

Article

Metal complexes of pyrazoline dithiocarbamate type ligands, synthesis, physio-chemical and liquid crystal studies

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Available from: <http://dx.doi.org/10.21931/RB/CSS/2023.08.03.84>

Abstract

For this study, metal complexes of thiocarbamate ligand derived from pyrazoline were synthesized in two steps. In the first step, pyrazoline was synthesized from chalcone. In the second step, the ligand (pyrazoline) was reacted with CS₂ and metal salt in a 1:2:1 mole ratio in a one-pot reaction to give metal complexes. All compounds were characterized by physio-chemical techniques, which revealed a bidentate behavior of the thiocarbamate and a tetrahedral geometry around metal centers except the chromium ion, which shows an octahedral shape. Hot-stage microscopes studied the liquid crystalline properties of the synthesized compounds. The compound [II] exhibited Nematic mesophase, while the complexes showed different crystalline properties

Keywords: Pyrazoline, Dithiocarbamat, Complexes, polar group, Liquid crystal.

Introduction

Pyrazoline is a nonaromatic five-membered ring from heterocycle fields having two adjacent nitrogen atoms within the ring¹. Pyrazolines are dihydro-pyrazoles, with only one double bond (imine bond),^{2,3} and their chemistry is closely related to pyrazoles. According to heterocyclic nomenclature, pyrazolines require the nitrogen atoms to be numbered 1 and 2 in each structure. There are three well-known tautomeric structures for pyrazolines: 1-pyrazoline, 2-pyrazoline, and 3-pyrazoline (Figure 1). However, among these tautomeric structures, 2-pyrazoline is the most common⁴. They could be easily prepared by the reaction of α,β -unsaturated aldehydes or ketones with hydrazine derivatives⁵. Pyrazoline derivatives are electron-rich nitrogenous heterocycles, which play an essential role in the diverse biological activities^{6,7,8}. Among its derivatives, 3-substituted pyrazolines seem to be the most attractive pyrazoline-type derivatives⁴.

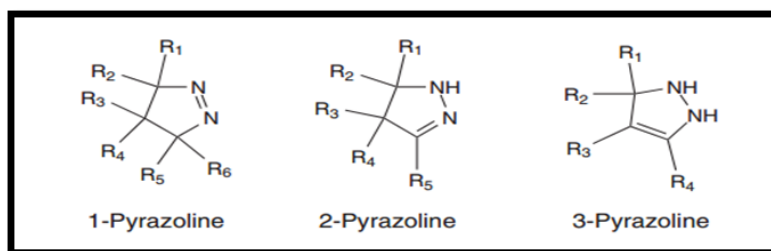


Figure 1: Tautomeric structures for pyrazolines.

Pyrazole-type ligands are relevant in organometallic chemistry due to their wide usage area^{9,10} as a ligand in organometallic chemistry. Pyrazolate is the conjugate base of pyrazole and has three coordination modes—*anionic monodentate*, *endo-bidentate* and *exo-bidentate*, as seen in Figure (2). *Exobidentate* is the most common mode in organometallic chemistry and prompted pyrazolates to bridge two metallic centers¹¹.



Figure 2: Coordinate modes of pyrazole.

Dithiocarbamate (DTC) groups are highly nucleophilic, which leads to a large number of derivatives. DTC forms stable complexes with all the transition elements¹². Dithio ligands are considered soft donors showing excellent coordination ability. They form stable complexes with the transition as well as non-transition metal ions¹³ and exhibit a variety of coordination modes in homo and hetero-nuclear complexes depending on the binding modes of the ligands towards the metal center¹⁴.

The design and development of liquid crystalline systems have gained considerable research interest over the past decade¹⁵. Few factors influence the formation of different liquid crystals: the length of the alkyl terminal chain, inter/intra-molecular interaction, presence of spacer, spacer length, polarization effects, odd-even effects, and the presence of an electron-withdrawing group or an electron-donating group. Liquid crystal technology is an ideal system to be applied to products to maximize their use, especially in the electronic and medical areas. Understanding the structure–property relationship is required to understand the interconnections between the core system, linking unit, and terminal group¹⁶. The presence of strongly polar, highly polarizable terminal groups in some of these compounds makes them potentially attractive for their ability to exhibit second-order non-linear optical properties¹⁷. Al-Obaidi and Tomma synthesized new mesogenic compounds containing pyrazoline unit¹⁸.

