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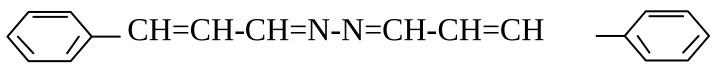
Study of Thermal Properties as a Function of Temperatures for anew Liquid Crystals Prepared from Schiff Bases and some complexes

دراسة الخواص الحرارية كدالة لدرجة الحرارة لبلورات سائله جديدة محضرة من قواعد شيف وبعض من معقداتها

ShaymaJabbarAbdulrazaq
* Department of Physics –College of Educationfor Girls- University of Kufa
E-mail: shayma_altaee@yahoo.com ,mobile: 07806187438

Abstract :

The ligand [Di(1-phenyl propanaldehyde) Hydrazone]was prepared from Schiff bases as symbol (Z) and complexes with ions (Co^{+3}) as symbol (CZ1), and (Cr^{+3}) as symbol (CZ2)as the following structure:



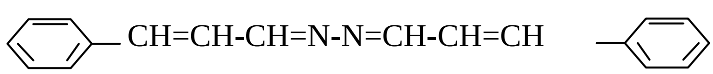
Di (1-phenyl propanaldehyde) Hydrazone

The legand and their complexes have been characterized by a spectrophotometer Infrared (IR), Ultra violet (UV), and polarizing microscope equipped with heating stage, this techniques were found all compounds have shown a nematic phase (Enantiotropic) by heating and cooling.The study thermal conductivity behavior of compounds as a function of temperaturesof the raising (298-323 K). It has been observed that the results obtained from these compoundspossess low thermal conductivityand increases with increasing temperatures. Calculated specific heat and thermal diffusivity values, as results show that the specific heat is increasing slightly with higher temperatures, and the thermal diffusivity of this compounds is decreasing slightly with the higher temperatures. The legand have high thermal stability, complexed less matter stability.

Key words: Schiff Bases, thermal conductivity, liquid crystals .

الخلاصة :

تم تحضير اليكاند[Di(1-phenyl propanaldehyde) Hydrazone] منقواعدشف(Z)، وعقد هذا الليكاندمع ايون الكوبلت الثلاثي التكافؤ(CZ1) وايون الكروم الثلاثي التكافؤ (CZ2)، وتكون الصيغة التركيبية لليكاند كالاتي:



Di (1-phenyl propanaldehyde) Hydrazone

تم تشخيص المركبات المحضرة بواسطة طيف الأشعة تحت ألحمراء (IR)،طيف الاشعة فوق البنفسجية (UV) و المجهر الضوئي المستقطب المجهز بلوح تسخين وقد تبين ان هذه المركبات المحضرة من قواعد شف ومعقداتها تمتلك الصفة البلورية السائلة ذات الطور النيماتي الاعتيادي (ثنائي الحالة الوسطية). وقد تم دراسة سلوك التوصيل الحراري كدالة لدرجات الحرارة بمدى من ($298 - 323^{o}K$)، وقد لوحظ من النتائج المستحصلة ان المركبات المحضرة ذات توصيل حراري واطئ، إذ يزداد التوصيل الحراري لها بارتفاع درجات الحرارة، وحسبتقيم الحرارة النوعية والانتشار الحراري وتبين ان الحرارة النوعية لهذه المركباتواطئة إلا إنها تزداد زيادة طفيفة بارتفاع درجات الحرارة والانتشار الحراريتتناقصبشكل طفيف بارتفاع درجات الحرارة،وكذلك لوحظ إن الليكاند ذات استقرار حراري عاليوان التعقيد يقلل من استقراريةالليكاند.

Introduction:

Schiff base ligands can be easily synthesized by reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed and they can used as complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics [1].

Heat transfer by conduction involves the transfer of heat energy (molecular and atomic motions by direct physical contact between molecules,atoms or their parts when they are at different temperatures. the rate of heat transfer by conduction is proportional to the area perpendicular to the direction of heat flow and temperature gradient . The proportionality factor is called the thermal conductivity . Its numerical value depends on the chemical composition (size,shape,inner structure of molecules or atoms) and physical stato (structure) of the investigated materials . Closer contact between molecules, atoms and their parts within the body of uniform chemical composition offers higher possibility of transfer of molecular and atomic motions among neighboring molecules and results in higher thermal conductivity [2].

