Study of Magnetic and Electrical Property for Different Types of Prepared Mesogenic Organo – Semiconductors

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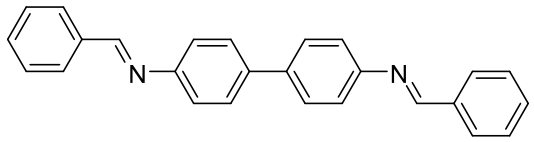
Abstract:

Synthesis and characterization were achieved for three mesogenic complexes of Schiff's base (mesogenic legand) with ions of (Cu^{+2}, Co^{+2}, and Mn^{+2}) as the following structure:



Di-Benzylidene Benzidine (DBB)

The legand and their complexes have been characterized by a spectrophotometer Infrared (IR), Ultra violet (UV), polarizing microscope equipped with heating stage, and Differential scanning calorimeter (DSC), techniques were found to be nematic (enantiotropic).

The magnetic sensitivity of these compounds has been investigated. Molar conductivity for the legand have shown that the free liquid crystal compound (twin dimmer) is non electrolyte solution while their complexes are electrolyte, that means the negative ions are swimming out of coordinated ball, as the following: $[DBB\text{-}Mn^{II}].Cl_n.X$; $[DBB\text{-}Cu^{II}].Cl_n.X$; $[DBB\text{-}Co^{II}].Cl_n.X$

The legand effect of complexation with (Cu^{+2}, Co^{+2}, and Mn^{+2}) on the (D.C) and (A.C) values have been clear when the (D.C) electrical conductivity ranged from (10^{-12}) to (10^{-9}) $(ohm.cm)^{-1}$ lies in the usual range of organic semiconductors.[14,15] The (A.C) electrical conductivity increases in the range of (10^{-11}) to (10^{-6}) $(ohm.cm)^{-1}$.

However, the measurements of magnetic sensitivity for the complexes are refer to have a paramagnetic property and have single electrons in outer electronic levels of the metal atoms, these compounds have the following trend: ($DBB\text{-}Mn^{+2}$) > ($DBB\text{-}Cu^{+2}$) > ($DBB\text{-}Co^{+2}$).

Key words: Schiff's base, magnetic sensitivity, semiconductors.

Physics classification : QC170-197

Introduction:

Recently, new types of organic compounds had been appeared including transitional elements have ability to bosses liquid crystalline behavior because their molecules can be arranged in several coordinated geometrical shapes; these compounds are called 'metallic mesogens'.[1]

Liquid crystalline complexes had studied widely because their importance at different industrial applications, especially those connected with Copper (II) because it has geometrical shape like square planar in all mesomeric compounds and that makes these molecules have ability to be aligned, these complexes have paramagnetic properties as one of the properties of liquid crystalline materials, there are many studies attained with complexes of Copper (II) that showed the relation between molecular structure and mesogenic properties, that could be obtained from derived systems of (2,4-dihydroxy benzaldehyde).[2]

In 1984,[3] first mesogenic complexes were prepared with Copper (II) and it gives textures of smectic phase (enantiotropic) and shape of square planar. However, there are several publications,[4,5] showed preparation of complexes that which derived from Schiff's bases and metallic ions, also they had explained the length effect of an aliphatic chains and substituted groups on the mesogenic properties, and how those groups that gives supporting to bosses or loses liquid crystalline behavior and magnetic sensitivity.

In 2004,[6,7] there was a study of the magnetic, electrical, and optical properties for nematic liquid crystalline molecules which have prepared from Schiff's bases with complexes of some transitional elements and found that liquid crystalline behavior had been loosed after complication.[8]

In 2006, there are several publications have showed the possibility to synthesis of new types of liquid crystalline semiconductors which have derived from benzidine as a mesogenic core.[9,10]

In 2010,[11] a study of magnetic sensitivity in order to characterization of complexes of transitional metals and its effect on an occupation of the outer electronic levels with single electrons and that gives information on compound that related with electronic distribution, oxidation state for transitional metals ions, and *Para* and *Diamagnetic* properties.

In this work, the prepared legand have liquid crystalline behavior and its complexes with metallic ions such as (Cu^{+2}, Co^{+2}, and Mn^{+2}) have been prepared and study their molar conductivity and magnetic properties.