A highly porous Zn-based metal–organic framework (MOF) IRMOF-3 was covalently decorated with pyridine-2-aldehyde. The free amine group of IRMOF-3, upon condensation with pyridine-2-aldehyde, affords a bidentate Schiff-base

moiety in the porous matrix. The Schiff base moieties can anchor copper (II) ions to display the catalyst's utility towards catalytic reactions.¹⁹ The metal-containing liquid crystalline behavior has been reported and studied²⁰. A series of copper(II) complexes derived from unsymmetric 1,3,4-thiadiazoles exhibiting mesogenic properties were noted by Liao et al.²¹. This work aims to synthesize and investigate the mesomorphic behavior of pyrazoline ligand and their complexes.

Materials

All chemicals were supplied from BDH, Himedia, sigma and Aldrich Chemicals Co. and used as received.

Instruments

FT-IR spectra were recorded using a potassium bromide disc on a Shimadzu (Ir prestige-21) FTIR spectrophotometer. ¹H-NMR spectra were obtained with Bruker spectrophotometer model ultra-shield at 400 MHz using tetramethylsilane (TMS) as internal standard and DMSO-d₆ as solvent. Uncorrected melting points were determined by using the Hot-Stage Gallen Kamp melting point apparatus. Using digital conductivity, measurements were taken for complexes with a 10⁻³ mol. L⁻¹ in DMSO. (Balance Johnson Matthey) evaluated the magnetic susceptibility of all complexes. Ultraviolet-visible (UV) spectra of the ligand and its complexes were recorded using a solvent DMSO-d₆ at 1x 10⁻³ M using a device of type (UV 160A Shimadzu apparatus). Metal analysis for complexes was measured using a Shimadzu atomic absorption spectrophotometer (AA) 680G in Ibn Sina Company, Ministry of Industry Baghdad, Iraq. Elemental analyses (C, H, N, and S) for complexes were carried out on a Heraeus instrument (Vario EL) at the University of Tehran, Islamic Republic of Iran. The mass spectra were measured using electron impact (EI), Italy, 70eV mass, using a Model of MS: 5973 Spectro meter at Central Lab, Tehran University. Hot-Stage Polarizing optical microscopy model Leica DM2500M was used to record transition temperatures and textures of the mesophases in the College of Education for Pure Science Tikrit University and College of Science-AL-Nahrain University.

Synthesis of (2E,2'E)-3,3'-(1,4-phenylene)bis(1-(4-bromophenyl)prop-2-en-1-one)chalcone [I].

The title compound was synthesized using 4-Bromo acetophenone (0.02 mol) and Terephthalaldehyde (0.01 mol), dissolved in a minimum amount of alcohol. A sodium hydroxide solution of 40% (0.78g, 0.02 mol in 1.95 mL of water) was added slowly, and the mixture was then cooled. The product was poured slowly onto 200 mL of iced water with constant stirring and kept in a refrigerator for 24 hrs^{22,23}. The precipitate obtained was filtered, washed and recrystallized from ethanol to yield chalcone [I]. Yield (84 %); m.p = 308-311 °C, color: Light yellow. The FTIR (cm⁻¹): 3033 (CH_{aromatic}); 1656(C=O); 1603(C=C); 1583 (C=C benzene ring), 765 (C-Br).

3-(4-bromophenyl)-5-(4-(5-(4-bromophenyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl)-4,5-dihydro-1H-pyrazole [II].

A mixture of chalcone [I] (0.01 mol) and hydrazine hydrate (0.5g, 0.01 mol) in ethanol (15 mL) was heated under reflux for 6 hours. After cooling, the produced

pyrazoline was filtered off, dried, and crystallized from ethanol[24], yielding (82.4 %); m.p = 285-290 °C, color: Yellow. The FTIR (cm^{-1}): 3433 ($\text{NH}_{\text{pyrazoline}}$), 3180 ($\text{CH}_{\text{pyrazoline}}$), 3003 ($\text{CH}_{\text{aromatic}}$); 1670(C=N); 1608 (C=C benzene ring), 771 (C-Br).