Developed the researchers (Kiyoshi Torizuka, and Hiroyuki Tajima, 2005)a technique to measure the thermal conductivity, which enables them to measure for organic samples over a wide temperature range between 4 K and room temperature. In this technique, two heaters and three thermometers are installed unlike the conventional one-heater-two-thermometer configuration. They have succeeded in measuring the thermal transport of organic molecular crystals with the conductivity of the order of,1 W / K m, by employing different method [3].

The researcher (Pankaj B. Kaul, and *et.al*., 2007) prepared sample for the three omega method of polyaniline films of three thicknesses (5 m and ultrathin 110 nm films of polyaniline as well as a thin 300 nm film) of low temperature plasma enhanced chemical vapor deposited SiO2 as a function of temperature were measured and found that the polyaniline films exhibit an increase in thermal conductivity with temperature, which is largely due to increasing heat capacity. The thick film thermal conductivity is many times the value corresponding to the thin film, which is likely due to significant phonon boundary scattering present in the ultrathin film [4].

Studied the researcher (Takashi Kato, and Takashi Nakamura, and *et.al.*, 2007) the relation between the thermal conductivity and the PLC network styles from through prepare Mixtures consisting of mono-functional polymerizable liquid crystals (PLC) having a polymerizable moiety on the molecular short axis terminal and a bi-functional PLC having the polymerizable moieties on the molecular long axis terminals,and preparation Uniaxially aligned films from the PLC mixtures by photo polymerization after aligning the molecular directions by the rubbing method, and found that the relation between them was investigated from the aspect of the molecular order [5].

The research aims to prepare the three compounds from schiff bases compounds and then characterized the type of phase liquid crystal by polarizing microscope and study the thermal properties of these compounds by measuring the thermal conductivity and applied to find thespecific heat values thermal diffusion, for the large and growing importance of these compounds in the areas of applied and industrial.

Theoretical Part:

Thermal conductivity is the phenomenon of heat transfer which is the transfer of energy from one location to another due to excitation of the atoms or molecules of material due to change in a media temperature. Thermal conductivity is known as the amount of heat that passing through unit area of the material for the unit of time, thermal conductivity directly proportional to the difference between the temperatures external surfaces of the material and inversely with the thickness, so the flow of heat does not depend on absolute temperature, but the difference in the degree of double-sided heat, Basic equation of thermal conductivity (Fourier equation) is as follows [6]:

$\lambda = Q X / A t (\Delta T)$ ……………….. (1)

Where (X) represents thickness of the sample, (A) cross-section area of the sample, (ΔT)difference in temperature on both sides of the sample, where the measured (λ) in units of (W / cm . K), (Q/t) Represents the heat flow through the sampleand given by the following equation [6]:

$Q = I V$ ………………… (2)

The specific heat is the quantity of heat required to change the temperature of unit mass of the substance by one degree, if a quantity of heat (ΔQ) is required to produce a temperature change (ΔT) in a mass (m) of substance, then the specific heat is [7]:

$C = \Delta Q / m \Delta T$ ………………… (3)

where the specific heat (C) in units of (gm . k / w),

Can extract the thermal diffusion values(α) after calculating density (ρ), where the density is equal the mass ratio (m) to the volume ($V = \pi R^2 L$),were (L) is equal to the thickness of the sample (0.4 cm), (R) is the radius of the sample and is equal to (0.8 cm). Therefore, this sample volume is equal to (0.8 cm^3)[8].If the mass of this sample is (m = 1.5 gm), the density becomes (ρ = 1.86 gm/cm^3).So the thermal diffusion equation is as follows[5]:

$\alpha = \lambda / \rho c$ ………………… (4)