Experimental [9,10]

1. Preparation of the legand (benzylidine benzidine; mp. 240 C^{o}) by a reaction of one mole of benzidine and two mole of benzaldehyde using Ethanol as a solvent during reflux process.
2. Preparation of the complexes by a reaction of the prepared legand and metal ions of (Cu^{+2}, Co^{+2}, and Mn^{+2}) using molar ratio (1:1) and Ethanol as a solvent during reflux process.
3. Preparation of the samples for molar conductivity measurements by prepares solutions with concentrations of (0.001 M) from the prepared complexes in solvent of DMF.

Characterization of the compounds and Results:

1. UV-Visible spectra: the prepared legand shows absorption peaks at (320-290) nm because the electronic transition of (π-π^*) and (σ-σ^*) for the aromatic (C=C) bonds, and at (400-375) nm because the transitions of (n-π^*) for the azomethane (CH=N) bond; while for the complexes they showed a broad band (410-470) nm at visible field.
2. IR spectra of the prepared compounds have vibration band (1600) cm^{-1} for the aromatic double bond, (1570) cm^{-1} for the (CH=N).
3. Textures of the liquid crystalline compounds: all compounds have shown a nematic phase by heating and cooling:

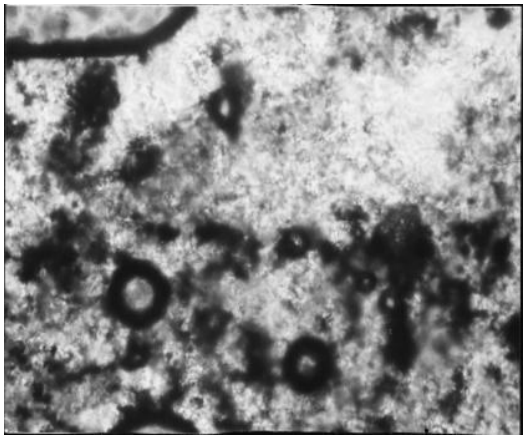


Photo (1): Marble texture of nematic phase of legand (DBB) by heating process.

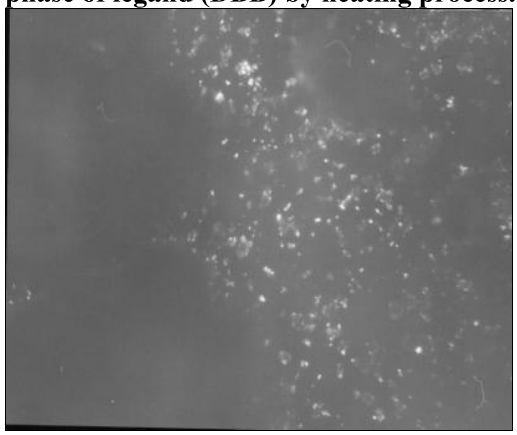
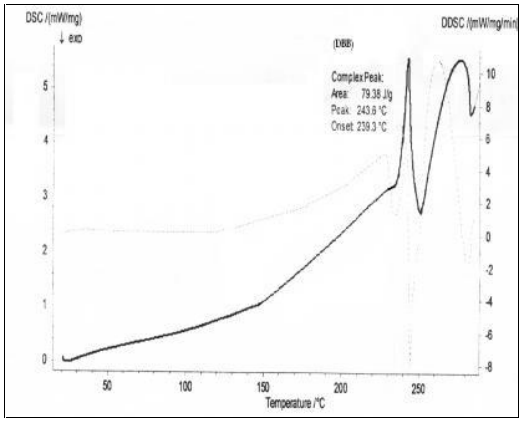


Photo (2): Marble texture of nematic phase of complex (DBB-Cu^{II}) by heating process.

4. DSC spectra for the legand and their complexes are showed two peaks for the transitions of crystal phase to liquid crystal phase and from liquid crystal phase to an isotropy (liquid phase):



Scheme (1): DSC spectra for the legand (DBB) .

5. Molar conductivity of the complexes is an electrolyte solution and that explain the negative ions (Chloride ions) are swimming out of the coordinate ball for these complexes at solution. So, the suggested forms of compounds are: $[DBB\text{-}Mn^{II}].Cl_n.X$; $[DBB\text{-}Cu^{II}].Cl_n.X$; $[DBB\text{-}Co^{II}].Cl_n.X$,where (X: coordinated molecules of water).

