# Preparation, Characterization and Liquid Crystalline properties of some Compolexes Schiff Base Derived from 4-(4-Alkoxy benzoyloxy)-2-hydroxy Benzaldehyde

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**Abstract:**

Two series of thermotropic liquid crystal dimers were prepared and characterized, the first series: α,β-bis (4-(4-Alkoxy benzoyloxy)-2-hydroxy Benzylidene) diamino ethane($nO_2On$).The second series, the copper(II) complexes of these dimers α,β-bis (4-(4-Alkoxy benzoyloxy)-2-hydroxy Benzylidene) diamino ethane copper (II) (Cu $nO_2On$). In these materials the length terminal alkyl chain is varied from 1 to 7 carbon atoms. The liquid crystalline properties of these materials have been investigated using differential scanning calorimetry and optical microscopy. This study revealed that these material exhibit nematic and smectic A.

**الملخص:**

حضرت وشخصت سلسلتين من البلورات السائلة الثرموتروبية الدايمرية. السلسة الاولى هي دايمر ( α، β- بس(4-(4-الكوكسي بنزويلوكسي)-2-هيدروكسي بنزلدين)) ثنائي أمينو **ايثان** $nO_2On$ . السلسلة الثانية هي معقدات النحاس الثنائية للدايمرات المحضرة: ( α، β- بس (4- (4-الكوكسي بنزويلوكسي)-2-هيدروكسي بنزلدين)) ثنائي امينو ايثان النحاس Cu $nO_2On$.

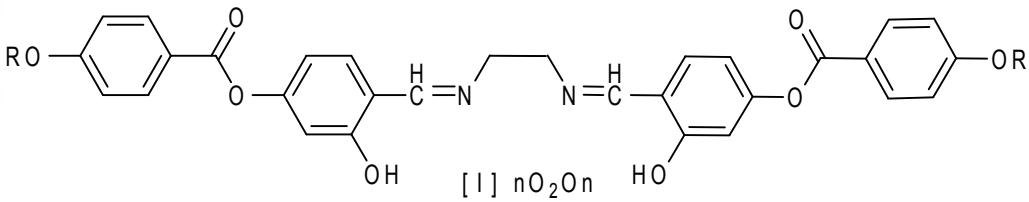
في هذه المركبات يتغير طول السلسلة الطرفية من 1 الى 7 ذرة كاربون . فحصت الصفات البلورية السائلة بواسطة المسح المسعري التفاضلي والمجهر ذو الضوء المستقطب ، دلت هذه الدراسة على امتلاك هذه المركبات اطوار وسطية نيماتية وسمكتية.

## Introduction:

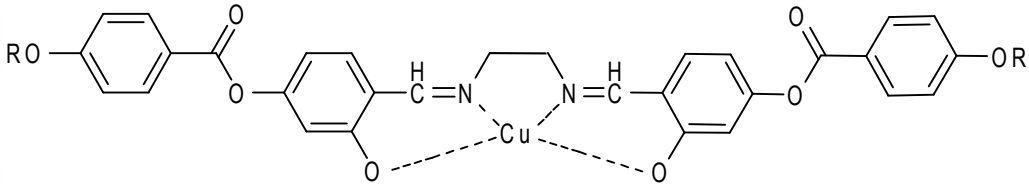
The earliest liquid crystal which contained a metal as integral part of the structure was a diphenyl mercury (II) compound reported in 1923 by Daniel Vorlander (1). Not much happened then until the late 1970 with the discovery of the matel dithiolenes by Anne-Marie Giroud and Ulrich Mueller-Westerhoff (2), but in mid-1980, the field really started to take off. There are many reasons why one might want to include a metal in a liquid crystalline structure, quite apart from nature curiosity.

For example, metals are stable radicals, their complexes are colored there are centers of polarizable electron density and they are centers of reactivity (3-5). If just two mesogen units, however, are linked through a flexible spacer, yielding the so called liquid crystal dimers, then the transition properties are found to be critically dependent on the length and parity of the alkyl spacer in a manner reminiscent of the behavior observed for polymeric systems (6-7).

