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Research Article

SYNTHESIS OF SERIES CHEMICAL COMPOUNDS AND STUDYING OF THEIR APPLICATIONS (LIQUID CRYSTAL, THERMO-PHYSICAL), BIOLOGICAL ACTIVITY, COMPLEXATION WITH PB (II)

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ABSTRACT

Objective: Series new organic compounds were synthesized and identified in our paper via types of reactions represented by condensation reaction, alkylation reaction, and cyclization reaction.

Methods: Preparation of many compounds through various reactions which studied several applications such as liquid crystal (LC), differential scanning calorimetry (DSC)-measurement, complexation with ion Pb, and other chemical studies such as conditions of complex.

Results: The structure of the newly compounds were investigated using thin-layer chromatography-plate and many techniques (Fourier transform-infrared, ^{1}H nuclear magnetic resonance, ultraviolet-visible, determination of optimal conditions, ratio of ligand:metal [L: M], molar conductivity measurements, some physical characterization) then studying the biological activity of compounds.

Conclusion: All compounds appeared application in LC, as ligands with lead ion Pb (II), it gave mole ratio of L:M (1:1) as a complex, they have been appeared high stability in DSC-measurements and gave good activity in biostudying against bacteria.

Keywords: Liquid crystal, Differential scanning calorimetry, Azo, Schiff, Pb, Biological active, Formazan.

INTRODUCTION

Liquid crystals (LCs) are a state, which has properties between the liquid and crystal. For instance, an LC may flow like a liquid, but its molecules may be oriented in a crystal-like way. There are various types of LC phases; it can be distinguished by their different optical properties such as birefringence. When showed under a microscope via a polarized light source, types of LC phases will appear to have distinct textures [1-4].

In general, LC materials have many common properties. Among these are rod-like molecular structures, rigidness of the axis, and strong dipoles or simple polarizable groups.

The distinguishing characteristic of the LC state is the tendency of the molecules (mesogens) to point along a common axis. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, compounds are highly ordered and have little translational freedom. The characteristic orientational order of the LC state is between the traditional solid state and liquid phases, and this is the origin of the name mesogenic state [5-9].

The Fig. 1 illustrating the thermal process of phases is placed just above the temperature axis (at one atmosphere pressure). This contains a crystal to LC phase (Smectic A) transition at 50°C followed by a barely detectable Smectic A phase to nematic phase transition at 70°C and finally the nematic to isotropic (NI) transition near 90°C. The upper, cooling, curve shows a slight displacement of the NI transition, partially due to high cooling and partially instrumental hysteresis attributable to the temperature scan rate. The Smectic A to crystal transition is depressed strongly due to high cooling of the Smectic A phase [10-14]. The phase figure for the cooling process and heating are shown in Fig. 2.

METHODS

Instrumentation

1. Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected
2. Fourier transform-infrared (FT-IR) spectra were recorded using FTIR 8300 Shimadzu in the range 400-4000/cm as KBr discs
3. Ultraviolet-visible (UV-VIS) spectra
4. ^{1}H nuclear magnetic resonance (NMR) - spectra in dimethyl sulfoxide-solvent were carried out in Canada
5. Differential scanning calorimetry (DSC) - thermal analysis in Canada
6. Polarized optical microscope (POM) in Canada
7. Molar conductivity measurements in Canada
8. Physical with analytical studies and biological studies carried out in Baghdad and Kufa Universities.

Procedures

Synthesis of compound (1)

P-hydroxy benzoic acid (0.01 mole) was reacted with 0.01 mole of pentyl chloride (3 hrs) in the presence of potassium carbonate in absolute ethanol as a solvent according to literature [15-17], to yield precipitation which filtered and dried then recrystallized to yield compound (1).

Synthesis of compound (2)

Compound (1) is (0.01 mole) refluxed with ethanol for 4 hrs in the presence of concentrated H_2SO_4 acid according to literature [16], precipitation which filtered and dried then recrystallized to yield ester compound (2).

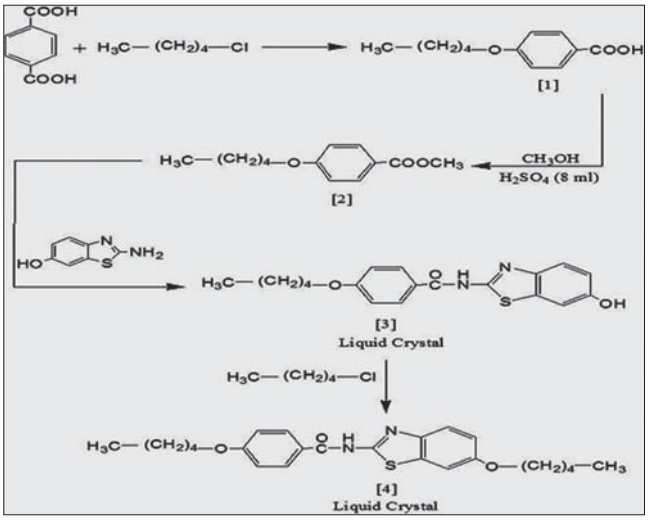
Synthesis of compound (3)

A mixture of 0.01 mole compound (2) with 0.01 mole of 4-hydroxy-2-amino benzothiazole was reacted, with refluxing for 5 hrs in absolute ethanol according to literature [16], after that it gave precipitation, filtered and dried then recrystallized to yield compound (3).

Synthesis of compound (4)

Compound (1), which has (OH)-terminal (0.01 mole), was reacted with 0.01 mole of pentyl chloride (4 hrs) in the presence of potassium carbonate in absolute ethanol as a solvent according to

literature [15-17], to yield precipitation which filtered and dried then recrystallized to yield compound (4).