6. Measurements of magnetic sensitivity of the complexes by device model (M.S.B) Auto. College of Science, Al-Nahrain University are referred to the property of paramagnetic sensitivity and these compounds have the following trend according to an active magnetic moment as: $(DBB\text{-}Mn^{+2}) > (DBB\text{-}Cu^{+2}) > (DBB\text{-}Co^{+2})$.

$$X_g = C \times L / 109m \times (RR_o) \quad \ldots\ldots(1)$$

$$X_m = X_g \times M.Wt \quad \ldots\ldots(2)$$

$$X_A = X_m \times D \quad \ldots\ldots(3)$$

$$\mu_{eff} = 2.828 \sqrt{X_A \times T} \ (B.M) \quad \ldots\ldots(4)$$

Where:

C: constant (0.5); *L*: Sample height (1cm); *m*: Sample Wt.; X_g: Wt. sensitivity; X_m: Molar sensitivity; X_A: Atomic sensitivity; *T*: absolute temperature (K^o); *D*: Factor of diamagnetic correction; μ_{eff}: Active magnetic momentum; *(B.M)*: Unit of magnetic momentum.

So, the outer electronic levels at conductive band will have occupied with single electrons which are responsible for conductivity of semiconductors. However, this property makes the complexes take the structure of square planar and that support

the appearance of liquid crystalline behavior for the complexes. This structure gives regular an arrangement for the molecules of complexes. in general the results agree with the source [12].

Conclusions:

1. Study the texture of liquid crystals materials and its complexes by a polarized optical microscope, it was found that it exhibited nematic phase liquid crystal, enantiotropic mesophases.
2. The study of magnetic sensitivity for the complexes with ions of (Cu^{+2}, Co^{+2}, and Mn^{+2}), it was have a paramagnetic property.
3. The study of molar conductivity in solutions, it was found that the electrical conductivity lies in the usual range of organic semiconductors and it was found the electrical conductivity increased because of the complexity .

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دراسة الخواص المغناطيسية لأنواع مختلفة من أشباه موصلات عضوية ميزوجينية محضرة

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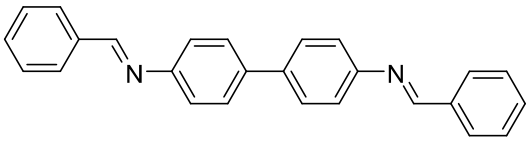
الخلاصة :

تم تحضير ووصف ثلاث معقدات ميزوجينية لقواعد شيف (ليكاند ميزوجيني) مع ايونات الكلوريد والكوبلت والمنغنيز الثنائية (Cu^{+2}, Co^{+2}, and Mn^{+2}) كما في الصيغة التركيبية التالية :



Di-Benzylidene Benzidine
(DBB)

ولقد شخص هذا الليكاند ومعقداته بواسطة طيف الاشعة تحت الحمراء (IR) , طيف الاشعة فوق البنفسجية (UV) ,المجهر الضوئي المستقطب المجهز بلوح تسخين ,المسح المسعري التفاضلي (DSC) وقد تبين ان هذه المركبـــات تمتلك الصفـــة البلورية السائلة ذات الطور النيماتي (الاعتيادي) . ولقد حققت الحساسية المغناطيسية لهذه المركبات . ينت التوصيلية المولارية لليكاند ان المركب البلوري السائل (ثنائي التناظر) ليس محلول الكتروليتي بينما معقداته هي محاليل الكتروليتية , هذا يعني ان الايونات السالبة تسبح خارج الكرة التناسقية كالاتي :

$[DBB\text{-}Mn^{II}].Cl_n.X$; $[DBB\text{-}Cu^{II}].Cl_n.X$; $[DBB\text{-}Co^{II}].Cl_n.X$

تأثير تعقيد الليكاند بأيونات (Cu^{+2}, Co^{+2}, and Mn^{+2}) على قيم التوصيلية الكهربائية المستمرة والمتناوبة كان واضح من خلال مدى التوصيلية الكهربائية المستمرة من (10^{-9}) الى (10^{-12}) (اوم . سم)$^{-1}$ والذي يقع ضمن المدى الاعتيـــادي لأشباه الموصلات العضوية . تزداد التوصيلية الكهربائية المتناوبة بمدى من (10^{-11}) الى (10^{-6}) (اوم . سم)$^{-1}$. على أي حال ,تشير قياسات الحساسية المغناطيسية الى ان هذه المركبات تمتلك خواص بارامغناطيسية و الكترونات منفردة في المستويات الالكترونية الخارجية للذرات الفلزية , ترتيب الحساسية المغناطيسية لهذه المركبات يعطى كالاتي :

$(DBB\text{-}Mn^{+2}) > (DBB\text{-}Cu^{+2}) > (DBB\text{-}Co^{+2})$

الكلمات المفتاحية: قواعد شيف, الحساسية المغناطيسية, اشباه الموصلات

Physics classification : QC170-197