^1H NMR (DMSO-d_6), (δ ppm): (2.7,3.5) for H_a and H_b at C5, (4.92) for H_x at C4 in pyrazoline ring, (7.3-8.28) (m,12 H, Ar-H), 8.69 (s,2H ,2NH pyrazoline). The mass spectrum for [II] exhibited parent ion [M^+] at $m/z=524$.

Synthesis of macrocyclic complexes via a one-pot reaction.

A general method was conducted to obtain the bimetallic dithiocarbamate-based macrocyclic complexes^{25,26}. To a solution of the 3-(4-bromophenyl)-5-(4-(5-(4-bromophenyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl)-4,5-dihydro-1H-pyrazole [II] in MeCN/ H_2O mixture (9:1), with stirring, an excess of KOH (4eq) was added. Carbon disulfide (4 equivalents) was added to 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 adding two equivalents of metal ions. The mixture was stirred for 18 h; water was added for precipitation, filtered, washed with methanol, and dried to give the macrocyclic complex.

[Cu_2L_2].

Green powder; yield (93 %); mp:250 °C dec. ; FT-IR(ν cm^{-1}): 3035 ν (CH aromatic), 1681 ν (C=N), 1620 ν (C=C aromatic), 1417.6 ν (N-CS_2), 1215, 966 ν (C-S,C=S), 777 ν (C-Br). Calculation of the atomic absorption of the compound (9.55 calculated – 8.95 practical)%.

[Cr_2L_2] Cl_2 .

Light green powder; yield (89.7 %); mp: 198-200 °C ; FT-IR(ν cm^{-1}): 3084 ν (CH aromatic), 1676 ν (C=N), 1585 ν (C=C aromatic), 1415.7 ν (N-CS_2), 1284, 982 ν (C-S,C=S), 761 ν (C-Br). Calculation of the atomic absorption of the compound (7.9 calculated – 7.37 practical)%.

[Co_2L_2].

Yellow powder; yield (93.5 %); mp: 228-230 °C . ; FT-IR(ν cm^{-1}): 3030 ν (CH aromatic), 1683 ν (C=N), 1639 ν (C=C aromatic), 1413.7 ν (N-CS_2), 1244, 935 ν (C-S,C=S), 773 ν (C-Br). Calculation of the atomic absorption of the compound (8.87 calculated - 7.94 practical)%.

[Ni_2L_2].

Light brown powder; yield (96.5 %); mp: 238-240 °C ; FT-IR(ν cm^{-1}): 3001 ν (CH aromatic), 1686 ν (C=N), 1630 ν (C=C aromatic), 1419.5 ν (N-CS_2), 1211, 964 ν (C-S,C=S), 779 ν (C-Br). Calculation of the atomic absorption of the compound (8.87 calculated – 8.35 practical)%.

[Cd_2L_2].