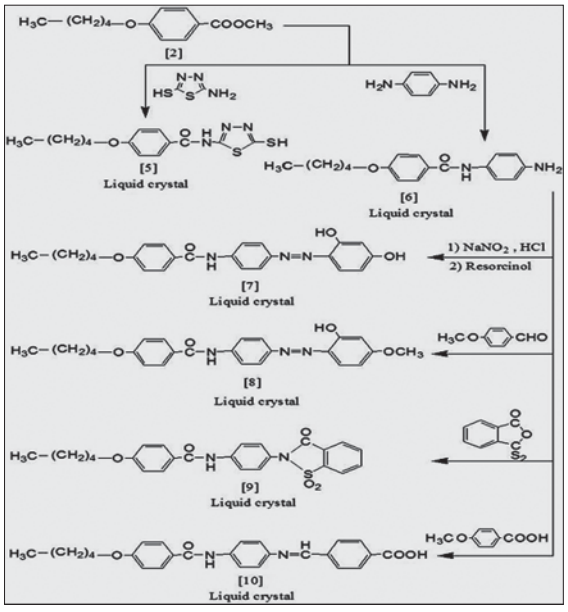
Preparation of compounds (1–4)

Synthesis of compounds (5) and (6)

0.01 mole of compound (2) was refluxed with 0.01 mole of (5-mrcapto-2-amino thiadiazol, p-phenylene diamine), respectively, in the presence of ethanol as a solvent, according to studies [16], then it gave precipitation which filtered and dried then recrystallized to produce compounds 5 and 6, respectively.

Synthesis of compounds (7-10)

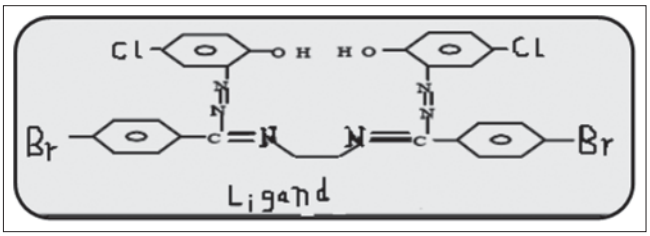
Compound (6) was dissolved in 2 ml of hydrochloric acid, then solution of sodium nitrite was added at 0-5°C, then added to solution of resorcinol according to studies [15-17], after 48 hrs gave precipitation which filtered and dried then recrystallized to yield azo-ether compound (7), while compound (6) reacted with p-methoxy benzaldehyde in presence of absolute ethanol as a solvent and (drops) of glacial acetic acid, to produce compound (8), to prepare compound (9), 0.01 mole of compound (6) was heated with sulfobenzoic acid in presence of acetone as a solvent at 180°C to give compound (9), compound (6) reacted with 0.01 mole from p-benzoic benzaldehyde in refluxing for 4 hrs, then it produced precipitation which filtered and dried then recrystallized to yield compound (10).



Preparation of compounds (5–10)

Synthesis of ligand (11)

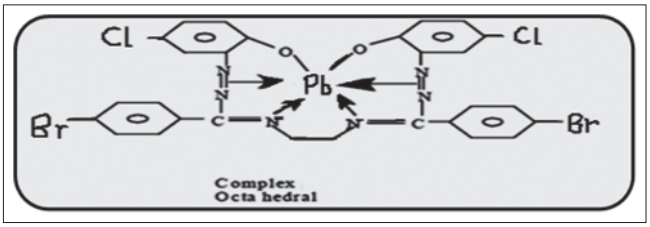
0.01 mole of hydrazine was refluxed with 0.02 mole of p-bromo benzaldehyde for 3 hrs in presence of glacial acetic acid, to yield precipitation which filtered and dried then recrystallized to yield initial compound, which reacted in ethanol in beaker, while 4-chloro-2-amino phenol dissolved in 3 ml of hydrochloric acid, then solution of sodium nitrite was added, after that reaction with mixture solution according to paper [19], after 36 hrs gave precipitation which filtered and dried then recrystallized to yield ligand (11).



Preparation of ligand (11)

Preparation of complex with (Pb^{2+})

According to procedure [19], the complexation of ligand was prepared through mixed of the hot solution of ligand of formazan (11) was mixed with of lead chloride ($PbCl_2$) according to optimal conditions which tested in this work with mole ratio metal:ligand (M:L) (1:1), after mixing and stirring for 1.5 hrs, the precipitate was precipitated, dried, and recrystallized to give complexes (Pb [ligand]).



Preparation of complex [Pb (ligand)]

RESULTS

All formatted compounds (1-11) and complex will identify them by spectral methods such as FTIR and H NMR**.**

Organic investigation

The FT-IR investigation

Absorption bands appeared at 1170-1198/cm in all compounds (1-10) due to ether (C-O-C) group, and other bands are appeared at 3287-3200/cm for (NH) amide of groups in compounds (3-10), and amine (NH_2) at 3240, 3375/cm for amine group [15-19] in compound (6). While compound (7) and ligand (11) appeared bands at 1467-1496/cm for azo [19] groups (-N=N-), and other bands listed in Table 1 and some Figs. 3-5.

This is the first evidence of preparation of compounds (1-11), which gave good results about the appearance of functional groups in these compounds in our work through sharp frequency for active groups such as amine (NH), thiol (SH), carbonyl of ester, or carbonyl of carboxylic acids in the Figs. 3-5 and Table 1 which indicates to right procedures for preparation of compounds through comparison with past studies in same fields.

The ^1H NMR-spectra

Showed peaks at Б {δ (13.08, 13.23) for proton of (COOH) carboxyl groups in compounds (1,10), respectively. While compounds (3,7) showed signal at Б (11.02, 11.17) for protons of (OH) phenol, compound (6) appeared peak at Б (5.12) for NH_2 group}. However, compounds (3-10) showed signals at Б (10.04-10.27) for proton of (-CO-NH) amide groups, respectively, and other signals in Table 2 and Figs. 6-8.

