



Synthesis, Spectroscopic and Liquid Crystalline Studies of Dithiocarbamate Derivatives of Pyrazole Type Ligands and their Metal Complexes

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Abstract

In this study, two chalcone compounds were synthesized from the reaction of (diketone [I]a,b) with (4- methoxy benzaldehyd). In the second step two pyrazoles type preligands were synthesized from the reaction of prepared chalcones [II]a,b with (Hydrazine Hydrate) in a 1:2 ratio. The compounds characterized by FT-IR and NMR spectroscopic methods. Metal complexes of pyrazoles thiocarbamate were synthesized via a one pot step reaction of preligand, metal salt and CS₂ with (2:2:4) mole ratio. All complexes characterized by physiochemical and spectroscopic techniques (FT-IR, ¹H-NMR, magnetic susceptibility, conductivity, atomic absorption spectrophotometer (A.A), melting points and elemental analysis CHN), which revealed tetrahedral geometry around metal centers. The liquid crystalline behavior for prepared compounds studied via Hot-Stage Polarizing optical microscope (POM) and Differential Scanning Calorimetry (DSC). The preligands showed enantiotropic Nematic mesophase with a wide thermal stability range and some of the complexes also showed liquid crystalline properties.

Keywords: Pyrazole, Dithiocarbamate, Complexes, Liquid crystal.

1. Introduction

pyrazole derivatives represent an important class containing of nitrogen atoms in five membered heterocyclic compounds that has attracted great interest in recent years due to wide spread applications as pharmaceutical agents, synthetic scaffolds in combinatorial and medicinal chemistry, photographic couplers, chelating agents in coordination chemistry and agrochemical products.(1) The pyrazole unit is an integral part of many biologically active natural products.(2)

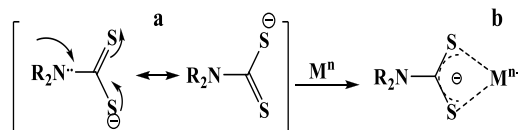
A common approach relies on the use of suitable ligands to form a metal complex. One of the most studied ligands is pyrazole, which occupies a special position as a building block in chemistry.(3) Pyrazolate is the conjugate base of pyrazole and has three coordination modes anionic monodentate, endo-bidentate and exo-bidentate, as seen in

Fig. 1.(b). Exobidentate is the most common mode in organometallic chemistry, and the one that prompted the use of pyrazolates for bridging two metallic centers.(4)

Coinage metals are unique among the transition metals as they are capable of forming binary metallic pyrazolates [M(□-Pz)]_n.(5)



Figure (1). (a) Deprotonation of 1H-pyrazole to produce pyrazolate, (b) Coordination modes of pyrazolate to a metal, in organometallic chemistry.



Figure(2). Resonance hybrid of metal-dithiocarbamates

Dithiocarbamates are one of a range of compounds; dithiocarbamate, xanthate, thioxanthate and dithiophosphate.(10,11) These can be prepared from

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reaction of carbon disulfide with nucleophiles (Z^-) such as nitrogen, oxygen, sulfur and phosphorus. The reaction of carbon disulfide and either primary or secondary amines in the presence of alkali base (NaOH, KOH) or excess of amine resulted in the formation of dithiocarbamates. (12,13) liquid crystals can act as an important component in various applications such as liquid crystal displays, solar cells, sensors, modulators, etc.(14) Additionally, liquid crystals are useful in medicine, biology, food production and for oil recovery.(15,16) For example to pyrazole complexes application in liquid crystal. More.The reserchers Barbera, Gimenez, Serrano and Villalba were synthesizing the liquid crystalline behavior of 1-(4-n-decyloxyphenyl)-3-(4-X-phenyl) propan-1,3-diones and their pyrazole derivatives. The 4-substituents (X) were decided to include a range of different polar and non-polar substituents: H, OCH₃, Cl, Br and CN. These compounds showed only SMA phase. Recently Al-Obaidi and Tomma were synthesis new mesogenic pyrazoline-2-on compound. The aim of our present work is the synthesis and study the misogynic behavior of pyrazole complexes.

Experimental:

Materials. All chemicals were supplied from BDH, Himedia, sigma and Aldrich chemicals co. and used as received.

