain size) has been estimated using equation (1), were found to be (24-70) nm. Figure (4) shows XRD spectrum of (A_1) compound.

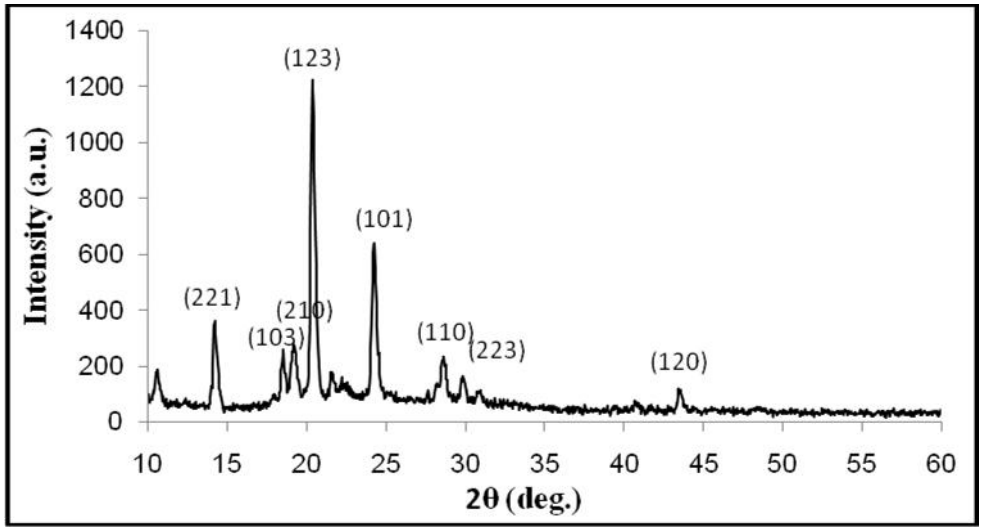

Figure 4. XRD spectrum of (A_1) compound.

4.5. Molar conductance measurements:

Molar conductivity measurements of the complexes in DMF solutions lie in the (235–144.1) (Ω^{-1} mol^{-1} cm^2) range, indicating their electrolytic behavior [14], this result was clearly indicated that complexation of their ligands were happened by ratio (1:1), and chloride ions were responsible for charge transfer by their swimming outside coordination sphere in the solution.

5. Conclusions:

From this paper we was concluded that the ligands and its complexes with Ni^{II}, and Zn^{II} exhibit nematic phase at heating and cooling, UV-VIS spectra of two ligands show two bands at (270) nm, and (420-560) nm,while the complexes showed one broadband between (400-470) nm, FT-IR spectra showshift bands to lower wave numbers indicated that complexation with the metal ions was occur, XRD spectra show polycrystalline structure of compounds (A_1), while monoclinic structure of complexes (M_1A_1, and M_2A_1), andmolar conductance shows electrolytic behavior of complexes are in the range of organic semiconductors and the complexes have square planar.

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