

## Preparation and Structural Properties of Liquid Crystalline Materials and its Transition Metals Complexes

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Received: 31 August 2018;

Accepted: 14 October 2018;

Published online: 31 December 2018;

AJC-19215

Two ligands have been synthesized from hydrazine and benzidine derivatives. These ligands were mixed with metal ions such as [Cd(II) and Zn(II)] to synthesize liquid crystalline complexes. By using polarizing optical microscopy, these compounds have a liquid crystalline behaviour. The complexes were characterized by physical and chemical techniques such as spectroscopic (UV-visible, FT-IR, X-ray powder diffraction) and molar conductivity. The results show enantiotropy nematic phase (marble and schleiren textures through heating and cooling, respectively) for all compounds. Compounds have polycrystalline amorphous structure with square planar geometry.

**Keywords:** Liquid crystalline materials, Hydrazine, Benzidine derivatives, Mesogenic complexes.

### INTRODUCTION

Liquid crystals are intermediate state between solid and liquid state. It is often called a mesomorphic state, which is a state of matter in which the degree of molecular order is intermediate between the perfect three-dimensional, 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].

Liquid crystals have been implemented in 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 [2]. In the last decade, 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 that does not exhibit liquid crystal properties leads to a new complex with liquid crystal properties [3].

In this paper, two ligands were synthesized, which are [dicinnamylidene benzidine] ( $A_1$ ), (*bis*-4-methoxybenzylidene hydrazine) ( $A_2$ ) and their complexes with  $Cd^{2+}$  and  $Zn^{2+}$ . These compounds are characterized by polarizing optical

microscopy (POM), UV-visible, FT-IR, XRD and molar conductivity. The physical and chemical properties have been discussed according to physical investigations in order to discover new mesogenic organic semiconductor.

### EXPERIMENTAL

Powder X-ray diffraction (XRD) is one of the primary techniques used by mineralogists and solid 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, a crystalline size (average grain size) has been calculated using Debye-Scherrer formula [4,5]:

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

Layer spacing (d) values were obtained from the inner meridional arc by using Bragg equation [6]:

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

where  $\lambda$  is wavelength of X-ray (0.15405 nm),  $\beta$  is FWHM (full width at half maximum in rad.),  $\theta$  is the diffraction angle, ( $G_s$ ) is crystalline size, ( $n$ ) is integer that indicates the order of the reflection and ( $d$ ) is layer spacing.

**Physical measurements:** Liquid crystalline properties were investigated by polarizing optical microscopy 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 ( $1 \times 10^{-3}$ ) 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)  $\text{cm}^{-1}$  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.

**Synthesis:** Compounds were prepared using a method reported in the literature [7].

**Synthesis of dicinnamylidene benzidine (A1):** Dicinnamylidene benzidine was prepared by mixing (1.84 g, 0.01 mol) of benzidine dissolved in 10 mL of absolute ethanol with (2.64 g, 0.02 mol) of cinnamaldehyde in 10 mL of absolute ethanol, then added to the prepared mixture three drops of glacial acetic acid. Reaction mixture was refluxed for 2 h, resulted yellow solid product. The crystal product filtered and washed with absolute ethanol repeatedly and recrystallization was done by absolute ethanol.

**Synthesis of bis-4-methoxybenzylidene hydrazine (A2):** Dicinnamylidene benzidine was prepared by mixing (1.84 g, 0.01 mol) of benzidine dissolved in 10 mL of absolute ethanol with (2.64 g, 0.02 mol) of cinnamaldehyde in 10 mL of absolute ethanol, then, three drops of glacial acetic acid were added to the prepared mixture. The reaction mixture was refluxed for 2 h, and a yellow solid product was performed. The crystal product was filtered and washed with absolute ethanol repeatedly and recrystallization was done by absolute ethanol.

**General synthesis of complexes:** The complexes were prepared using the reported procedure [8] (0.001 mol) of both Cd(II) and Zn(II) were dissolved in 10 mL of absolute ethanol and mixed with (0.001 mol) of A<sub>1</sub> and A<sub>2</sub>, where the ratio of reactants (1:1). The reaction mixture was refluxed for 1 h and the produced mixture was filtered and washed with absolute ethanol repeatedly and recrystallization was done by absolute ethanol.