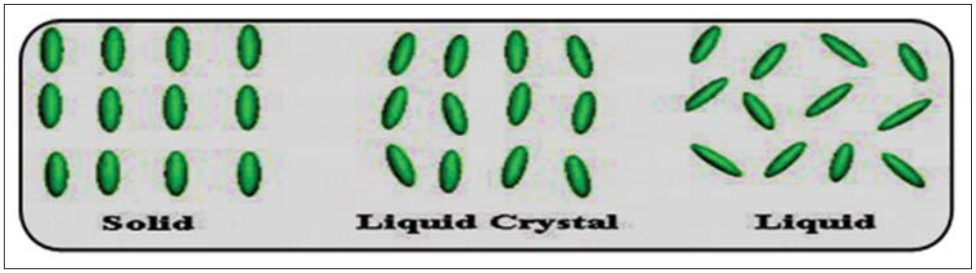


Fig. 1: The phases of liquid crystals

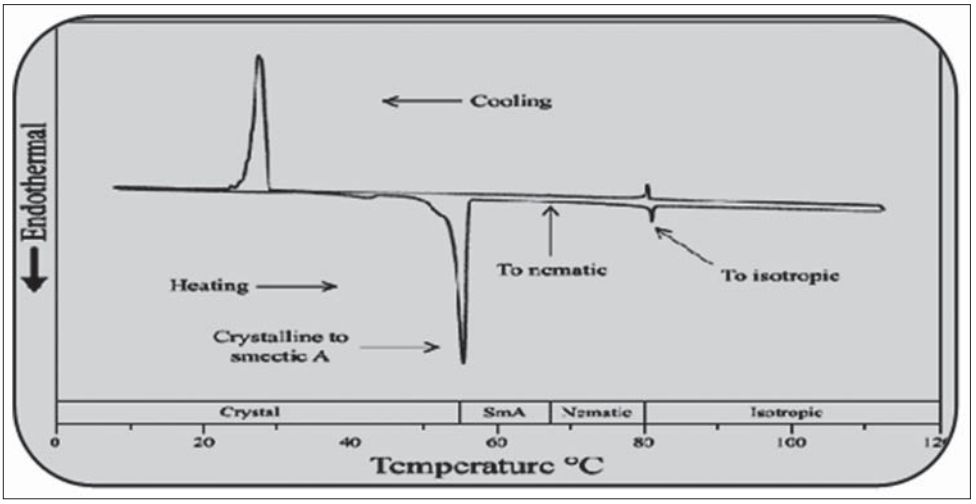


Fig. 2: The cooling process and heating

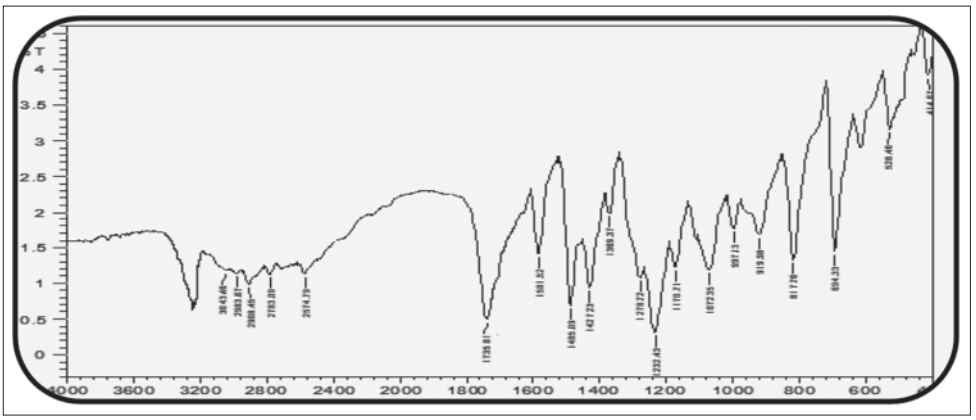


Fig. 3: Fourier transform-infrared of compound (1)

Table 1: FT-IR-data (cm^{-1}) of compounds (1-11) and complex

Compounds	IR $_{(KBr)}$ (only important groups)
1	CO-O- of carboxyl group: 1714, OH of carboxyl group: 2630-3100, C-O-C ether: 1170
2	CO-O- of carbonyl of ester group: 1723, C-O-C ether: 1198
3	OH: 3456, C-O-C ether: 1176, CO-NH amide: 3287, -CO amide: 1678, C-S: 677
4	C-O-C ether: 1185, CO-NH amide: 3266, -CO amide: 1683, C-S: 689
5	SH: 2410, C-O-C ether: 1187, CO-NH amide: 3278, -CO amide: 1690, C-S: 692.
6	NH_2: 3244, 3256, C-O-C ether: 1181, -CO amide: 1684
7	OH: 3493, C-O-C ether: 1179, CO-NH amide: 3197, -CO amide: 1696, -N=N- azo: 1467, 1496
8	C-O-C ether: 1173, CO-NH amide: 3213, -CO amide: 1694, C=N imine group: 1617
9	C-O-C ether: 1181, CO-NH amide: 3263, -CO amide: 1686, SO_2 sulphone: 1378
10	C-O-C ether: 1175, CO-NH amide: 3236, -CO amide: 1685, C=N imine group: 1614, CO-O- of carboxyl group: 1726, OH of carboxyl group: 2643-3120
Ligand 11	C=N imine group: 1620, OH: 3487, -N=N-: 1496, 1480
Complex (Pb[Ligand])	C=N imine group: 1607, -N=N-: 1476, 1448, M-O: 576, M-N: 496

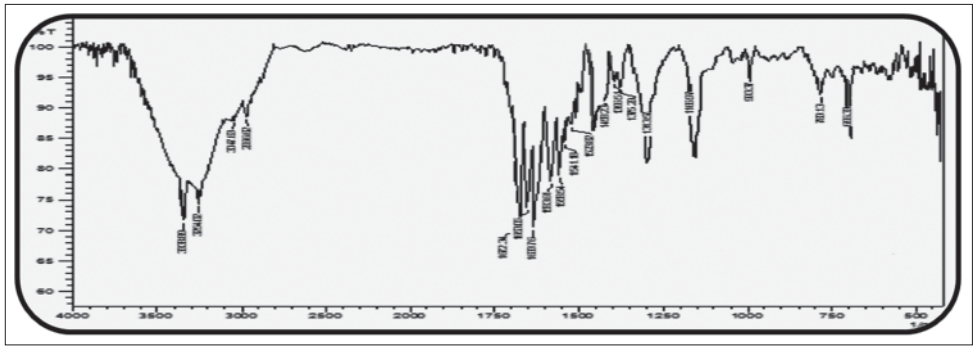


Fig. 4: Fourier transform-infrared of compound (6)