Instruments: FT-IR (Fourier Transform Infrared) spectra were recorded using potassium bromide disc on a Shimadzu (Ir prestige-21) FTIR spectrophotometer. ¹H-NMR (Proton Nuclear Magnetic Resonance) spectra. were obtained with Bruker spectrophotometer model ultra shield at 400 MHz using tetramethylsilane (TMS) as internal standard and DMSO-d₆ (dimethyl sulfoxide deuterated) as solvent. Uncorrected melting points were determined by using Hot-Stage Gallen Kamp melting point apparatus. Using digital conductivity, measurements were taken for complexes with a 10⁻³ mol. L⁻¹ in DMSO-d₆ (Balance Johnson Matthey) evaluated the magnetic susceptibility of all complexes. Metal analysis for complexes were measured using a Shimadzu atomic absorption spectrophotometer (A.A) 680G in Ibn Sina Company, Ministry of Industry Baghdad, Iraq. Elemental analyses (C, H, and N) for complexes was carried out on a Heraeus instrument (Vario EL) at University of Tehran, Islamic Republic of Iran. The mass spectra were measured using of electron impact (EI), Italy, 70ev mass, the use of a Model of MS: 5973 Spectro meter at Central Lab, Tehran University, Islamic Republic of Iran. Hot-Stage Polarizing optical microscop model Leica DM2500M was used for recorded transition temperatures and textures of the mesophases in College of Education for pure Science tikrit University and college of Science-AL-Nahrain university.

Synthesis of 1, 2-bis [4-oxyacetophenone] ethane [I]_a and 1,3-bis [4- oxyacetophenone] Propane[I]_b.

These compounds were prepared according to the procedure that described by Ayyash et al.(19)

General method for synthesis of Chalcones [II]_{a,b}.(20)

Equimolar quantities of diketone acetophenone [I]_{a,b} (0.01 mol, 1.35g) and 4- methoxy benzaldehyde (0.02 mol, 2.48g) were dissolved in minimum amount of alcohol. Sodium hydroxide solution 40% (0.04 mol) was added slowly then cooled the mixture. The mixture was poured slowly onto 200 mL of ice water with constant stirring and kept in refrigerator for 24 h. The precipitate obtained was filtered, washed and recrystallized from ethanol.

Synthesis of 1,1'-(4,4'-(ethane-1,2-diylbis(oxy)) bis(4,1-phenylene)) bis(3-(4-methoxyphenyl) prop-2-en-1-one) [II]_a. White powder; yield (93 %); m.p: 178-180 °C; FT-IR(ν cm⁻¹): 3072 ν (CH aromatic), 2931, 2837 ν (CH aliphatic), 1670 ν (C=O), 1651 ν CH=CH), 1595 ν (C=aromatic), 1249 ν (C-O) .

Synthesis of 1,1'-(4,4'-(propane-1,3-diylbis(oxy)) bis(4,1-phenylene)) bis(3-(4-methoxyphenyl) prop-2-en-1-one) [II]_b.

This compound was prepared according to the procedure described by Insuasty et al. (21).

General method for synthesis pyrazole.

Mixture of chalcone[II]_{a,b} (0.01 mol, 5.35g) and Hydrazine Hydrate (1.36 g, 0.02 mol) in ethanol (15ml) was heated under reflux for 6hrs. After cooling the separated solid was filtered off dried and crystallized from ethanol (22).

Synthesis of 3-(4-methoxyphenyl)-5-(4-(2-(4-(5-(4-methoxyphenyl)-1H-pyrazol-3-yl)phenoxy)ethoxy)phenyl)-1H-pyrazole [III]_a.

White powder; yield (62%); m.p (260-270)⁰C; FT-IR(ν cm⁻¹): 3363 ν (NH), 3053 ν (CH aromatic), 2945, 2839 ν (H aliphatic), 1664 ν C=N), 1607 ν (C=C aromatic), 1244 ν (C-O); ¹HNMR (DMSO-d₆), (δ ppm): 4.29 (s,6H,OCH₃), 4.43 (s,4H,OCH₂), 6.93 (s,1H ,NH pyrazole), 7.08-7.94 (m,16 H, Ar-H). Elemental analysis of (C,H,N) C (68.91-(73.1 calc.)), H(6.48-(5.41calc.)) and N (11.64-(10.03 calc.)).

3-(4-methoxyphenyl)-5-(4-(3-(4-(5-(4-methoxyphenyl)-1H-pyrazol-3-yl)phenoxy)propoxy)phenyl)-1H-pyrazole [III]_b.

White powder; yield (75%); m.p (250- 260)⁰C; FT-IR (ν (cm⁻¹): 3340 ν (NH), 3072 ν (CH aromatic), 2963, 2841 ν (CH aliphatic), 1672 ν (C=N), 1600 ν (C=C aromatic), 1251 ν (C-O). ¹HNMR (DMSO-d₆), (δ ppm): 2.0 (t,2H,C-CH₂-C), 4.31 (s,4H,2OCH₂), 4.42(s,6H,2OCH₃), 6.16 (s,2H,2NH pyrazole), 6.92-7.95 (m,16 H, Ar-H).

one pot reaction.

A general method was conducted to obtain the bimetallic dithiocarbamate-based macrocyclic complexes. (23,24) To a solution of the bis (4-(5-(4-methoxyphenyl)-1H-imidazol-4-yl) phenoxy) ethane) (Pyrazole) in MeCN/H₂O mixture (9:1), with stirring, an excess of KOH (4eq) was added. Carbon disulfide (4 equivalents) was added into the solution, and the mixture was stirred for 10 minutes allowing the formation of the potassium dithiocarbamate salt. The complex was prepared *in situ* (ligand salt was not isolated) by the addition of two equivalent of metal ion. The mixture was stirred for 18 h; water was added for precipitation if required, filtered washed with methanol and dried to give the macrocyclic complex.