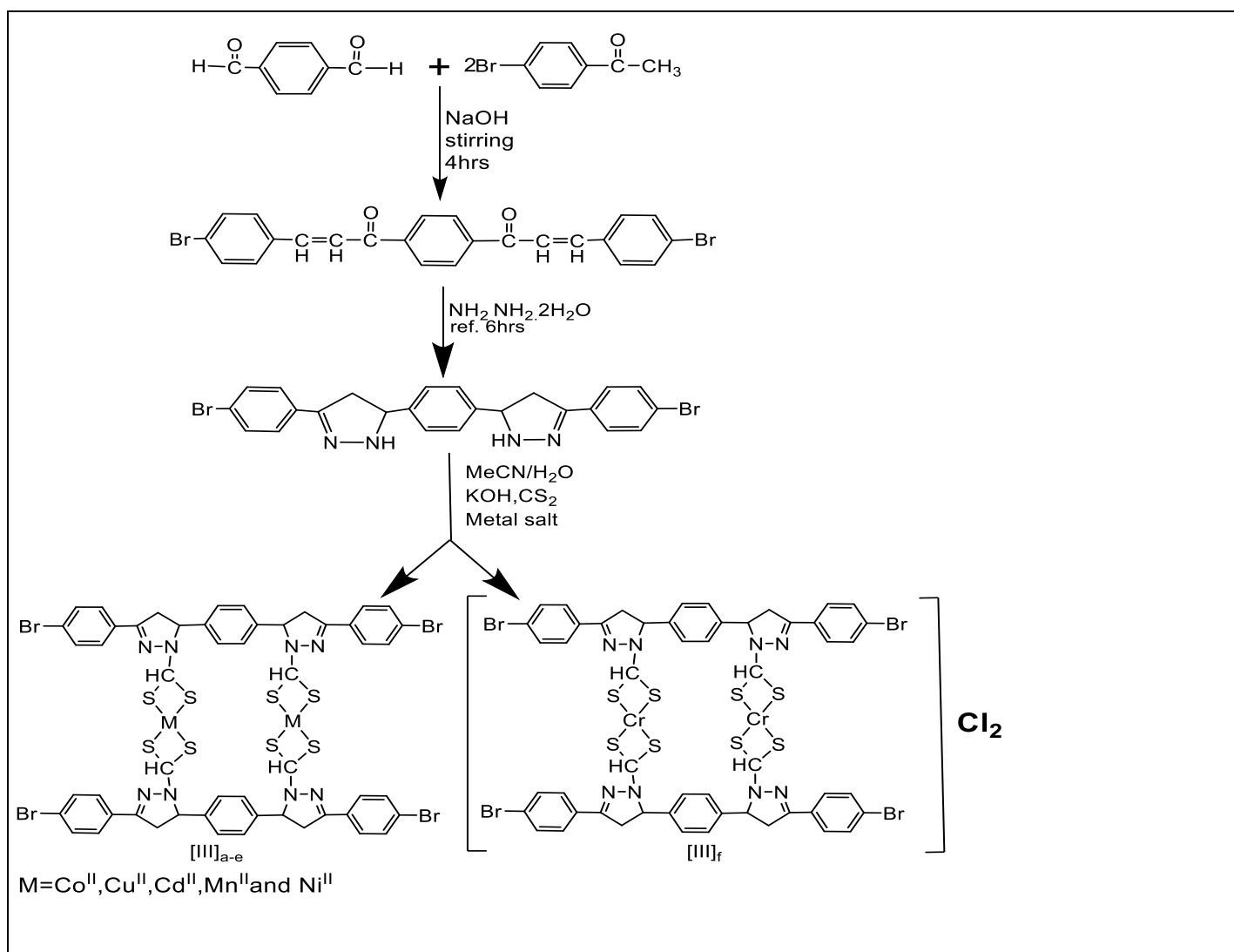
Yellow powder; yield (90 %); mp: 243-245 °C ; FT-IR(ν cm^{-1}): 3025 ν (CH aromatic), 1685 ν (C=N), 1639 ν (C=C aromatic), 1413.7 ν (N-CS_2), 1220, 937 ν (C-S,C=S), 764 ν (C-Br). Calculation of the atomic absorption of the compound (15.65 calculated – 14.29 practical)%.

[Mn_2L_2].

Brown powder ; yield (89.7 %); mp: 187-190 °C ; FT-IR(ν cm^{-1}): 3025 ν (CH aromatic), 1685 ν (C=N), 1639 ν (C=C aromatic), 1413.7 ν (N-CS_2), 1245, 931 ν (C-S,C=S), 779 ν (C-Br). Calculation of the atomic absorption of the compound (8.32 calculated – 8.025 practical)%.

n.	Symbol compound	Molar conductivity $M(\Omega^{-1}cm^2mol^{-1})$	Magnetic susceptibility	Yield %
1	[II]	1.06	-----	82
2	[Co ₂ L ₂]	1.56	4.09	93
3	[Mn ₂ L ₂]	0.75	6.13	89.7
4	[Cu ₂ L ₂]	1.88	0.0	92.5
5	[Ni ₂ L ₂]	0.92	2.87	85
6	[Cr ₂ L ₂]Cl ₂	53.65	3.48	89
7	[Cd ₂ L ₂]	1.78	0.0	92

Table 1: Physical properties for per ligand [II] and complexes.