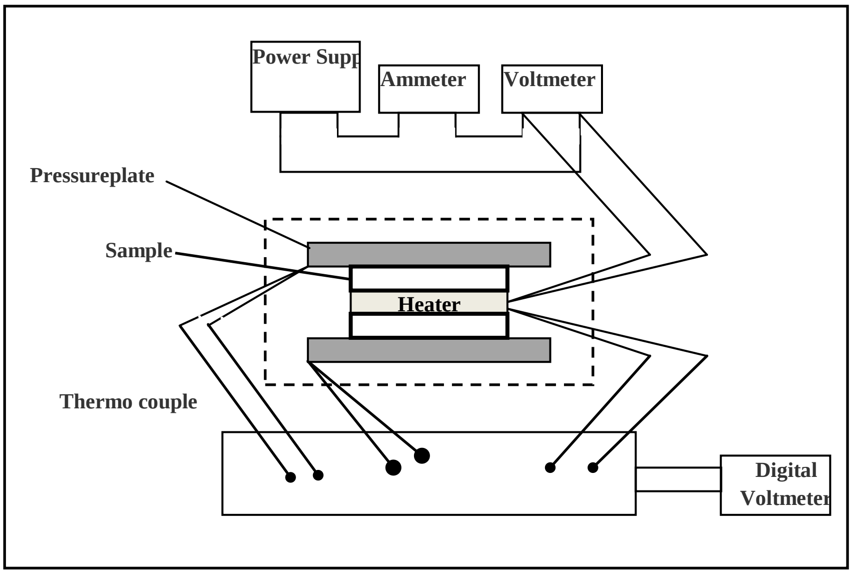
From calculation of thermal conductivity and specific heat, is obtained thermal diffusion values in units of (cm^2 / s).

Practical Part:

Preparation of Samples**:**Preparation of the legand (Di (1-phenyl propanaldehyde) Hydrazone) by a reaction of one mole of Hydrazine and two mole of Vanilline using Ethanol as a solvent during reflux process . Preparation of the complexes by a reaction of the prepared legand with metal ions of (Co^{+3}, Cr^{+3}) using molar ratio (1:1) and Ethanol as a solvent during reflux process[9,10].

The Method of Work: The thermal conductivity measuring deviceconsists of two main parts(heater,two pressure plate),Connecting the circuit as shown in the figure (1)with existence digital voltmeter and DC power supply of which is the heat equipped for the heater, has been studying the behavior of thermal conductivity for the samples for the samplesby change the temperature within the range of temperatures (298-323 K), the samples used were thick (0.4 cm) and diameter (1.6 cm) which was obtained by laboratory-yard and specifications fit the nature of the study of form, mass andmolecular weight, the accounts have been conducted in the advanced materials laboratory in department of Physics - college of Science - university of Babylon.

Install sample from prepared samples on the face of the heater by two pressureplate and then the device was placed inside a thermal oven, which has control on the temperature, and then prove the sample temperature at (298 K) by controlling oven programming with the help of thermal thermometer until a steady state of the device, then record the reading thermocouples that are sensitive of upper and lower plates temperatures.



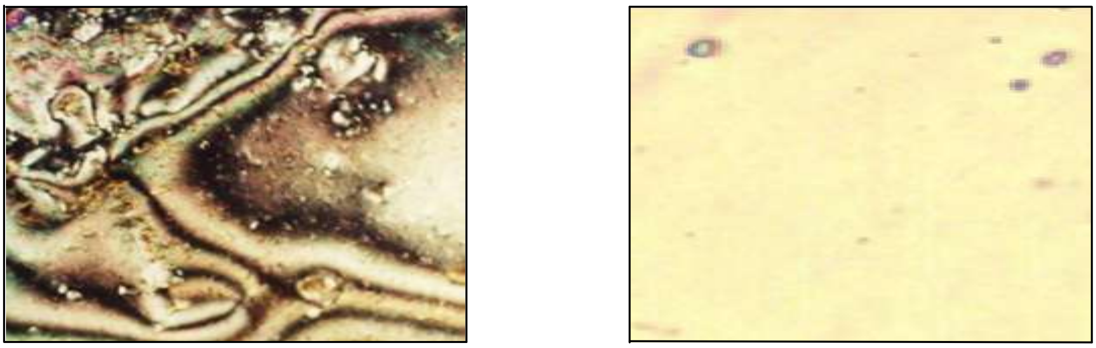
Figure(1): The circuit used in thermal conductivity measuring.