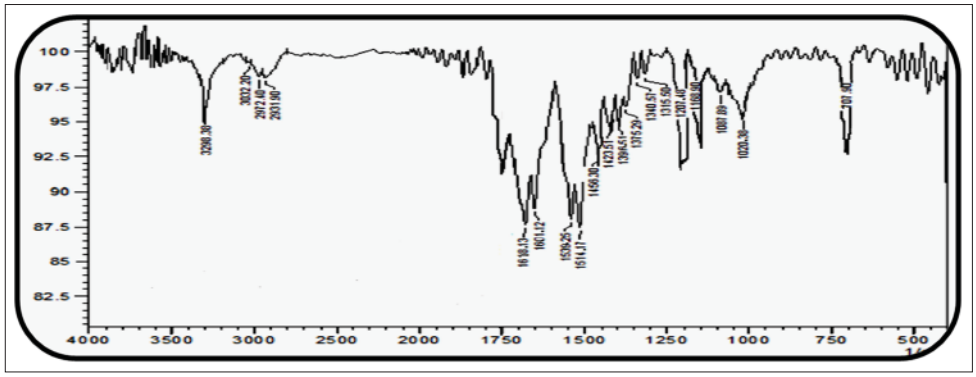


Fig. 5: Fourier transform-infrared of compound (8)

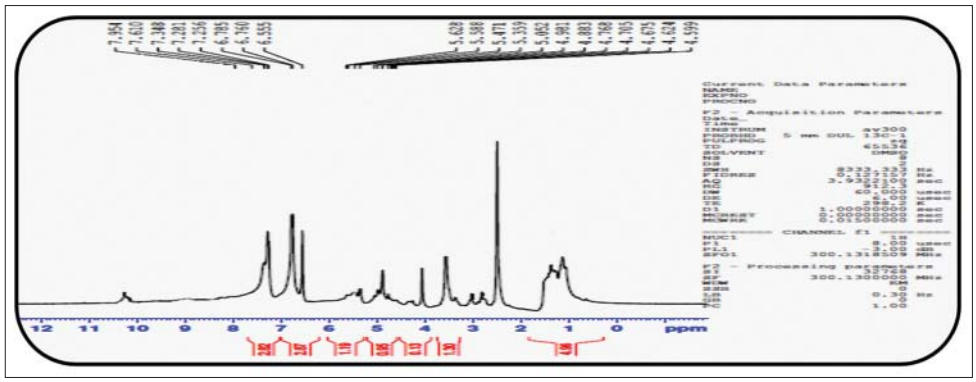


Fig. 6: H nuclear magnetic resonance of compound (4)

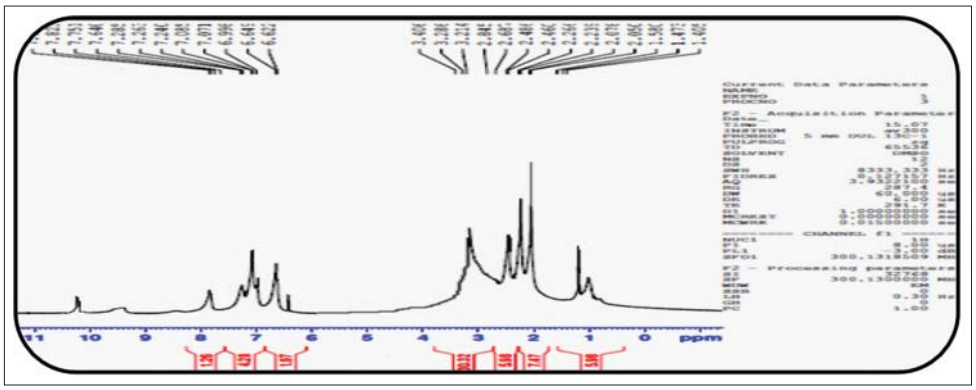


Fig. 7: H nuclear magnetic resonance of compound (9)

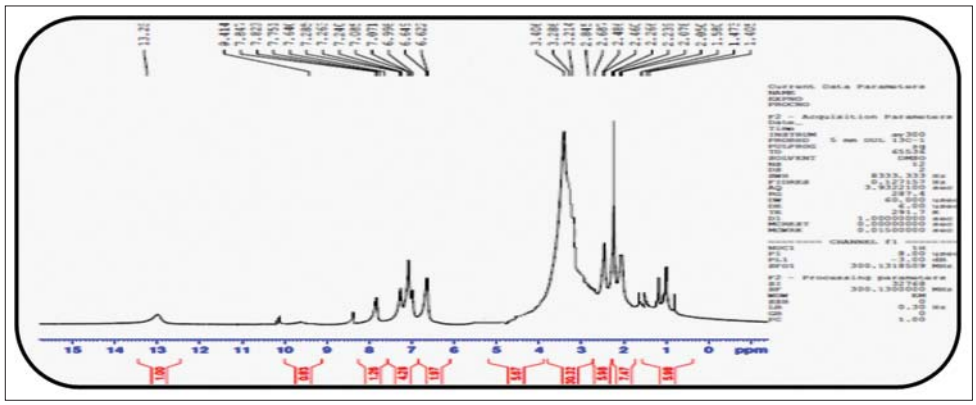


Fig. 8: H nuclear magnetic resonance of compound (10)

Table 2: H NMR-data (δ - ppm) of compounds (1-11) with complex

Compounds	H NMR ((important peaks))
1	CO-OH proton of carboxyl group: 13.08
2	CO-OCH_3 proton of methyl ester group: 3.32
3	OH proton of phenol: 11.02, CO-NH proton amide: 10.04
4	CO-NH proton amide: 10.22
5	CO-NH proton amide: 10.11, SH: 12.13
6	CO-NH proton amide: 10.21, NH_2 amine: 5.12
7	CO-NH proton amide: 10.28, OH phenol: 11.19
8	CO-NH proton amide: 10.14, CH=N proton of imine: 8.29
9	CO-NH proton amide: 10.25
10	CO-OH proton of carboxyl group: 13.23, CO-NH proton amide: 10.27, CH=N proton of imine: 8.24
Ligand 11	OH phenol: 11.33
Complex (Pb[Ligand])	Proton of phenol disappeared due to coordination

NMR: Nuclear magnetic resonance

The Figs. 6-8 and Table 2 appeared sharp signals due to active groups in synthesized compounds, which acts second indicators for formatted compounds, which gave good results about appearance of functional groups in these compounds in our work through sharp peaks for active groups such as hydroxyl of carboxylic acid (OH), mercaptan terminal (SH), amine, which indicates to right procedures for preparation of compounds through comparison with past studies in same fields.