Scheme 1: The synthesis pathway of the preligand and complexes.

Result

All of the synthesized compounds gave satisfactory analysis for the proposed structures, which

were confirmed based on their Fourier transform Infrared (FT-IR) spectra, proton nuclear magnetic resonance (¹HNMR) spectra and mass spectroscopy. The first step includes the reaction of terephthalaldehyde with 4-bromoacetophenone according to the aldol condensation reaction to produce chalcone [I]. The FT-IR

spectrum, as a sample, showed the stretching vibration bands for $\nu(\text{C}=\text{O})$ of chalcone in $(1656) \text{ cm}^{-1}$ and $\nu(\text{C}=\text{C})$ at $(1603, 1583) \text{ cm}^{-1}$. In the following step, the reaction of the compound [I] with hydrazine hydrate in (1:2) mole produces pyrazole derivative (preLigand) [II]. The structure of the pyrazoline [II] was identified by FTIR, ^1H NMR and Mass spectroscopy. The FT-IR spectrum of this compound showed the disappearance of two absorption bands of the $\text{CH}=\text{CH}$ and $\text{C}=\text{O}$ group of the chalcone [I] and the appearance of new absorption bands of $\text{N}-\text{H}$, $\text{C}-\text{H}$, and $\text{C}=\text{N}$ group at 3433 cm^{-1} , 3180 cm^{-1} and 1670 cm^{-1} (endocyclic), respectively. The mass spectrum for preligand [II] exhibited parent ion $[\text{M}^+]$ at $m/z=524$. Finally, complexes are prepared by the ligand, metal salt, and CS_2 reaction in a (2:2:4) mole ratio. Scrutinizing the FTIR spectrum of the complexes, the band $\nu(\text{C}=\text{N})$ in pyrazoline $(1670) \text{ cm}^{-1}$ was shifted and appeared in new positions in the complexes spectra $(1684-1676)$.

Liquid crystalline properties

The liquid crystalline properties of the synthesized compounds were investigated using POM. The phase transition temperatures and corresponding for compounds $[\text{III}]_{\text{a,b}}$, and their complexes were summarized in Table 1. The compound [II] exhibited Nematic mesophase. The formed mesophase showed a typical thread-like nematic texture under POM observation, as in Fig. 3. as in Fig. 4 of the 3D structure of the compound [II]. On heating at $211 \text{ }^\circ\text{C}$ for the compound [II].

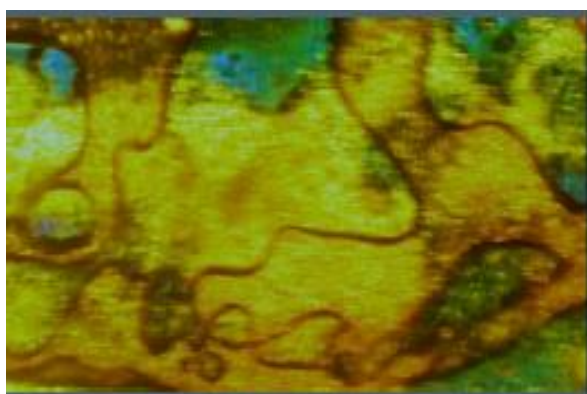


Figure 3: Nematic mesophase texture obtained.

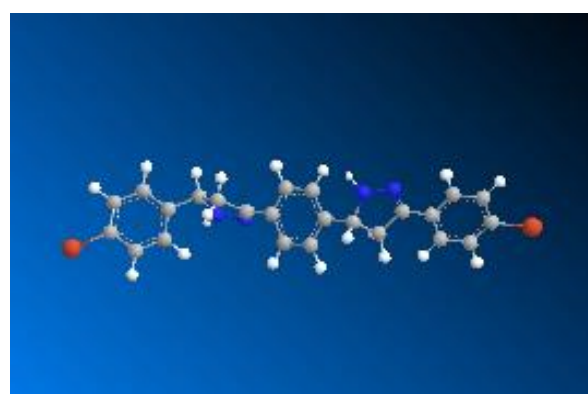


Figure 4: 3D structure of compound [II].