For the purpose of calculating the specific heat of the compounds prepared is to install the oven temperature at heat degree (298K) and the current is passed through the heater for a certain value by ammeter tied in a row with the heater, as well as the voltage across the heater, calculate the amount of heat flowing through the sample (Q) from the relationship (2), keep the temperature of the oven constant at (298 K) while change the temperature flowing through the sample by change the values of both current and voltage, shall be returned the process several times for different readings of the current and voltage, were calculated specific heat by using equation (3),Then calculates the thermal conductivity and thus the thermal diffusion.

Re the same previous work for the temperature (303 K), where they prove the degree of the thermal convection oven and set the amount of heat flowing through the sample and the same previous values that have been registered for the current and voltage at temperature (298 K), so for other temperature and up to the temperature (323 K).

Results and discussion:

All compounds have shown a nematic phase (Enantiotropic) by heating and coolingas in Figure (2):



heating process .

Photo (B): Marble textureby cooling process .

Figure (2): Marble of nematic phase of legand (Z) by heating and cooling process.

IR spectra of the prepared legand (Z) have absorption band (1664) cm-1 for the aromatic double bond, as well as showed abroad absorption band of complexes at (1560 - 1632) cm^{-1} as a result of the presence water molecules within the complex. UV-Visible spectra of the prepared legand (Z) shows absorption peaks at (332)nm ; while for the complexes they showed abroad band (278 - 363) nm for CZ(1), (289 - 357) nm for CZ(2) because the electronic transition of (n-π*) for the azomethane (CH=N) bond, and (σ-σ*), (π -π*) for the aromatic (C=C) bonds.

This paragraph includes the presentation of the results of thermal tests of three liquid crystal samples made in practice by some analytical devices in addition to the values that have been reached using mathematical relationships, where the results Include the values of thermal conductivity and heat flow and its relationship with temperature obtained within the range of degrees heat (298-323 K). The figure (3) shows the relationship of thermal conductivity with temperature for the legand (Z), from the figure (4) calculating the values of specific heat (C) of the legand (Z) from the relationship the amount of heat (ΔQ) and temperature difference (ΔT) in the temperature range (298-323K) through forms of (S1-S6), respectively.the relationship between each of the specific heat (C) and thermal diffusion (D) with temperature of the legand (Z) shows in the form (5) through two forms (S7) and (S8), respectively.

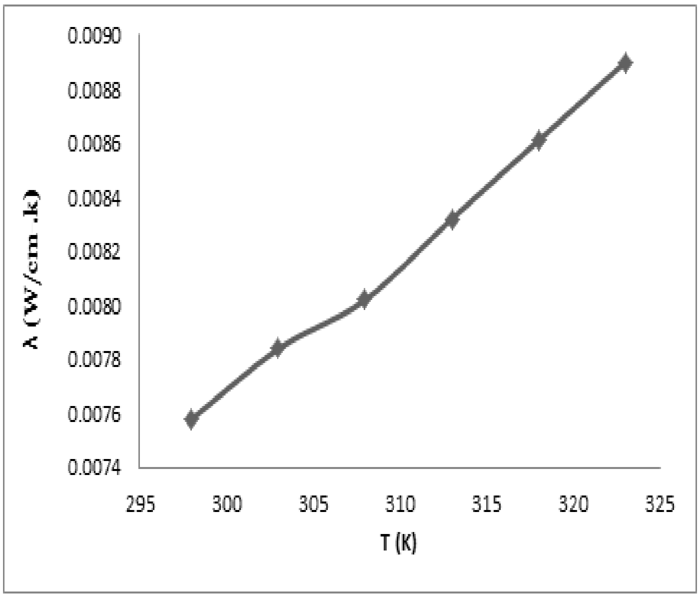
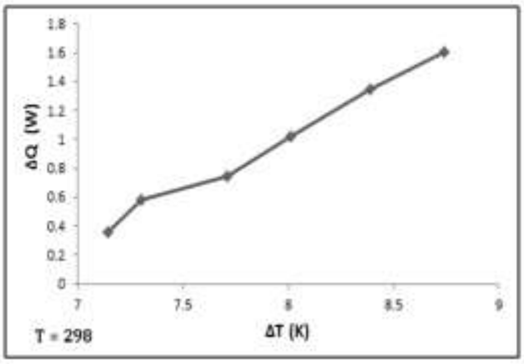
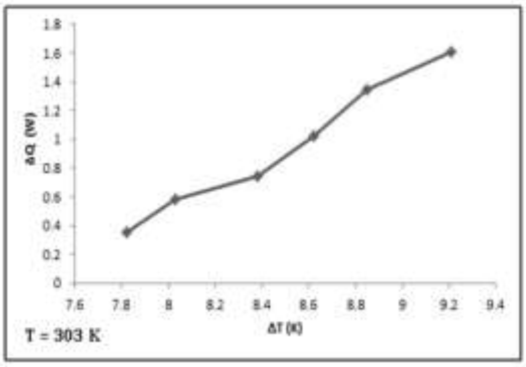