DISCUSSION

The present paper involved preparation of new compounds (1-11) and the complex will characterize them by a spectral method-like UV-VIS and study some of the physical and thermo analysis with chemical applications such as LC, thermo-analysis, the conductivity of ligand and complex, and biochemical studying.

Studying of POM

This work involved studying of phases of compounds, the behavior of compounds as an LCs by following with optical microscope through heating compounds with different temperatures.

From results some Figs. 9-11, we found compounds (3-10) are LCs, for some compounds by optical microscope measurements, which gave all phase for each of compounds at various temperatures represented by (solid phase, nematic phase, liquid phase, and LC phase) in clear photo under the microscope.

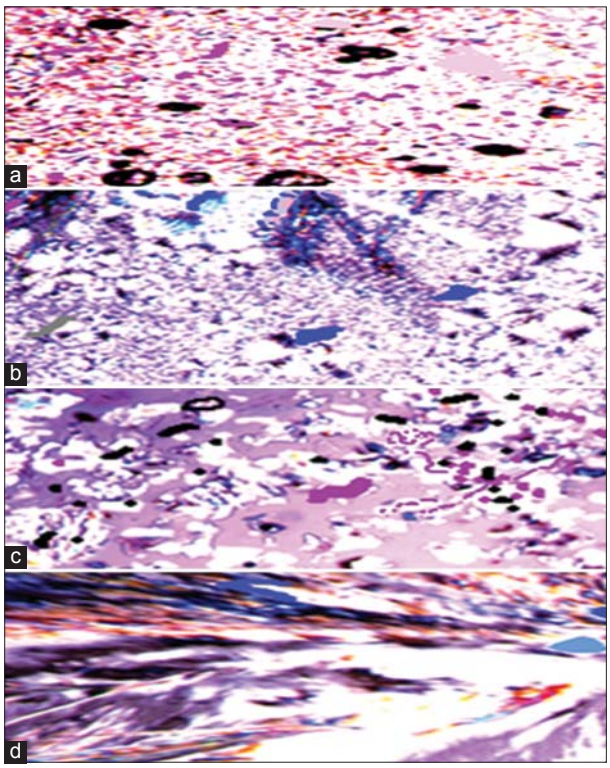


Fig. 9: (a) Crystal phase at 40°C for compound (3), (b) nematic phase at 85°C for compound (3), (c) liquid phase at 160°C for compound (3), (d) liquid crystal phase at 115°C for compound (3)

Thermal studying (DSC-measurements)

DSC-measurements of compounds (3-10) measured for the stability of hetero cycles-azo or azomethine compounds or ether compounds in some Figs. 12-14, DSC-curves showed high stability toward high temperature.

The Figs. 12-14 gave measurements of thermal studying for the stability of ether, azo, imine, thiazole compounds or cyclic compounds, DSC-curves showed a high stability toward high temperature; all prepared compounds appeared stability at various temperatures and high temperatures.

Physical and chemical properties [20,21]

Physical and chemical properties represented by R_f of thin-layer chromatography (TLC) - technique for following the reactions, type of solvent which is used in TLC-plate, and products from reactions %, all data are listed in Table 3.

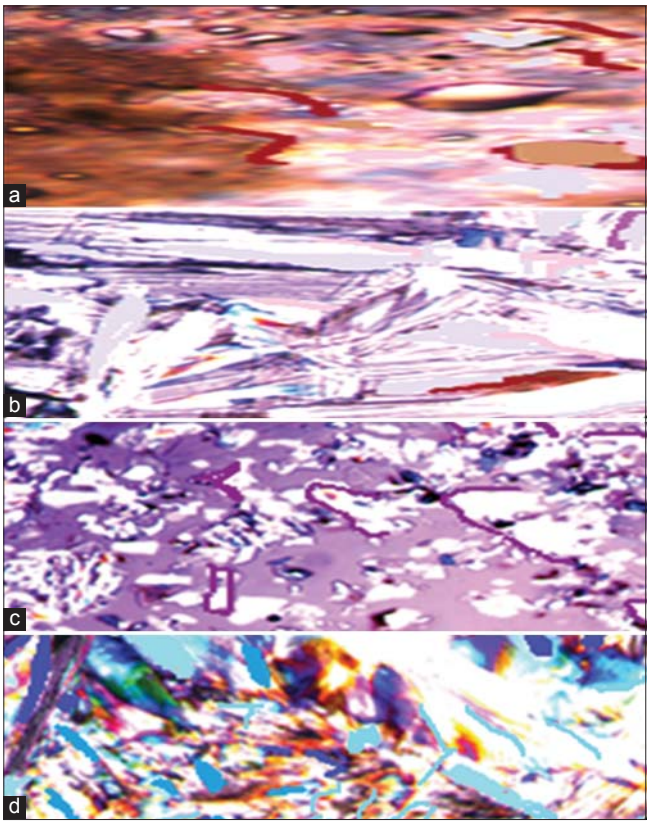


Fig. 10: (a) Crystal phase at 35°C for compound (8), (b) nematic phase at 80°C for compound (8), (c) liquid phase at 155°C for compound (8), (d) liquid crystal phase at 110°C for compound (8)

The procedures for preparation of all compounds gave a high percentage of products in high yield with good purity, and the used solvents depend on polarity and nature of formatted compounds in this work.

Coordination studying (complexation)

A. Testing of optimal conditions for complex:
Through this work, the optimal concentration for ligand and Pb ion, the optimal concentration of Pb2+=0.75×10−4 M, while concentration of ligand (0.5×10−3 M of formazan ligand) only this concentration gave best absorbance but higher than this concentration due to deviation in linearity of lambert –peer law.
While optimal pH of complexes were (pH=8 for complex) which acts best medium to remove proton of ligand to coordinate with ion.
while the stoichiometry of complex in mole ratio procedure [19] gave (M:L) ratio (1:1) for complex which indicate to each ligand coordinate with one metal ion through oxygen atom of hydroxyl and nitrogen atom of azo group and nitrogen atom of imine group , this appeared in absorbance of system of ultra-violet

B. Mole ratio and wavelength for ligand and complex:
Maximum wavelength was screened for ligand, and it complexes with Pb-ion by UV-VIS. All results (mole ratio, calibration curve, stoichiometry, and chemical spectra) and physical properties indicate that the Pb-complexes with all ligands were stoichiometry M: L (1:1) (Table 3 and Figs. 16-18).