[Cu₂L₂].

Dark brown powder ; yield (89 %) ; m.p: 250°C dec. ; FT-IR(ν cm⁻¹): 3068 ν (CH aromatic), 2918, 2891 ν (CH aliphatic), 1674 ν (C=N), 1508 ν (C=C aromatic), 1251.7 ν (C-O) attach with cycle, 1172 ν (C-O) ether, 1417 ν (N-CS₂), 1041,960 ν (C=S,C-S). Calculation of the atomic absorption of the compound (8.36 calculated - 7.69 practical)%.

[Cr₂L₂]Cl₂.

Light green powder ; yield (88.5 %) ; m.p: 245-250°C; FT-IR(ν cm⁻¹): 3009 ν (CH aromatic), 2918,2889 ν (CH aliphatic), 1676 ν (C=N), 1508 ν (C=C aromatic), 1251 ν (C-O) attach with cycle, 1172 ν (C-O) ether, 1419 ν (N-CS₂), 1041,960 ν (C=S,C-S). Calculation of the atomic absorption of the compound (7.47calculated-7.667 practical)%.

[Co₂L₂].

Dark brown powder; yield (88.9 %) ; m.p: 300°C dec.; FT-IR(ν cm⁻¹): 3003 ν (CH aromatic), 2954,2887 ν (CH aliphatic), 1674 ν (C=N), 1510 ν (C=C aromatic), 1256 ν (C-O) attach with cycle, 1170 ν (C-O) ether, 1419 ν (N-CS₂), 1030,982 ν (C=S,C-S). Calculation of the atomic absorption of the compound (8.39 calculated- 7.69 practical)%.

[Ni₂L₂].

Green powder ; yield (77.4 %) ; m.p: 300 °C dec.; FT-IR(ν cm⁻¹): 3070 ν (CH aromatic), 2920,2891 ν (CH aliphatic), 1676 ν (C=N), 1596 ν (C=Caromatic), 1251 ν (C-O) attach with cycle, 1172 ν (C-O)ether, 1418 ν (N-CS₂), 1041,961 ν (C=S,C-S). Calculation of the atomic absorption of the compound (8.39 calculated - 7.42 practical)%.

[Cd₂L₂].

Yellow powder; yield (76 %) ; m.p: 310 °C dec.; FT-IR(ν cm⁻¹): 3070 ν (CH aromatic), 2947, 2883 ν (CH aliphatic), 1672 ν (C=N), 1508 ν (C=C aromatic), 1245 ν (C-O) attach with cycle, 1177 ν (C-O) ether, 1417 ν (N-CS₂), 1037,941 ν (C=S,C-S). Calculation of the atomic absorption of the compound (140.86calculated– 13.70 practical)%.

[Mn₂L₂].

Brown powder ; yield (90 %) ; m.p: 300 °C dec. ; FT-IR(ν cm⁻¹): 3045 ν (CH aromatic), 2941, 2879 ν (CH

aliphatic), 1672 ν (C=N), 1501 ν (C=C aromatic), 1244 ν (C-O) attach with cycle, 1176 ν (C-O) ether, 1416 ν (N-CS₂), 1040,937 ν (C=S,C-S). Calculation of the atomic absorption of the compound (140.86calculated – 13.70 practical)%.

[Cu₂L₂].

Black brown powder; yield (87 %) ; m.p: 135-140 °C; FT-IR(ν cm⁻¹): 3068.5 ν (CH aromatic), 2931,2877 ν (CH aliphatic), 1674 ν (C=N), 1601 ν (C=C aromatic), 1249 ν (C-O) attach with cycle, 1174 ν (C-O) ether, 1419 ν (N-CS₂), 1029,926 ν (C=S,C-S). Calculation of the atomic absorption of the compound (8.86 calculated- 7.86 practical)%.

[Cr₂L₂]Cl₂.

Light green powder; yield (79 %) ; m.p: 230-245 °C; FT-IR(ν cm⁻¹): 3060 ν (CH aromatic), 2945, 2873 ν (CH aliphatic), 1676 ν (C=N), 1601 ν (C=Caromatic), 1247 ν (C-O) attach with cycle, 1174 ν (C-O) ether, 1413 ν (N-CS₂), 1006,954 ν (C=S,C-S). Calculation of the atomic absorption of the compound (7.32 calculated - 7.62 practical)%.

[Co₂L₂].

Dark brown powder; yield (88.9 %) ; m.p: 300°C dec.; FT-IR(ν cm⁻¹): 3003 ν (CH aromatic), 2954,2887 ν (CH aliphatic), 1674 ν (C=N), 1510 ν (C=C aromatic), 1256 ν (C-O) attach with cycle, 1170 ν (C-O) ether, 1419 ν (N-CS₂), 1030,982 ν (C=S,C-S). Calculation of the atomic absorption of the compound (8.39 calculated-7.69 practical)%.