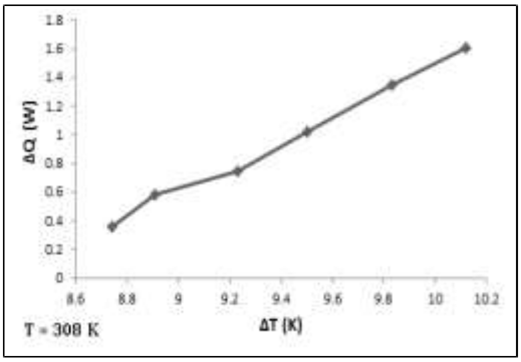
Figure (3):Relationship between thermal conductivity and temperature of Ligand (Z).



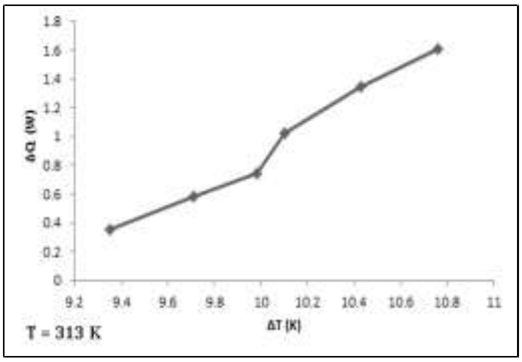
(S1)



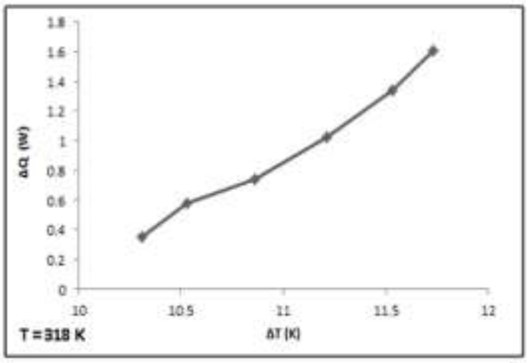
(S2)



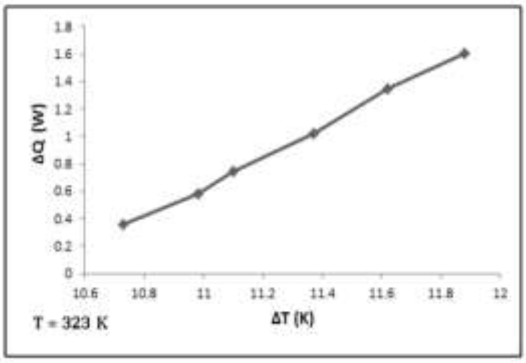
(S3)



(S4)