The compounds ($[\text{Cu}_2\text{L}]$, $[\text{Mn}_2\text{L}]$, and $[\text{Cd}_2\text{L}]$) did not show any mesogenic properties but only covered from solid to liquid phase. The complex $[\text{Ni}_2\text{L}_2]$ showed only Nematic mesophases on heating, while the complex $[\text{Co}_2\text{L}]$ showed Smectic A and Nematic mesophases on heating. Finally, on heating, the complex $[\text{Cr}_2\text{L}]$ showed Smectic A, Smectic C and Nematic mesophases Fig. 5. The change of element type in the complexes from Cu, Mn or Cd in (complex ($[\text{Cu}_2\text{L}_2]$, $[\text{Mn}_2\text{L}]$ and $[\text{Cd}_2\text{L}]$) by Ni, Co or Cr as in complexes ($[\text{Co}_2\text{L}_2]$, $[\text{Ni}_2\text{L}_2]$ and $[\text{Cr}_2\text{L}_2]$) may be lead to change in interaction forces and change in the molecule geometrical shape, especially in complex $[\text{Cr}_2\text{L}_2]$.

Compound No.	Transition temperatures
[II]	Cr $\xrightarrow{203^\circ\text{C}}$ N $\xrightarrow{248^\circ\text{C}}$ I
$[\text{Ni}_2\text{L}_2]$	Cr $\xrightarrow{236^\circ\text{C}}$ N $\xrightarrow{260^\circ\text{C}}$ I

[Cr ₂ L ₂]Cl ₂	Cr $\xrightarrow{140^{\circ}\text{C}}$ Sm A $\xrightarrow{174^{\circ}\text{C}}$ N $\xrightarrow{280^{\circ}\text{C}}$ I
[Cu ₂ L ₂]	Cr $\xrightarrow{200^{\circ}\text{C}}$ I(dec.)
[Co ₂ L ₂]	Cr $\xrightarrow{189^{\circ}\text{C}}$ Sm A $\xrightarrow{207^{\circ}\text{C}}$ N $\xrightarrow{219^{\circ}\text{C}}$ I
[Mn ₂ L ₂]	Cr $\xrightarrow{190^{\circ}\text{C}}$ I
[Cd ₂ L ₂]	Cr $\xrightarrow{240^{\circ}\text{C}}$ I

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

Table 2: Liquid crystalline transition temperature (°C) of preligand and complexes.

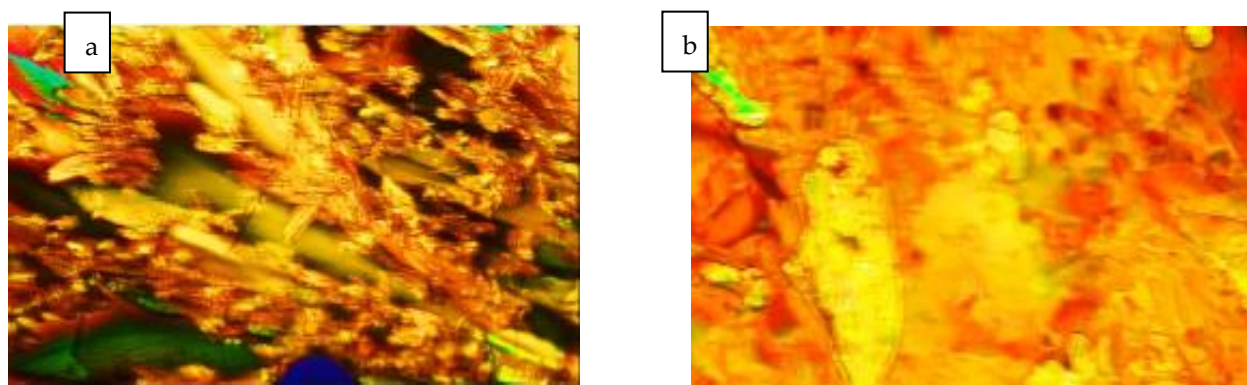


Figure 3: a) Smectic A at 140 °C b) Nematic mesophase texture obtained on heating at 245 °C for the complex [Cr₂L₂]Cl₂.