To extend such studies, were prepared and studied the transition behavior of dimeric mesogens the α,β-bis (4-(4-Alkoxy benzoyloxy)-2-hydroxy Benzylidene) diamino ethane [1] and organometallic dimeric [II]:



[I] $nO_2On$

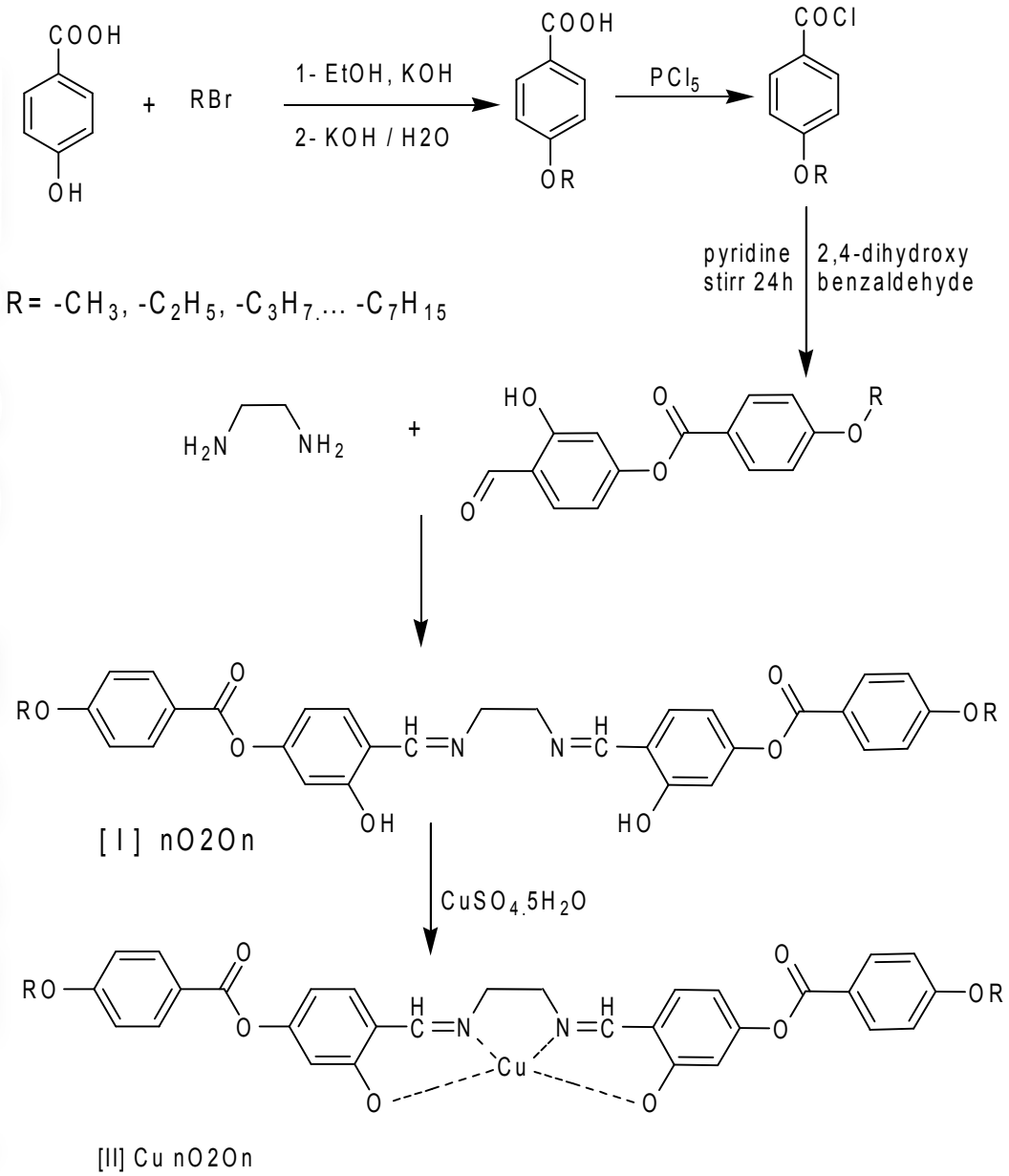


[II} Cu $nO_2On$

The main in these works is given to investigation of the influence of the structure of the mesogenic groups, conformation of complexes of liquid crystal and the length of the terminal alkyl chain on the nature of the mesomorphic state in dimer.