From Table 3 and Figs. 16-18, the stoichiometry of complex in mole ratio procedure [19] gave (M: L) ratio (1:1) for complex, and other chemical and physical measurements of complex in Fig. 18.

C. The conductivity of complexes:
From results of physical measurements such as molar conductivity measurements for ligand and its complex which was 1.36 ohm^{-1}. $mole^{-1}.cm^2$ with concentration (1×10^{-3} M) solution which indicates that the Pb-complexes is non-electrolytic in nature (Table 4).

Table 4 appeared conductivity of complex (1.36), this is evidence that the complex (non-electrolyte), which gave a good indicator that there is no chloride ion in the complex.

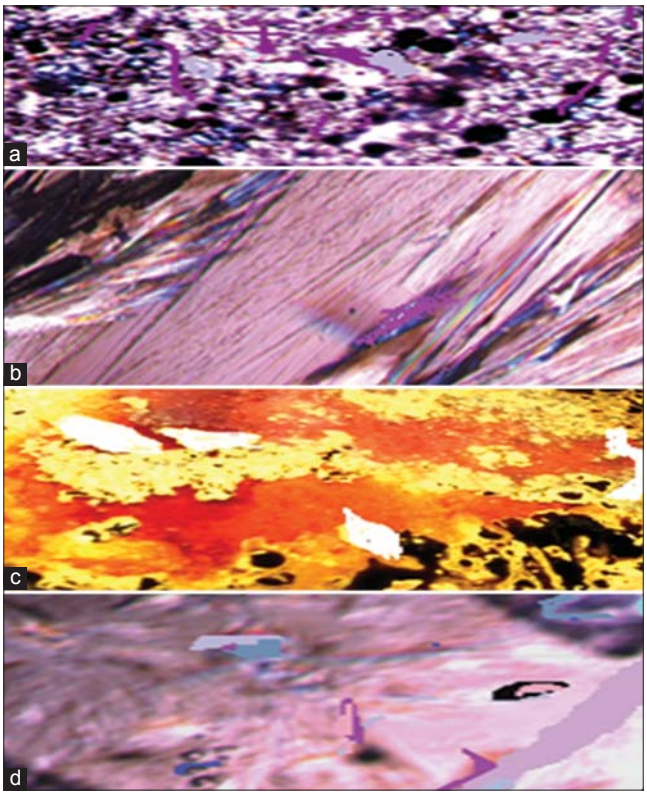


Fig. 11: (a) Crystal phase at 30°C for compound (10), (b) nematic phase at 85°C for compound (10), (c) liquid phase at 145°C for compound (10), (d) liquid crystal phase at 100°C for compound (10)

Table 3: Some physical and chemical properties for compounds (1-11)

Compounds	Products %	R_f	Solvents of TLC
1	77	0.74	Ethanol: Hexane
2	72	0.68	Ethanol: Hexane
3	76	0.66	Ethanol: Hexane
4	76	0.78	Ethanol: Hexane
5	70	0.70	Ethanol: Hexane
6	80	0.68	Ethanol: Hexane
7	74	0.82	Ethanol: Hexane
8	70	0.62	Ethanol: Hexane
9	82	0.76	Ethanol: Hexane
10	80	0.60	Ethanol: Hexane
Ligand 11	84	0.66	Ethanol: Hexane

TLC: Thin-layer chromatography

Table 4: Spectral and chemical data for ligands with complexes

Ligand and complex	MP (C°)	$ohm^{-1}.cm^2.mole^{-1}$ conductance
Ligand 11	176	-
Complex (Pb [Ligand])	168	1.36

MP: Molecular formula

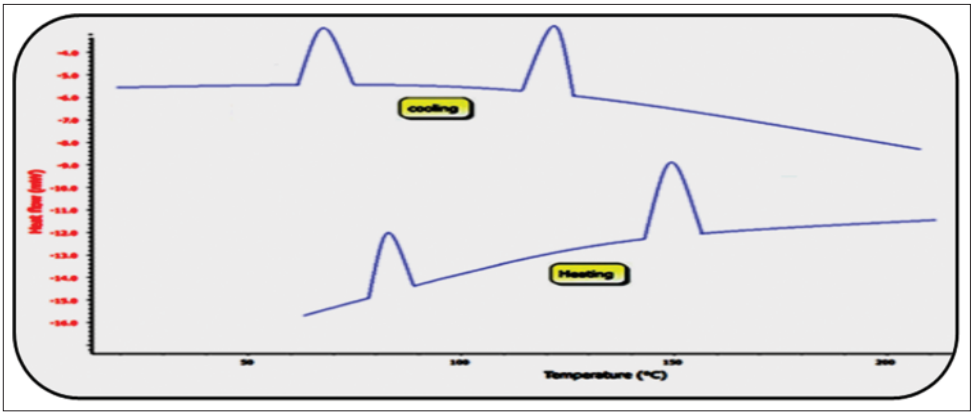


Fig. 12: Differential scanning calorimetry of compound (3)

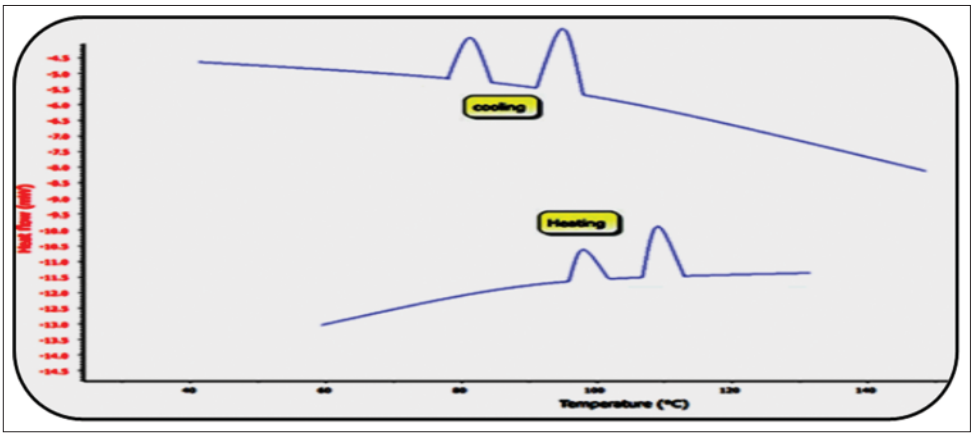


Fig. 13: Differential scanning calorimetry of compound (8)