[Ni₂L₂].

Green powder ; yield (83.9 %) ; mp: 120-125°C; FT-IR(ν cm⁻¹): 3055 ν (CH aromatic), 2943, 2883 ν (CH aliphatic), 1672 ν (C=N), 1606 ν (C=C aromatic), 1251 ν (C-O) attach with cycle, 1176 ν (C-O) ether, 1419 ν (N-CS₂), 1037,939 ν (C=S,C-S). Calculation of the atomic absorption of the compound (8.22 calculated - 7.52 practical)%.

[Cd₂L₂].

Yellow powder ; yield (84.8 %) ; m.p: 310 °C dec.; FT-IR(ν cm⁻¹): 3045 ν (CH aromatic), 2945,2877 ν (CH aliphatic), 1645 ν (C=N), 1603 ν (C=C aromatic), 1247 ν (C-O) attach with cycle, 1176 ν (C-O) ether, 1415 ν (N-CS₂), 1011,989 ν (C=S,C-S). Calculation of the atomic absorption of the compound (14.85calculated– 13.25

practical)%. ¹HNMR (DMSO-d₆), (δ ppm): 1.96 (t,2H,C-CH₂-C), 4.20 (s,4H,2OCH₂) and (s,6H,2OCH₃), 7.00-7.93 (m,16 H, Ar-H) and (s,1H ,CH pyrazole).

[Mn₂L₂].

Light brown powder; yield (74 %) ; m.p: 300 °C dec.; FT-IR (ν cm⁻¹): 3045 ν (CH aromatic), 2935,2881 ν (CH aliphatic), 1670 ν (C=N), 1605 ν (C=C aromatic), 1245 ν (C-O) attach with cycle, 1176 ν (C-O) ether, 1413 ν (N-CS₂), 1010,993 ν (C=S,C-S). Calculation of the atomic absorption of the compound (7.71calculated – 6.57 practical)%.

Table (1): Physical properties for perligands [III]_{a,b} and complexes:

Symbol compound	Molecular formula	Molar conductivity $\Lambda_M(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$	Magnetic of susceptibility	Atomic Absorption % (calc)	Yield %	Color	M.P. °C
1-[III] _a	C ₃₄ H ₃₀ N ₄ O ₄	0.96	-----	-----	85.7	Yellow	260-263
2-[Co ₂ L ₂]	C ₄₈ H ₅₆ N ₈ O ₈ S ₈ Co ₂	1.16	4.12	7.69 (8.39)%	88.9	Dark brown	250*
3-[Mn ₂ L ₂]	C ₄₈ H ₅₆ N ₈ O ₈ S ₈ Mn ₂	6.23	6.0	7.82 (6.74)%	90	Brown	300
4-[Cu ₂ L ₂]	C ₄₈ H ₅₆ N ₈ O ₈ S ₈ Cu ₂	6.96	0.0	8.53 (9.03)%	83.9	Dark brown	270*
5-[Ni ₂ L ₂]	C ₄₈ H ₅₆ N ₈ O ₈ S ₈ Ni ₂	9.52	2.95	7.42 (8.39)%	77	Green	300*
6-[Cr ₂ L ₂] ₂ Cl ₂	C ₄₈ H ₅₆ N ₈ O ₈ S ₈ Cr ₂	50.86	3.5	7.67 (7.47)%	88.5	Light green	245-250
7-[Cd ₂ L ₂]	C ₄₈ H ₅₆ N ₈ O ₈ S ₈ Cd ₂	3.94	0.0	13.7 (14.86)%	75	Yellow	310*
8-[III] _b	C ₃₅ H ₃₂ N ₄ O ₄	1.21	-----	-----	76.9	Pale yellow	270-273
9-[Co ₂ L ₂]	C ₅₀ H ₆₀ N ₈ O ₈ S ₈ Co ₂	3.85	4.00	7.30 (8.22)%	87	Brown	230-233
10-[Mn ₂ L ₂]	C ₅₀ H ₆₀ N ₈ O ₈ S ₈ Mn ₂	3.35	6.23	6.57 (7.71)%	74	Light brown	300*
11-[Cu ₂ L ₂]	C ₅₀ H ₆₀ N ₈ O ₈ S ₈ Cu ₂	3.06	0.0	7.86 (8.86)%	87	Black	135-137
12-[Ni ₂ L ₂]	C ₅₀ H ₆₀ N ₈ O ₈ S ₈ Ni ₂	0.19	3.0	7.52 (8.22)%	83.9	Green	120-123
13-[Cr ₂ L ₂] ₂ Cl ₂	C ₅₀ H ₆₀ N ₈ O ₈ S ₈ Cr ₂	67.32	3.8	7.62 (7.32)%	79	Light green	240-242
14-[Cd ₂ L ₂]	C ₅₀ H ₆₀ N ₈ O ₈ S ₈ Cd ₂	10.95	0.0	13.25 (14.58)%	84.8	Yellow	310

* = Decomposed.