Experimental:

The two series were prepared using the synthetic route show in scheme (1):




Scheme 1: Preparation of dimeric liquid crystals

Preparation of 4-alkoxy benzoic acid (8)

A mixture of 4-hydroxy benzoic acid (0.1 mmol), alkyle bromide (0.17 mmol) and potassium hydroxide (0.2mmol) in ethanol was refluxed for 24 h. Then 20% potassium hydroxide 160 mL was added to the same reaction vessel. The mixture was refluxed for 4h. After cooling, the solution was neutralized wit 10% hydrochloric acid. The crude product was filtered and washed with distilled water and recrystallized from ethanol (yield 60-85%).

Preparation of 4-(4-alkoxybenzoyloxy)-2-hydroxy benzaldehyde [nM] (9)

4-Alkoxy benzoyl chloride was synthesized from 4-alkoxy benzoic acid (0.02mmol) was mixed with phosphorous pentachloride (0.02mmol) and was

stirred at 60oC for 25 min to give liquid product. Then the POCl3 (side product) is distilled off by vacuum distillation. 2,4-dihydroxy Benzaldehyde (0.013mmol) was dissolved in 10mL pyridine. A solution of 4-alkoxy benzoyl chloride (0.01mmol) in 10 mL pyridine was added drop wise to this solution, after the addition was complete, the reaction mixture was stirring for 24h. The crude product was filtered off and washed with 10% hydrochloric acid then several times with distilled water then dried. The product was recrystallized from ethanol (yield 60-70%).Typical IR spectrum shown in Figure 1.

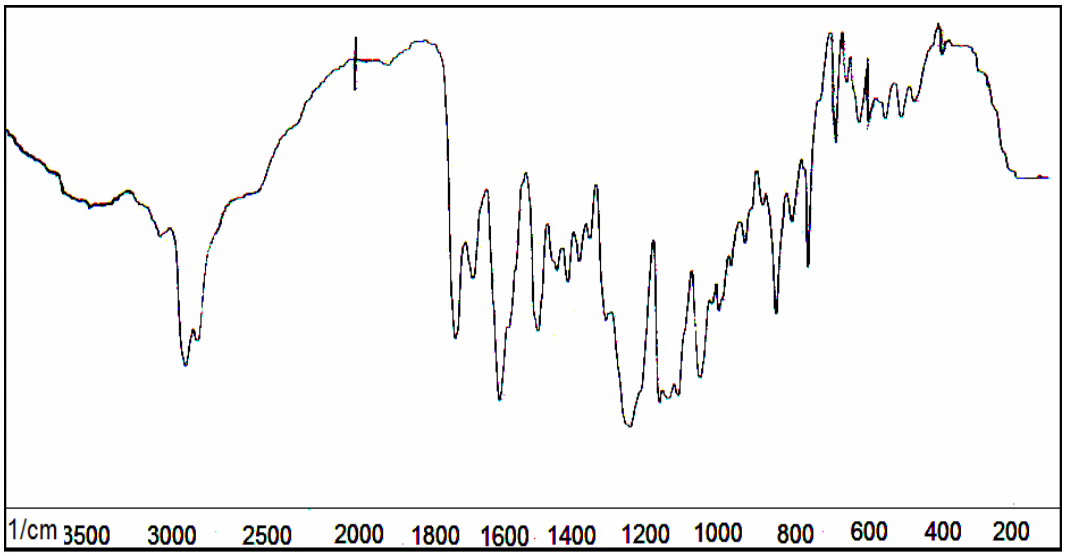



Figure 1: The IR spectra of compound 5M

Preparation of dimer Schiff base (nO2On) (10)

1,2-Diamino ethane (0.01mmol) was added stepwise to a hot solution of 4-(4-alkoxybenzoyloxy)-2-hydroxy benzaldehyde (0.02mmol) in 30mL absolute ethanol while cooling to roomtemperature are the mixture was stirred for 1h. Yellow precipitate formed which was filtered off and recrystallized from ethanol.(yield 80-90%).

Preparation of complexes (Cu nO2On) (4)

Copper sulfate five hydrates (0.01mmol) were added to a hot solution of dimer (0.01mmol) in 100mL methanol and the mixture was stirred for 1h. After cooling, the mixture was stirred for 1h. Green precipitate formed which was filtered off and washing several time with hot ethanol.(yield 60-85%).