## RESULTS AND DISCUSSION

**Molar conductance:** Molar conductivity measurements of the complexes in DMF solutions lie in 23.8-134.1  $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$  range, indicating their electrolytic behaviour [9]. This result clearly indicated that complication of their ligands was happened by ratio (1:1) and chloride ions were responsible for charge transfer by their presence outside coordination sphere in the solution (Table-1).

**Mesomorphic properties:** The compounds examined by (POM) showed a marble form by heating nematic phase, while exhibited a schleiren texture by cooling from isotropic liquid

TABLE-1  
MOLAR CONDUCTANCE AND MELTING POINTS  
OF LIGANDS AND THEIR COMPLEXES

Compounds	Colour	m.p. (°C)	$\Lambda \times 10^{-3}$ ( $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$ )
C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> (A <sub>1</sub> )	Yellow	270.3	–
C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> (A <sub>2</sub> )	Yellow shining	165.0	–
[Cd(C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> )]Cl <sub>2</sub> .X (M <sub>1</sub> A <sub>1</sub> )	Dark yellow	240.5	132.3
[Zn(C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> )]Cl <sub>2</sub> .X (M <sub>2</sub> A <sub>1</sub> )	Orange	263.5	123.8
[Cd(C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )]Cl <sub>2</sub> .X (M <sub>1</sub> A <sub>2</sub> )	Yellow	230.0	134.1
[Zn(C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )]Cl <sub>2</sub> .X (M <sub>2</sub> A <sub>2</sub> )	Yellow	198.0	107.2

by separation of distinct droplets grow to form large coloured flooring when continued cooling, this distinguishes nematic phase [8]. Fig. 1 shows a nematic phase of A<sub>1</sub> compound at heating and cooling. Reason of exhibited nematic phase in heating and cooling attributable in ligands and its complexes to presence of four aromatic rings in the molecular structure, and to presence of nitrogen atoms linked directly in the case of resonant in center of the molecule, aromatic rings and nitrogen atoms give a suitable length of the molecule and high hardness, in addition to the breadth of sequencers electronic on the long axis of the molecule, which leads to increased polarity molecule resulting from terminal attractive forces [9-15].

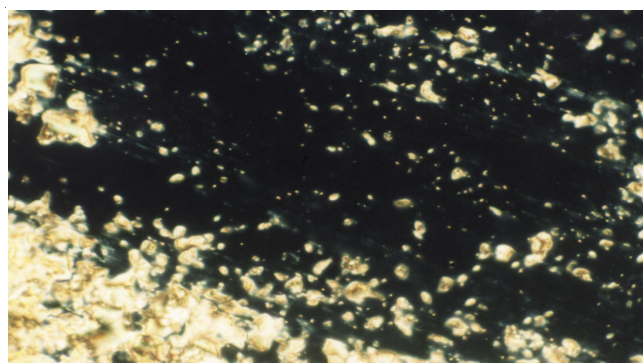


Fig. 1. Nematic phase of ligand (A<sub>2</sub>)

**UV-visible analysis:** The UV-visible spectra of ligands showed two bands at 370 nm assigned to ( $\sigma \rightarrow \sigma^*$ ), ( $\pi \rightarrow \pi^*$ ), and (420-560) nm assigned to ( $n \rightarrow \sigma^*$ ) while the UV-visible spectra for the prepared complexes showed one broadband between 400-470 nm (Figs. 2 and 3) [16].