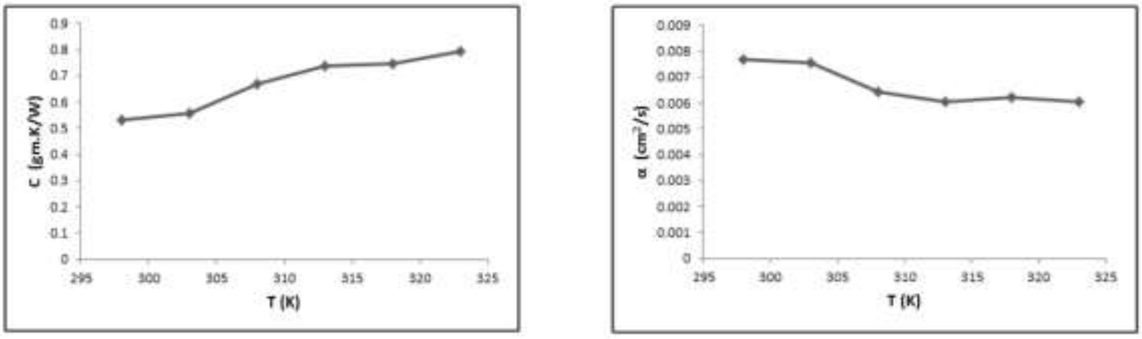


(S5)



(S6)

Figure(4): Relationship between thermal quantity ΔQ(W) and temperature difference ΔT(K) for Ligand (Z) at temperature range T=(298-323K).



(S$_7$) (S$_8$)

Figure(5): Relationship between specific heat , diffusion heat and temperature for Ligand (Z).

The figure (6) shows the relationship of thermal conductivity with temperature for the legand (Z), from the figure (7) calculating the values of specific heat (C) of the legand (z) from the relationship the amount of heat (ΔQ) and temperature difference (ΔT) in the temperature range (298-323K) through forms of (S$_9$-S$_{14}$), respectively. the relationship between each of the specific heat (C) and thermal diffusion (D) with temperature of the legand (Z) shows in the form (8) through two forms (S$_{15}$) and (S$_{16}$), respectively.

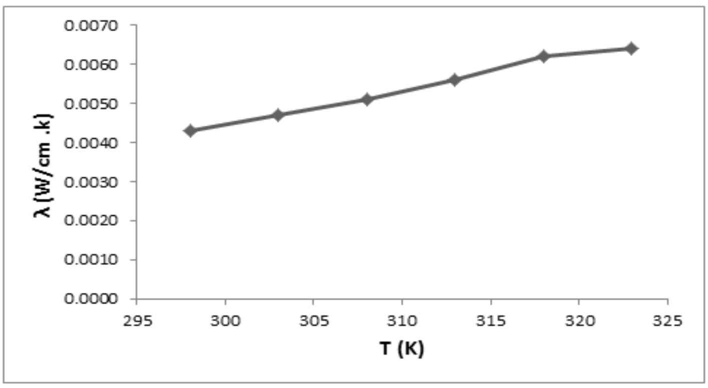
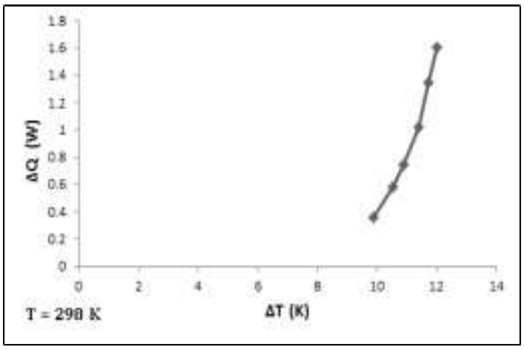
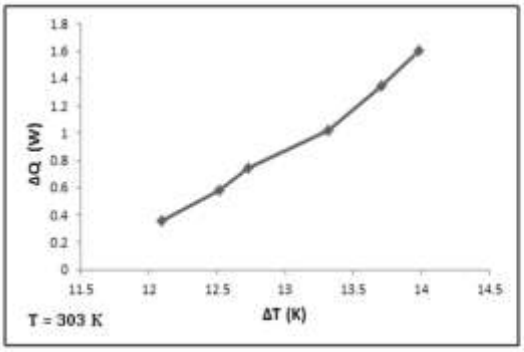


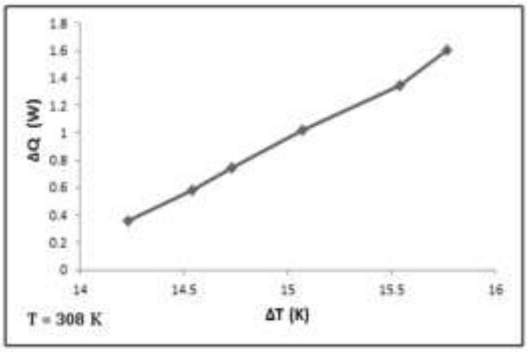
Figure (6):Relationship between thermal conductivity and temperature of complex (CZ1).