Techniques

Melting point was measured on a Gallen Kamp melting point apparatus. Elemental analysis was performed by EA1108 Elemental analyzer. Infrared spectra were recorded on apye unicam model sp3-300s spectrophotometer. UV-Visible spectra were measured by Thermospectronic Helios

αV4.6(England).Measurement of transition temperatures were made using a Perkin-Elmer DSC -7 differential scanning calorimeter (DSC) . The instrument was calibrated with indium of purity (99.99). Polarizing optical microscopy studies were carried out on alaborlux 12 pols polarizing microscope to gather with a Leitz 350 a hot stage and Leitz vario othomatic. The Grondjeanplaner texture used in measurement was obtained by shearing the sample between to glass slides.

Characterization of compounds

The elemental analysis of two series nO2On and Cu nO2On are in a good agreement with the calculated value as shown in table1 and 2.

Table (1): The elemental analysis of complexes nO2On

| Dimer | Calculated | | | Found | | |
|---|---|---|---|---|---|---|
| | %C | %H | %N | %C | %H | %N |
| 1O2O1 | 67.60 | 4.92 | 4.92 | 67.51 | 4.83 | 4.87 |
| 2O2O2 | 68.04 | 5.15 | 4.81 | 68.01 | 5.17 | 4.79 |
| 3O2O3 | 68.45 | 5.37 | 4.69 | 68.41 | 5.29 | 4.61 |
| 4O2O4 | 68.85 | 5.57 | 4.59 | 68.72 | 5.56 | 4.54 |
| 5O2O5 | 69.23 | 5.76 | 4.48 | 69.18 | 5.72 | 4.43 |
| 6O2O6 | 69.59 | 5.95 | 4.38 | 69,47 | 5.89 | 4.41 |
| 7O2O7 | 69.93 | 6.13 | 4.29 | 69.86 | 6.08 | 4.33 |

Table (2): The elemental analysis of complexes Cu nO2On

| Dimer | Calculated | | | Found | | |
|---|---|---|---|---|---|---|
| | %C | %H | %N | %C | %H | %N |
| Cu 1O2O1 | 61.04 | 4.13 | 4.45 | 61.24 | 4.08 | 4.34 |
| Cu 2O2O2 | 61.58 | 4.35 | 4.35 | 61.45 | 4.41 | 4.28 |
| Cu 3O2O3 | 62.10 | 4.56 | 4.26 | 62.27 | 4.49 | 4.21 |
| Cu 4O2O4 | 62.59 | 4.76 | 4.17 | 62.71 | 4.83 | 4.21 |
| Cu 5O2O5 | 63.06 | 4.96 | 4.08 | 63.14 | 4.86 | 4.01 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cu 6O2O6 | 63.61 | 5.15 | 4.01 | 63.52 | 5.05 | 4.11 |
| Cu 7O2O7 | 63.95 | 5.32 | 3.92 | 63.81 | 5.26 | 3.84 |

The most important vibration bands observed in the infrared spectra for the dimers and complexes are listed in table 3 and table 4 respectively. Typical IR spectrum for dimers nO2On and Cu nO2On are shown in Figure 2 and 4 respectively. The appearance of N=CH stretching vibration of azomethine groups and disappearance of O-H stretching vibration of hydroxyl groups in complexes of dimer indicated that the preparation of these material is successful.

The UV-Visible spectra for nO2On explain three absorption peaks. The first transition from type (n-π*) at 314nm related to electronic transition for azomethine groups with alkyl groups. The other transition for type (π-π*) at 332nm related to electronic transition for azomethine with phenyl groups and at 40nm related to electronic transitions for benzene ring which linking to alkoxy groups.

The UV-Visible spectra for Cu nO2On gave two absorption peaks. The first transition at 485nm related to eg(xy,yz) b1g(x2-y2) and the second transition at 675nm related to b2g(x,y) b1g(x2-y2). This two peaks related to allowed transition spin in symmetry D4h. Typical UV-visible spectra for dimeric and complex in Figure 4 and 5 respectively.

Table3: The location of the most important absorption bands (cm-1) for the IR spectra of dimers nO2On.

| Group | O-H hydroxy | C-H Aliph. | C-H Arom. | C=O ester | N=CH azomethine | C=C Arom. | C-O-C ether |
|---|---|---|---|---|---|---|---|
| Stretching vibration | 3250 W | 3010-3020 W | 2820-2930 M | 1715-1720 S | 1615-1625 M | 1580-1595 S | 1170-1180, 1250-1260 |