Table (2): FTIR spectral data (wave number) cm⁻¹ for preligand [III]_a.

Comp.	ν (N-H)	ν (CH)arom	ν (C-H)aliph.	ν (C=N)	ν (C=C)	$\nu_{\text{asy}}(\text{C-O})$	$\nu_{\text{sy}}(\text{C-O})$	ν (C=S), ν (C-S)	P-Sub.	ν (N-CS ₂)
(L ¹)[III] _a	3393	3053	2945,2839	1664	1607	1244	1173	-----	823	----
[Co ₂ L ₂]	---	3003	2954,2887	1674	1510	1256	1170	1030,958	821	1419
[Cr ₂ L ₂]	---	3009	2918,2889	1676	1508	1251	1172	1041,960	854	1419
[Cu ₂ L ₂]	---	3068	2918,2891	1674	1508	1251	1172	1041,960	833	1417
[Ni ₂ L ₂]	---	3070	2920,2891	1676	1596	1251	1172	1041,961	837	1418
[Cd ₂ L ₂]	---	3070	2947,2883	1672	1508	1245	1177	1237,941	833	1417
[Mn ₂ L ₂]	---	3045	2941,2879	1672	1501	1244	1176	1040,937	833	1419

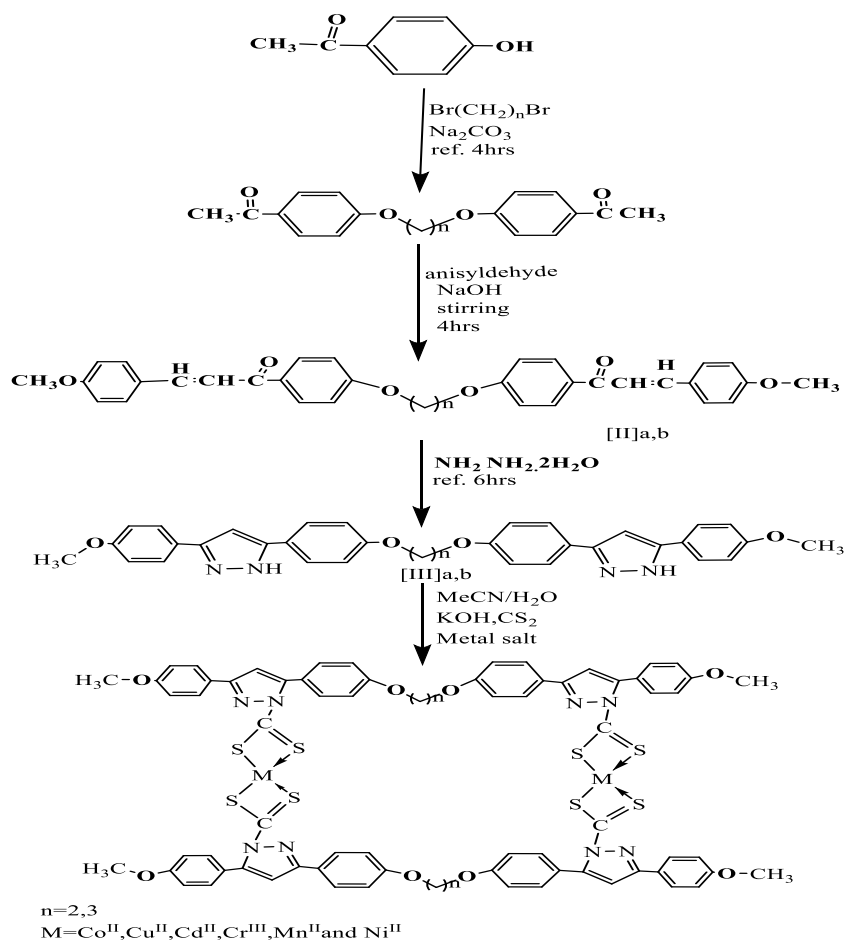
Table (3): FTIR spectral data (wave number) cm⁻¹ for preligand [III]_b.

Comp.	ν (N-H)py.	$\nu_{\text{ar}}(\text{CH})$ aro.	ν (CH) Ali.	ν (C=N)	$\nu_{\text{ar}}(\text{C=C})$	ν (C-O)cyc	$\nu_{\text{ar}}(\text{C-O})$ Ali.	ν (C=S), ν (C-S)	P-Sub.	ν (N-H)py
(L ²)[III] _b	3340	3072	2963,2841	1672	1600	1251	1174.7	-----	831	----
[Co ₂ L ₂]	---	3003	2954,2887	1674	1510	1256	1170	1030,982	829	1419
[Cr ₂ L ₂]	---	3060	2945,2873	1676	1601	1247	1174	1006,954	833	1413
[Cu ₂ L ₂]	---	3068.5	2932,2877	1674	1601	1249	1174	1029,926	833	1419
[Ni ₂ L ₂]	---	3055	2934,2883	1672	1606	1251	1176	1037,939	833	1419
[Cd ₂ L ₂]	---	3045	2945,2877	1645	1603	1247	1176	1011,989	833	1415
[Mn ₂ L ₂]	---	3045	2935,2881	1670	1605	1246	1176	1010,993	833	1413