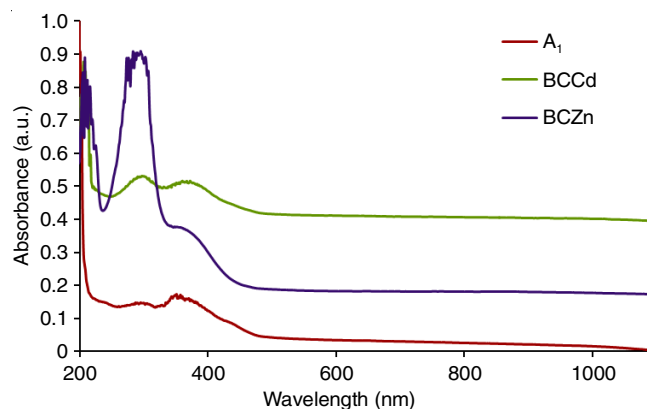


Fig. 2. UV-visible spectra of ligand (A<sub>1</sub>) and their complexes

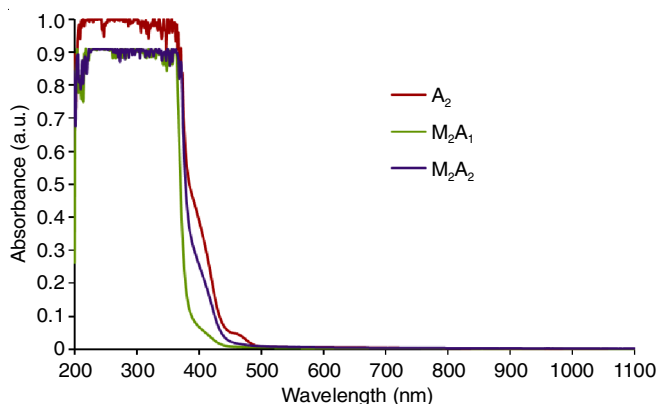


Fig. 3. UV-visible spectra of ligand ( $A_2$ ) and its their complexes

**FT- IR analysis:** The coordination sites of ligand have been determined by a careful comparison of IR spectra complexes with that of the parent ligand. The ligands ( $A_1$  and  $A_2$ ) showed intense absorption at  $1630$  and  $1664\text{ cm}^{-1}$ , which may be assigned to (C=C) aromatic in plane stretching vibration, and  $1605$  and  $1600\text{ cm}^{-1}$  for azomethine groups (CH=N), which are active groups [17]. These bands shift lower wave numbers in complexes indicating coordination through azomethane nitrogen of Schiff bases. Fig. 4 exhibited a band absorption of ligand ( $A_2$ ) and its complexes. The appeared new bands in the region  $522$ - $460\text{ cm}^{-1}$  are probably due to the formation of (M-N) [18]. Main characteristic FT-IR absorption bands of ligands and complexes are presented in Table-2.

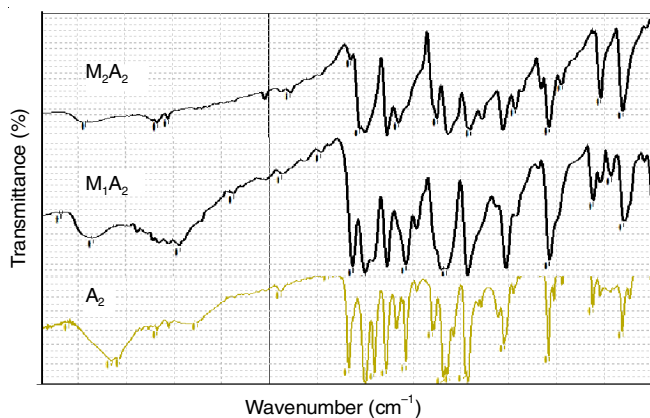


Fig. 4. FT-IR spectra of ligand ( $A_2$ ) and their complexes

Compounds	$\nu(\text{C}=\text{C})$ aromatic	$\nu(\text{C}=\text{N})$	$\nu(\text{M}=\text{N})$
$A_1$	1630	1605	–
$A_2$	1664	1600	–
$M_1A_1$	1625	1580	478
$M_2A_1$	1620	1581	460
$M_1A_2$	1650	1595	520
$M_2A_2$	1649	1590	522

**Structural properties:** Liquid crystal compounds and its complexes were examined by XRD to identify the crystalline composition. The examination found that ligands ( $A_1$  and  $A_2$ ) have polycrystalline structure, complex ( $M_2A_1$ ) have mono-

clinic structure, and complexes ( $M_1A_1$ ,  $M_1A_2$  and  $M_2A_2$ ) have amorphous structure [19] from this study, crystalline size (grain size) has been estimated using eqn 1, were found to be 13-67 nm.