W=weak, M=medium, S=strong

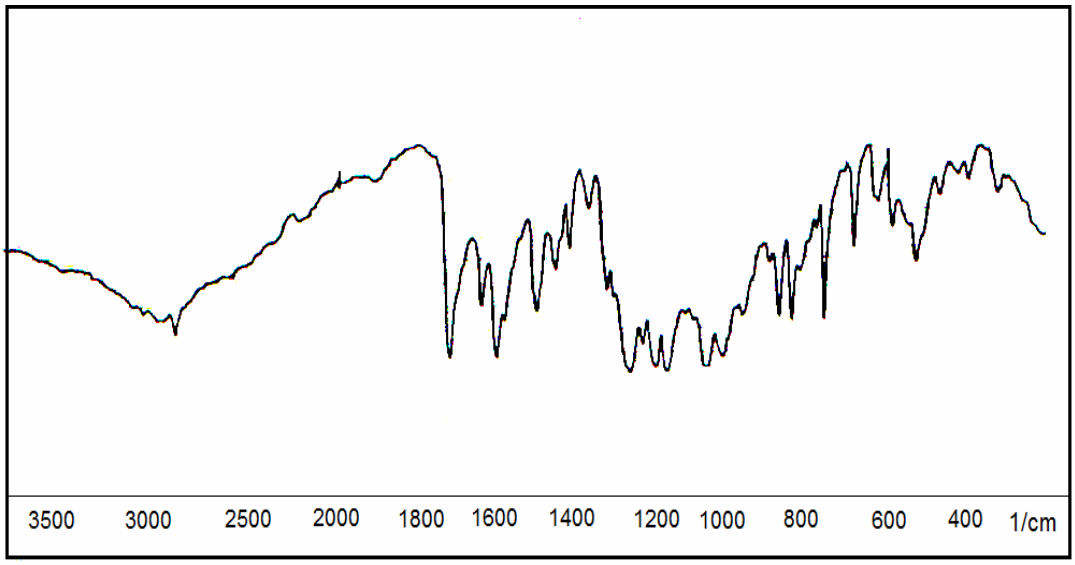



Figure 2 The IR spectra of 2O2O2 compound

Table3: The location of the most important absorption bands (cm-1) for the IR spectra of dimers nO2On.

| Group | O-H hydroxy | C-H Aliph. | C-H Arom. | C=O ester | N=CH azomethine | C=C Arom. | C-O-C ether |
|---|---|---|---|---|---|---|---|
| Stretching vibration | 3250 W | 3010-3020 W | 2820-2930 M | 1715-1720 S | 1615-1625 M | 1580-1595 S | 1170-1180, 1250-1260 |

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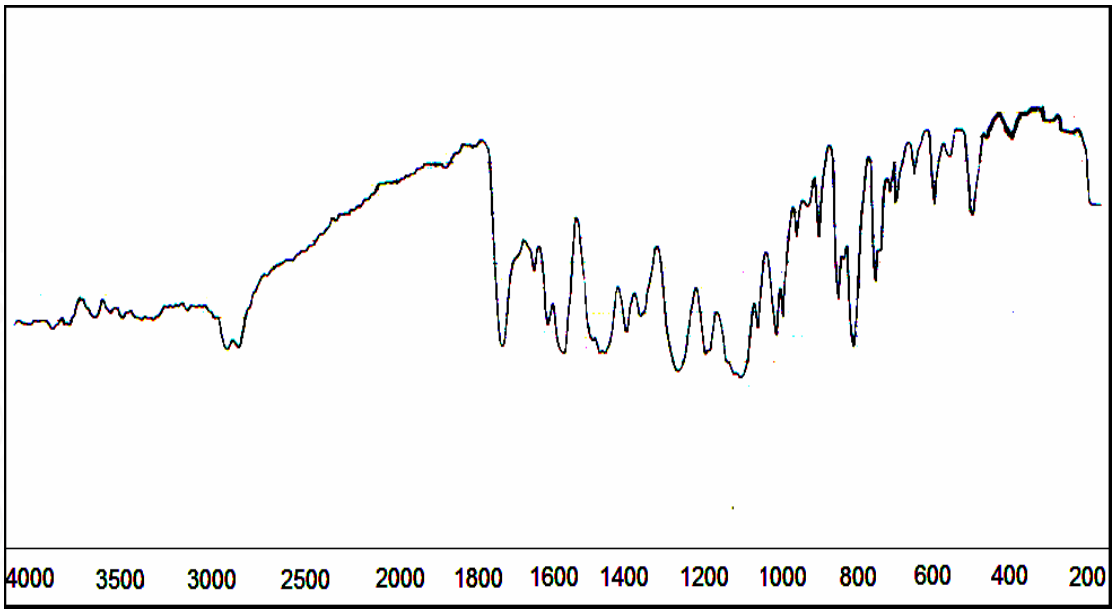