Results and discussion:

All of the synthesized compounds gave satisfactory analysis for the proposed structures, which were confirmed on the basis of their Fourier transform Infrared (FT-IR) spectra and proton nuclear magnetic resonance (¹H-NMR) spectra. The first step including reaction of diketones with 4- methyl benzaldehyde according to the aldol condensation reaction to produce chalcones [II]_{a,b}, the FT-IR spectrum as a sample, showed the stretching vibration band for $\nu(\text{C=O})$ of chalcone in the region (1676-1658) cm⁻¹

and $\nu(\text{C=C})$ in the region of (1654-1625) cm⁻¹ and the ¹H-NMR spectrum for [II] showed doublet signal at δ (7.11-7.99) ppm attributed to two protons attached to (C=C) (alkene) (26). In the next step reaction of compounds [II]_{a,b} with hydrazine hydrate in (1:2) mol to produce pyrazoles (preLigand) [III]_{a,b}. The current compounds [III]_{a,b} were diagnosed by FTIR and ¹H-NMR and show pyrazole rings have several bands of variable intensities within the range 1530-1013 cm⁻¹ because of ring stretching vibrations (25).



Scheme(1). The synthesis pathways of the L^1 and L^2 ligands and complexes

In this study, the vibrational mode of the azomethine group $\nu(C=N)$ has a delocalization of π -electron density in the ring, the IR spectra of pyrazole ligands show weak absorption bands in the range of $3087\text{--}3047\text{ cm}^{-1}$ (27) indicating the presence of the aromatic (C–H) stretching vibrations. Absorption bands at $2970\text{--}2860\text{ cm}^{-1}$ should be assigned to the stretching vibrations of the aliphatic (C–H). Another characteristic pyrazole bands in the range of $1672\text{--}1664\text{ cm}^{-1}$ (C=N), 1600 cm^{-1} (C=C), $1251\text{--}1209\text{ cm}^{-1}$ (C–O) (31). On other hand we noticed in pyrazole ring active group NH its appear in spectrum at $(3340)\text{cm}^{-1}$, $(3363)\text{cm}^{-1}$ in preligand. When comparison between NMR, FTIR spectra of these preligands and complexes (28,29). It was suggested coordination of thiocarbamate to metal centers has several effects. First, electron donation like nitrogen atom of the azole to the Lewis acidic metal center increases the acidity of the azole (N–H) group. This can lead to the formation of pyrazolate rather than pyrazole complexes. Even when stable pyrazole complexes can be prepared, the increase in the acidity of the (N–H) group due to pyrazole coordination can result in the deprotonation of the complexes in the presence of even very weak base (30). The IR spectral data of the

complexes showed stretching vibrations of aromatic (C–H) and aliphatic in the range of $3068\text{--}3049\text{ cm}^{-1}$ and $2960\text{--}2830\text{ cm}^{-1}$, respectively. The shift of the (C=N), (C=C), (C–O) attach with cycle and (C–O) of the preligand in complexes rings bands frequencies compared to that of the free ligands bonds (32) whereas appeared shifted of complexes and appeared in the range $1645\text{--}1676\text{ cm}^{-1}$ (C=N), $1609\text{--}1508\text{ cm}^{-1}$ (C=C), $1251\text{--}1226\text{ cm}^{-1}$ (C–O). Also there is some peaks appeared in complexes (N–CS₂) and (C–S)_{sy,asy} including the range $1432\text{--}1413\text{ cm}^{-1}$ and $1041\text{--}926\text{ cm}^{-1}$ respectively. Finally the presence of a new band in the $(430\text{--}408)\text{cm}^{-1}$ range assignable to $\nu(M\text{--}S)$ is another indication of the involvement of sulphur coordination (39). Proton Nuclear Magnetic resonance (¹H-NMR) spectra: ¹H-NMR spectrum of preligand [II]a were recorded in solution (DMSO)-d₆. NMR spectra were consistent with the signal values of the ligand and a slight shift was observed especially in ¹H-NMR values due to the binding to the metal. It was also confirmed that the number of hydrogen atoms attached to the aromatic ring was the same as the ligand (32). Shows the ¹H-NMR chemical shift values observed in ppm of the preligand and the complex in DMSO-d₆ at room temperature. On the other hand, the

absence of the NH-pyrazolic around (6.16) ppm a singlet signal suggests the presence of (N-CS₂) in the complex instead of NH pyrazole (33)

These values in table (1) indicate the non-electrolyte behavior of the complexes except Cram complexes which showed electrolyte behavior in (1:2) ratio. Also we observed in Magnetic moment measurements that the results confirm all complexes were Para magnetic except cadmium complexes showed diamagnetic properties.