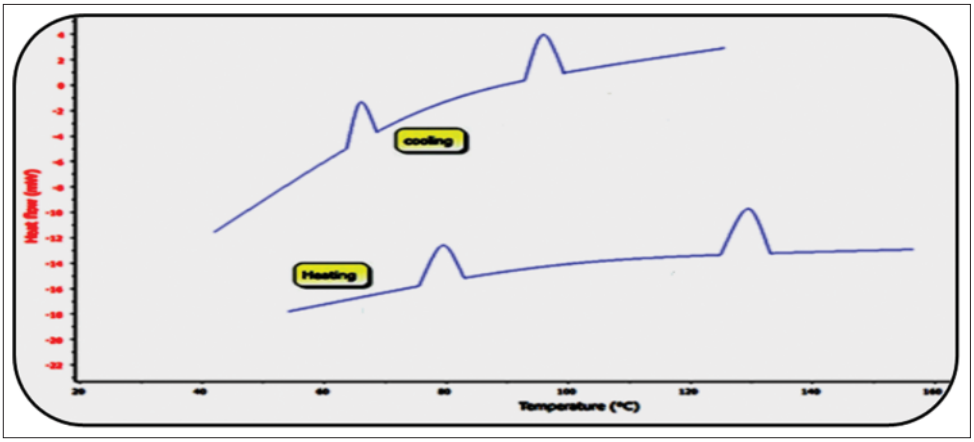


Fig. 14: Differential scanning calorimetry of compound (10)

Antimicrobial studying

The compounds (1-11) with complex were tested according to their action against bacteria are described in Table 5. The presence of heterocyclic rings such as benzothiazole and thiadiazole are reported to possess antibacterial effect may enhance or increase the biological activity of the sulfur derivatives.

The antimicrobial results are listed in Table 5 and (Figs. 19, 20). From results of antibacterial studies, it was found to be potentially activity against all types of bacteria, which gave evident from the results that the biological activity of all compounds has high biological activity which inhibits the growth of bacteria.

The compounds (5,9,4,3, complex) have higher activity than other compounds may be due to the fact that is an essential micronutrient during transcription and transformation of nuclei.

Acids which shown to inhibit cellular protein and RNA synthesis, they included some groups with sulfur atoms and hence inhibit the bacterial growth.