Figure 3 The IR spectra of Cu 4O2O4 compound

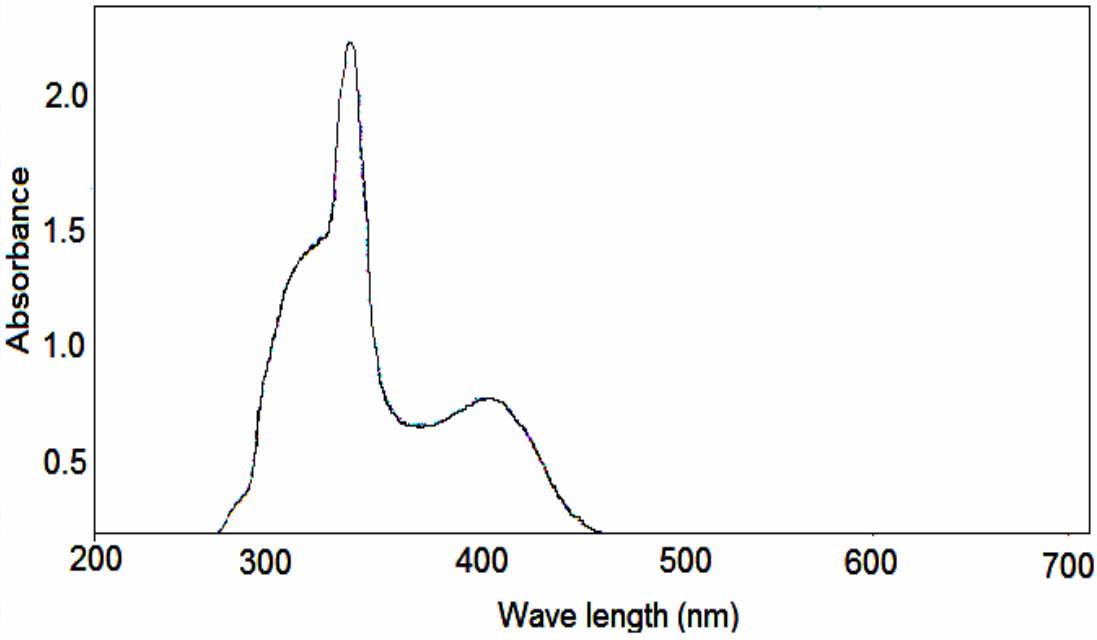


Figure 4 The UV-visible spectra of 3O2O3 compound

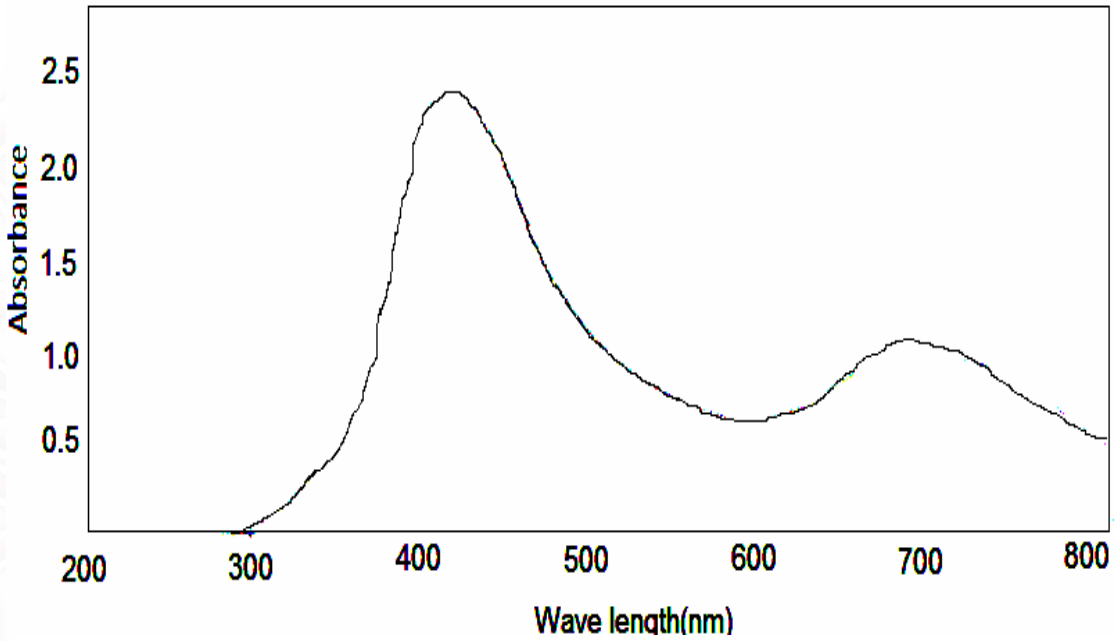


Figure 5 The UV-visible spectra of Cu 3O2O3 compound

Mesomorphic behavior

Mesogenic properties of dimeric series (nO2On) and complexes series (Cu nO2On) were examined by DSC and optical microscopy. The transition properties of the dimers and complexes are listed in table 3 and 4. All members of the dimers series exhibit an enantiotropic nematic phase with typical Schielern pattern as shown in Figure 6. While the series Cu nO2On exhibit smectic A phase typical small fan shape pattern.

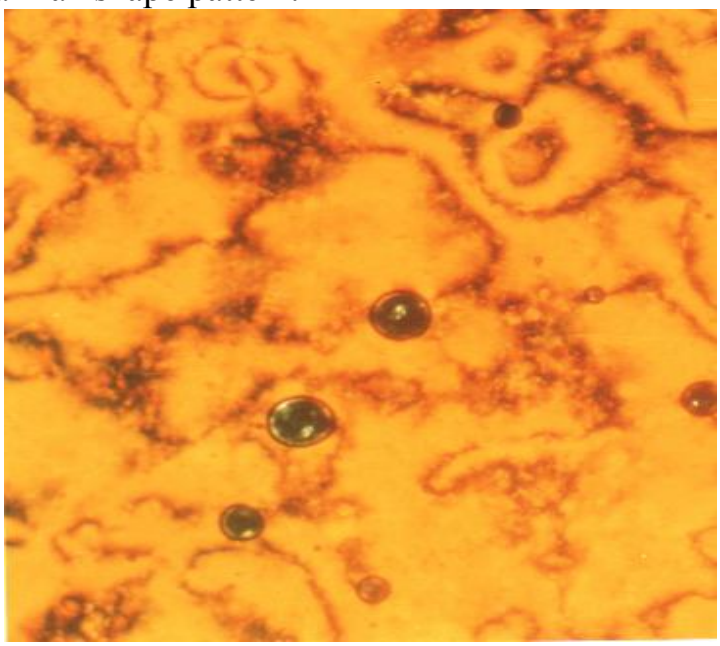

Figure 6 Texture of nematic phase of compound 4O2O4

The dependence of the transition temperature on the number of carbon atoms, n, in the alkoxy chain for the series nO2On and Cu nO2On is showed in