## Conclusion

It is concluded that the ligands and its metal complexes with Cd(II) and Zn(II) exhibited nematic phase at heating and cooling. UV-visible spectra of two ligands showed two bands at 370 nm, and 420-560 nm, while the complexes showed one broadband between 400-470 nm. FT-IR spectra showed shift bands to lower wave numbers indicated that complexation with the metal ions was occurred, XRD spectra show polycrystalline structure of compounds ( $A_1$ ,  $A_2$ ) and  $M_2A_1$  have monoclinic structure, while amorphous structure of complexes ( $M_1A_1$ ,  $M_1A_2$  and  $M_2A_2$ ), and molar conductance shows electrolytic behaviour of complexes are in the range of organic semi-conductors and the complexes have square planar.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

- J.-G. An, S. Hina, Y. Yang, M. Xue and Y. Liu, *Rev. Adv. Mater. Sci.*, **44**, 398 (2016).
- D. Yang and W. Shin, *Fundamentals of Liquid Crystal Devices*, John Wiley, pp. 1-37 (2006).
- C. Liliana, C. Csunderlik and C. Otilia, *J. Chem. Bull. Politehnic. Univ. Timisoara*, **50**, 1 (2005).
- J.S.J. Hargreaves, *Catal. Struct. React.*, **2**, 33 (2016); <https://doi.org/10.1080/2055074X.2016.1252548>.
- M. Bal, G. Ceyhan, B. Avar, M. Köse, A. Kayraldiz and M. Kurtoglu, *Turk. J. Chem.*, **38**, 222 (2014); <https://doi.org/10.3906/kim-1306-28>.
- M. Marcos, P. Romero, J.L. Serrano, C. Bueno, J.A. Cabeza and L.A. Oro, *Mol. Cryst. Liq. Cryst. Incorpor. Nonlinear Opt.*, **167**, 123 (1988); <https://doi.org/10.1080/00268948908037168>.
- K.K. Abid and S.M. Al-barody, *J. Liq. Cryst.*, **41**, 1303 (2014); <https://doi.org/10.1080/02678292.2014.919670>.
- K. Sanyucta, *J. World Medical Res.*, **3**, 1 (2014).
- M. Riyadh, I. Enaam, A. Hasan, and J. Mohamad, *J. Scientific World, Article ID 289805* (2013); <https://doi.org/10.1155/2013/289805>.
- K. Abdali, M.Sc. Thesis, College of Science, Babylon University, Babylon, Iraq (2010).
- A.K.H. Al-Khalaf, M.Sc. Thesis, College of Science, Babylon University, Babylon, Iraq (2010).
- A.K.H. Al-Khalaf, Ph.D. Thesis, School of Chemistry, Cardiff University, U.K. (2012).
- K. Smith, A.K.H. Al-Khalaf, G. El-Hiti and S. Pattison, *Green Chem.*, **14**, 1103 (2012); <https://doi.org/10.1039/c2gc16443d>.
- A.K.H. Al-Khalaf, S.M. Haddawi and O.M. Yasser, *Iraqi National J. Chem.*, **24**, 475 (2006).
- A.O. Mousa, A.K.H. Al-Khalaf, S.J. Abdul-Razzaq and Q.M. Sh. Al-Jomali, *J. Al-Qadisiyah Univ.*, **4**, 215 (2015).
- A.O. Mousa, A.K.H. Al-Khalaf and M.A. Zghair, *J. Babylon Univ. Pure Appl. Sci.*, **3**, 24 (2016).
- P.M. Krishna, B.S. Shankara and N.S. Reddy, *Int. J. Inorg. Chem., Article ID 741269* (2013); <https://doi.org/10.1155/2013/741269>.
- S. Chandra and P. Pipil, *J. Open Inorg. Chem.*, **4**, 30 (2014); <https://doi.org/10.4236/ojic.2014.42005>.
- M.A.E.M. Mohamed, O.B. Ibrahim and M.S. Refat, *Can. Chem. Transac.*, **2**, 108 (2014).