Discussion

The ¹H NMR spectrum of compound [II] shows the following signals: Twelve aromatic protons appeared as doublets at δ 7.3-8.28 ppm, a doublet at δ 8.69 ppm that could be attributed to the one proton of NH (pyrazoline). One proton H_x of CH-(pyrazoline) appeared as triplet ²⁷ at δ 4.92 ppm, while two protons of H_b and H_a for CH₂-(pyrazoline) appeared as two doublets at δ 2.7, 3.5 ppm, respectively ²⁴. However, the FT-IR spectra data of the complexes showed a shift in stretching vibrations bands of (3084-3010) cm⁻¹ ν (C-H) or (1684-1676) cm⁻¹ ν (C=N), (1639-1585) cm⁻¹ ν (C=C), (786-761) cm⁻¹ ν (C-Br), and (3191-3121) cm⁻¹ C-H_{pyrazoline} compared to that of the free preligand bands, indicating the interaction between metals and preligand thiocarbamate salt ²⁸. The greater shift of the azomethine band can be justified due to the coordination of the metal-ligand through C-S since the displacement can be attributed to the change in the bond order as a result of the delocalization of the π -electrons of the ring and hence in the weakening of metal-nitrogen coordination ²⁹. It is widely known that dithiocarbamate can exist as an equilibrium mixture of thione (C=S) and thiol (C-SH) tautomeric forms ³⁰. The spectrum for preligand does not display ν (S-H) in the range around 2500-2700 cm⁻¹ ^{31,32}, while in complexes FTIR spectrum, it was noticed stretching band of ν (C=S) at (981-935) cm⁻¹ ^{32,33}, and the splitting of ν_a (S-C-S) (1284-1211) cm⁻¹ confirms two non-equivalent C-S bonds from the dithiocarbamate ²⁹. In addition, in FT-IR spectra of complexes, the strong band of (N-H)_{pyr} within the ring (3260-3060) cm⁻¹ was absent due to the deprotonation beyond the thiocarbamate formation step. ^{31,32,34}.

Finally, the presence of a new band in the (430-408) cm^{-1} range assignable to $\nu(\text{M}-\text{S})$ indicates the involvement of sulfur coordination³⁵. The phase identification via Texture and Liquid crystal^{36,37} to assign each mesophase type. The broadening of the molecule by the pyrazoline ring reduces the lateral molecular interaction and increases the terminal interaction³⁹ besides the presence of bromine atoms in the terminals of the molecule) led to the formation of nematic phases^{40,41}.

Conclusions

The dithiocarbamate ligand proposed to behave as a bidentate ligand coordinating through sulfur atoms as the form.

The metal complexes are supposed to have a tetrahedral shape, except Cr(III) ion. The complexes ($[\text{Cu}_2\text{L}]$, $[\text{Mn}_2\text{L}]$, and $[\text{Cd}_2\text{L}]$) did not show any mesogenic properties, while the complex $[\text{Ni}_2\text{L}_2]$ showed only Nematic mesophase on heating, the complex $[\text{Co}_2\text{L}]$ showed Smectic A and Nematic mesophases on heating. Finally, the complex $[\text{Cr}_2\text{L}]$ showed Smectic A, Smectic C and Nematic mesophases.

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Received: May 15, 2023/ Accepted: June 10, 2023 / Published: June 15, 2023

Citation:AL-Satar, N.A.; Tomma, J.H; Hassan, H.A. Metal complexes of pyrazoline dithiocarbamate type ligands, synthesis, physio-chemical and liquid crystal studies. *Revis Bionatura* 2023;8 (3) 84.

<http://dx.doi.org/10.21931/RB/CSS/2023.08.03.84>