Figure 8. It is immediately apparent that the melting points, the nematic – isotropic temperatures, and thesmectic-isotropic temperature are show adramatic odd-even effect and it isattenuated on increasing n. The transition temperature which exhibited by the Cu nO2On compounds are generally higher than the temperature which exhibited by the nO2On compounds because increase the increasing the cohesive enrage which result from the hydroxyl groups in 2-position and azomethine groups leads to a strong chelating to copper metal by mean of intramolecular hydrogen bonding.

**Table (3): phase transition temperature for nO2On series**

| Compound | Nematic (N) | Isotropic (I) | ΔT |
|---|---|---|---|
| 1O2O1 | 175 | 210 | 45 |
| 2O2O2 | 170 | 225 | 55 |
| 3O2O3 | 160 | 203 | 43 |
| 4O2O4 | 165 | 216 | 51 |
| 5O2O5 | 155 | 197 | 42 |
| 6O2O6 | 162 | 209 | 47 |
| 7O2O7 | 153 | 194 | 41 |

**Table (4): phase transition temperature for Cu nO2On series**

| Compound | Smectic (N) | Isotropic (I) | ΔT |
|---|---|---|---|
| 1O2O1 Cu | 195 | 221 | 26 |
| 2O2O2 Cu | 203 | 241 | 38 |
| Cu 3O2O3 | 187 | 218 | 31 |
| 4O2O4 Cu | 195 | 230 | 35 |
| 5O2O5 Cu | 184 | 109 | 25 |
| Cu 6O2O6 | 187 | 219 | 32 |
| Cu 7O2O7 | 181 | 201 | 20 |