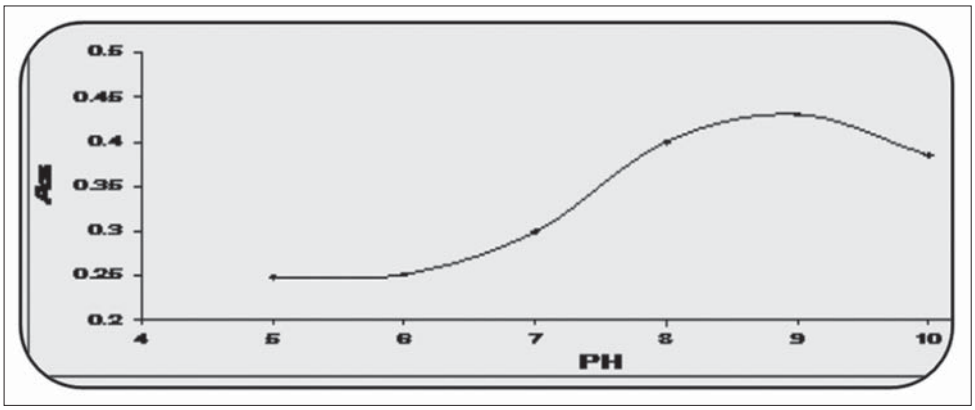


Fig. 15: Determination of optimal pH of complexes

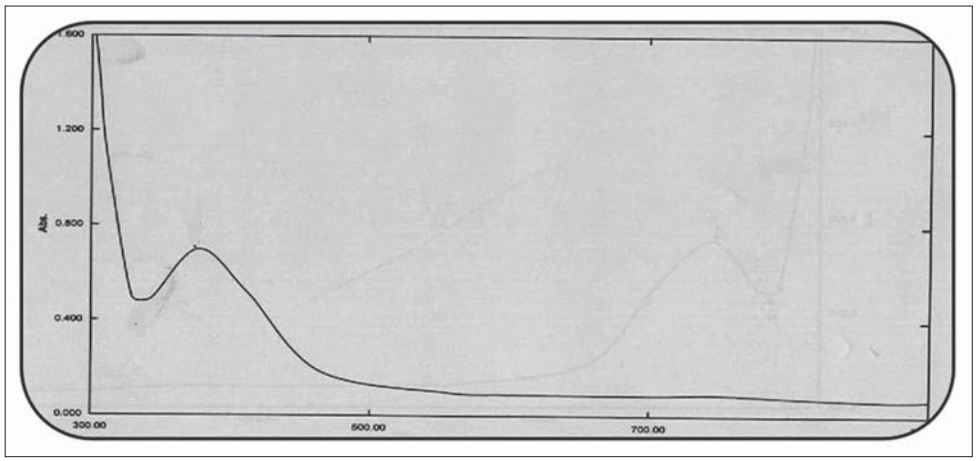


Fig. 16: Ultraviolet-visible of ligand

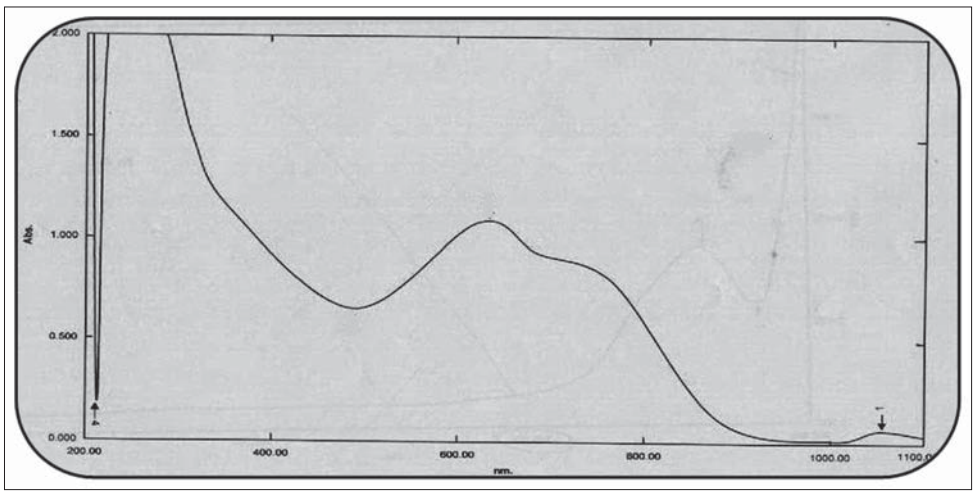


Fig. 17: Ultraviolet-visible of complex [Pb(ligand)]

Furthermore, the mechanism of action of the compounds may involve the formation of a hydrogen bond with the active centers of the cell constituents resulting in the interference with the normal cell process.

Hydrogen bonding and the antimetabolite action of the compound may be an important factor in antimicrobial activity. The prepared compounds gave excellent activity against bacteria.

CONCLUSION

The compounds (1-10) appeared in LC behavior, as ligands with lead ion Pb (II), which gave mole ratio of L: M (1:1) as a complex; they have been appeared high stability in DSC-measurements and gave good activity in biostudying against bacteria**.**

Table 5: Antibacterial activity of compounds (inhibition zone in mm) of compounds (1-11) and complex in concentration (150 mg.ml^{-1})

Compounds	*P. aeruginosa*	*B. subtilis*
1	10	6
2	10	8
3	24	14
4	24	16
5	28	22
6	12	6
7	14	8
8	16	10
9	24	20
10	16	12
Ligand 11	18	14
Complex	22	16

P. aeruginosa: *Pseudomonas aeruginosa, B. subtilis: Bacillus subtilis*

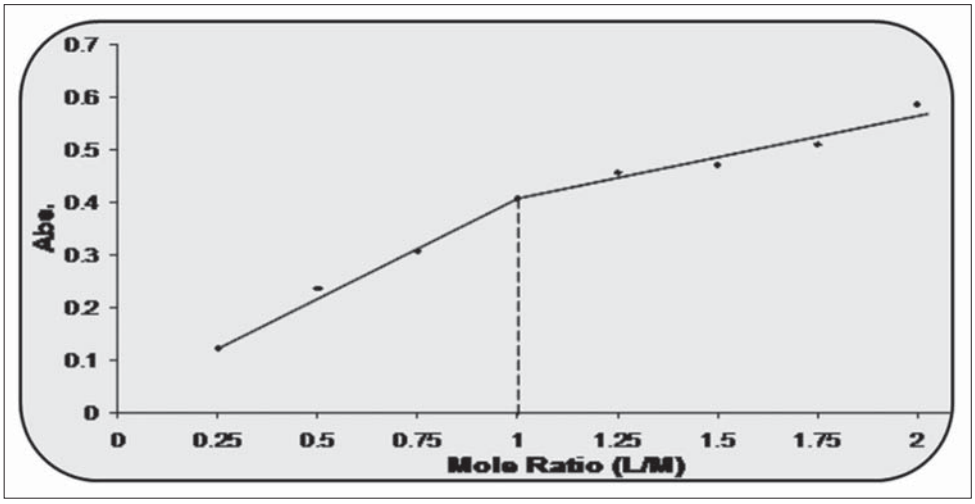


Fig. 18: Mole ratio of complex (Pb [ligand])

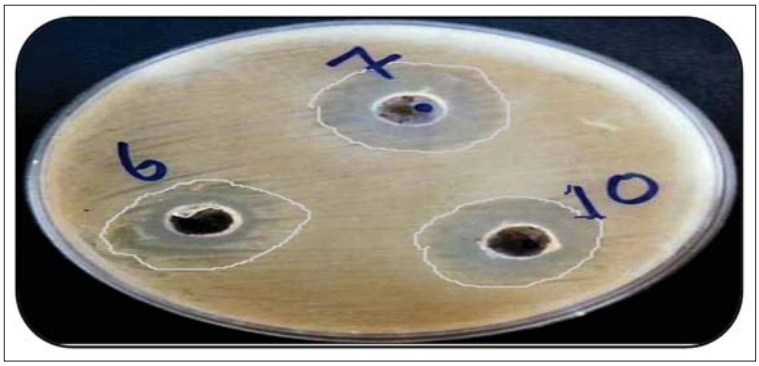


Fig. 19: Inhibition zone of compounds (6, 7, 10) against *Pseudomonas aeruginosa*

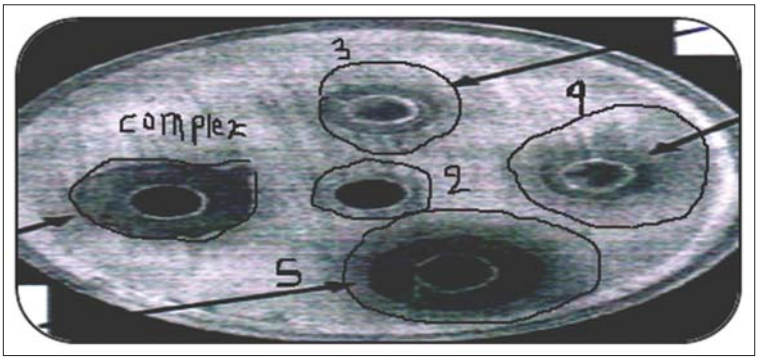


Fig. 20: Inhibition zone of compounds (2, 3, 5,9) against *Pseudomonas aeruginosa*

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