Liquid crystalline properties:

The liquid crystalline properties for the synthesized compounds were investigated using POM. The phase transition temperatures corresponding for compound [III]_{a,b}, and twelve complexes were summarized in Table (4). The phase identification via Texture and Liquid crystal (34,35) to assign each mesophase type. As shown in Table(4), compound [III]_{a,b} exhibited enantiotropic Nematic mesophase. The formed mesophase showed a typical thread-like nematic texture under POM observation, as in Figure (3) of compound [III]_a, while compound 2 showed

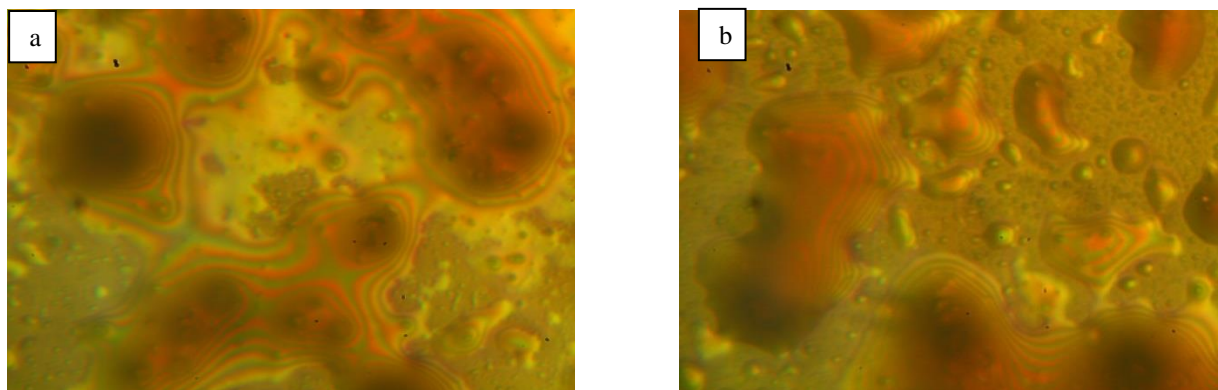
only droplet of Nematic phase, this could be explained to the rigid-rod (CH₂CH₂ in the centre of the molecule [III]_a) and banana hape (CH₂CH₂CH₂ in the center of the molecule [III]_b)(36), respectively. 3D structure of compound [VIII]_a and [IIIIV]_b shown in (Figure (4).

In spite of the liquid crystallinity of uncoordinated compounds [III]_{a,b}, not all of their corresponding M(II) complexes are liquid crystalline. The Optical observation shows that complexes [Cu₂L¹₂], [Co₂L¹₂], [Cd₂L¹₂], [Mn₂L¹₂], besides to [Cr₂L¹₂]Cl₂, [Cd₂L¹₂], [Mn₂L¹₂] did not show any mesogenic behaviour. These complexes have decomposition at isotropic phase. On the other hand complexes were mesogenic and exhibited enantiotropic Nematic phase with good thermal stability. Due to coordination geometry (37), the intermolecular interactions are slightly different, therefore it causes that mesomorphism (nematic phase) settle in [Ni₂L²₂] and [Cu₂L²₂] complexes but not in [Ni₂L¹₂] and [Cu₂L¹₂] complexes. By the same reason the [Cr₂L¹₂]Cl₂ complex give a nematic mesophases, Fig. 5.

Table(4) Liquid crystalline transition temperature (C°) of preligands and complexes.

Compound No.	Transition temperatures
[III] _a	Cr $\xrightleftharpoons{250^{\circ}\text{C}}$ N $\xrightleftharpoons{3450^{\circ}\text{C}}$ I
[Ni ₂ L ¹ ₂]	Cr $\xrightarrow{360^{\circ}\text{C}}$ I (dec.)
[Cr ₂ L ¹ ₂]Cl ₂	Cr $\xrightleftharpoons{175^{\circ}\text{C}}$ SmA $\xrightleftharpoons{>306^{\circ}\text{C}}$ I
[Cu ₂ L ¹ ₂]	Cr $\xrightarrow{300^{\circ}\text{C}}$ dec.
[Co ₂ L ¹ ₂]	Cr $\xrightarrow{310^{\circ}\text{C}}$ dec.
[Mn ₂ L ¹ ₂]	Cr $\xrightarrow{290^{\circ}\text{C}}$ dec.
[Cd ₂ L ¹ ₂]	Cr $\xrightarrow{320^{\circ}\text{C}}$ dec.
[III] _b	Cr $\xrightleftharpoons{200^{\circ}\text{C}}$ N $\xrightleftharpoons{335^{\circ}\text{C}}$ I
[Ni ₂ L ² ₂]	Cr $\xrightleftharpoons{130^{\circ}\text{C}}$ N $\xrightleftharpoons{>300^{\circ}\text{C}}$ I
[Cu ₂ L ² ₂]	Cr $\xrightleftharpoons{150^{\circ}\text{C}}$ N $\xrightleftharpoons{260^{\circ}\text{C}}$ I
[Cr ₂ L ² ₂]Cl ₂	Cr $\xrightarrow{250^{\circ}\text{C}}$ dec.
[Co ₂ L ² ₂]	Cr $\xrightarrow{350^{\circ}\text{C}}$ dec.
[Mn ₂ L ² ₂]	Cr $\xrightarrow{320^{\circ}\text{C}}$ dec.
[Cd ₂ L ² ₂]	Cr $\xrightarrow{310^{\circ}\text{C}}$ dec.