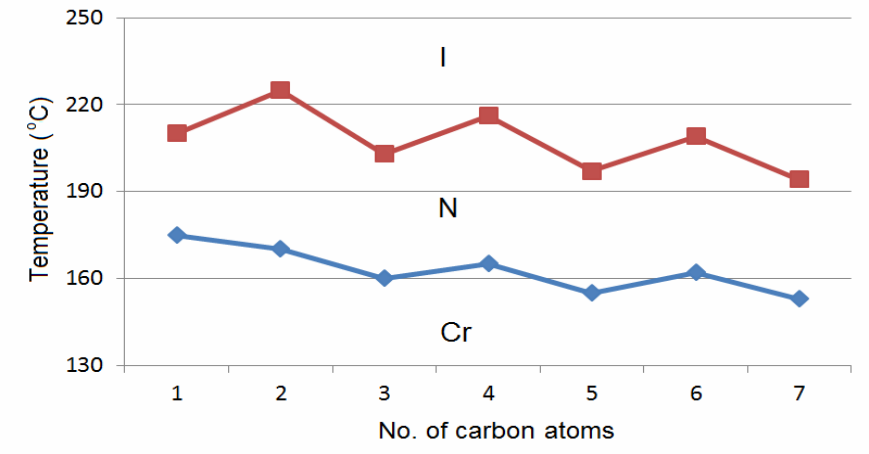


Figure 3 Represented the relationship between the number of carbon atoms and the transition temperature for the dimers nO2On

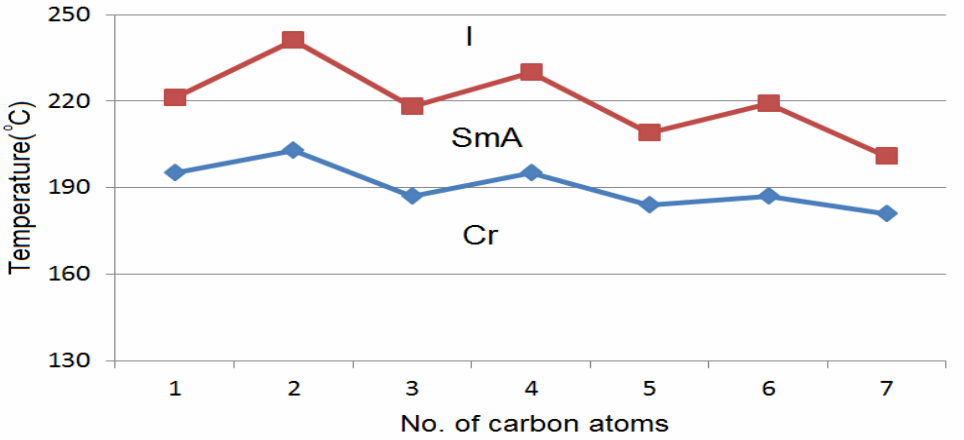


Figure 4 Represented the relationship between the number of carbon atoms and the transition temperature for the complexes Cu nO2On

References:

1- D. Bruce, K. Heyns and V. Vill, Liq.Cryst., 813,23,1997.
2- A.Giroud and V.Mueller-Westeroff, Mol.Cryst.Liq.Cryst.Lett.11, 41, 1977.
3- B.Donnin and D.Bruce, Structure and Bonding, Ed. D.M.P. Mingger, Springer- Verlag, P193, Chapter 5, 1999.
4- K.Binnemans and C.Gorller-Walarnd,Chem.Rev., 2303, 102, 2002.
5- L.Oriol, M. Pinol and L. Serrano, Prog.Polym.Sci., 873, 22,1997
6- C.T. Imire and G.R.Luckhurst, J.Mater.Chem.,1339, 8,1998.
7- A. Hameed, N. Saleh and A. Al- Dujaili, National J. Chem., 121, 5, 2002.
8- J. Dave and r.Vora, Liquid Crystals and Ordered Fluids, Plenum Press, NewYork, 477, 1970.
9- M. Marcose, P. Romero and J. Serrano, Chem. Soc. Chem. Commum., 1641, 21,1989.
10- P. Lemasurier and G. Luchurst, J.Chem. Soc. Faraday Trans., 1593, 94, 1998.