Cr=crystal, S=smectic, N=nematic, I=isotropic, dec.= decomposition



Figure(3). Nematic mesophase texture obtained a) on heating at 330 °C b) on cooling at 130 °C (200 × magnification) for the compound [III]_a.

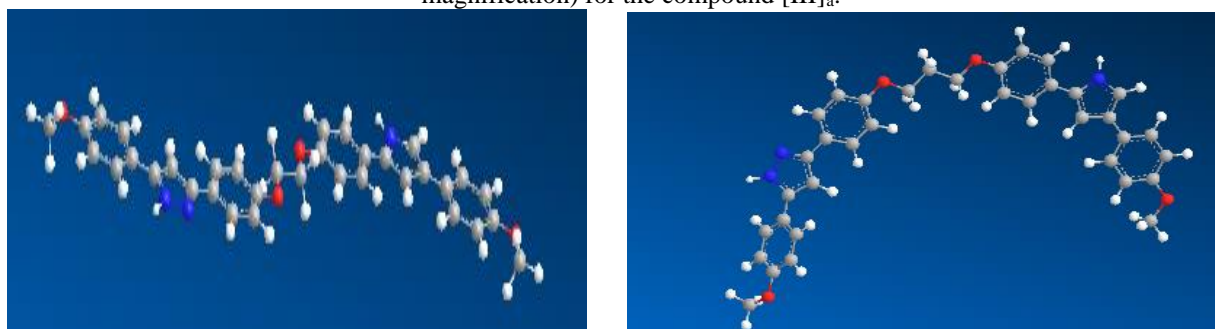


Figure (4). 3D structure of compound of a) [III]_a and b) [III]_b.

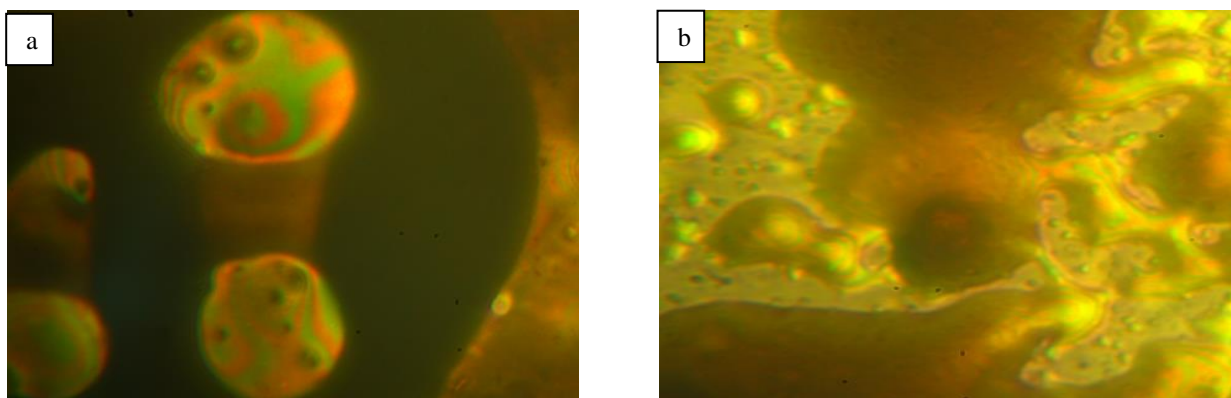


Figure (5). Nematic mesophase texture obtained a) on heating at 190 °C b) on cooling at 40 °C (200 × magnification) for the compound [Cu₂L₂]₂.

Conclusions:

- 1- The prepared intermediate compounds and preligands characterized with different spectroscopic methods and the results was in a good accordance with the proposed structures
- 2- All synthesized complexes proposed to have tetrahedral shap, the spectroscopic and analytical data revealed the geometry concluded.
- 3- The preligands (pyrazoles) showed enantiotropic nematic mesophase while the metal complexes appeared various behavior.

Some of them did not shows any mesomorphic behavior but decomposition at isotropic phase.

- 4- On the other hand, the molecular interaction and geometry led to appear a clear mesophese in other complexes [Cr₂L₂]¹Cl₂, [Ni₂L₂]² and [Cu₂L₂]².

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