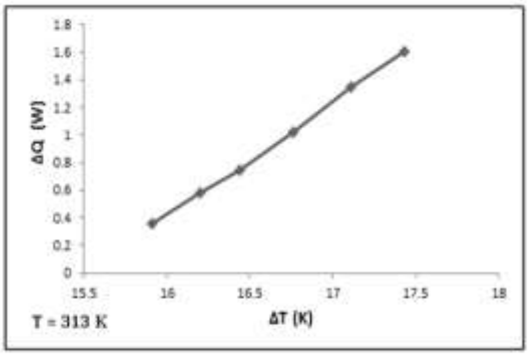
(S9)



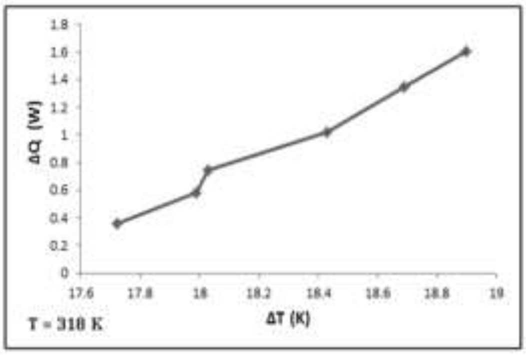
(S10)



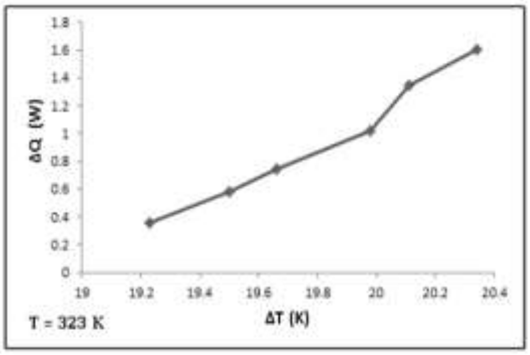
(S11)



(S12)

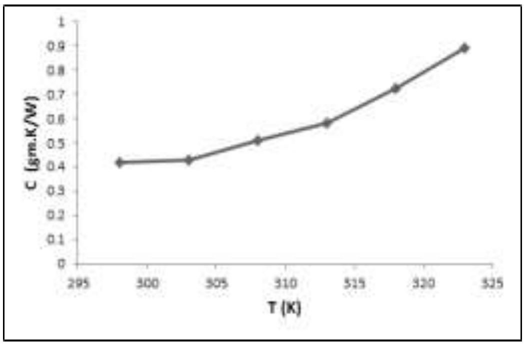


(S13)

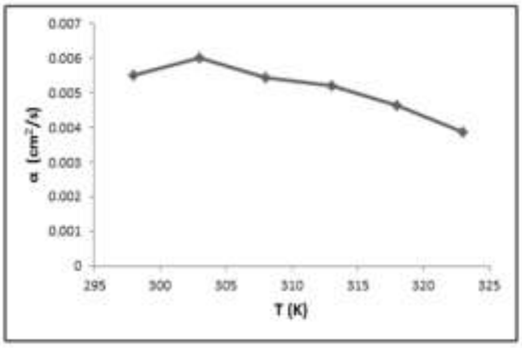


(S14)

Figure(7): Relationship between thermal quantity ΔQ(W) and temperature difference ΔT(K) for complex (CZ1) at temperature range T=(298-323K).



(S_{15})



(S_{16})

Figure(8): Relationship between specific heat , diffusion heat and temperature for complex (CZ1).
Photo (A): Marble texture by

The figure (9) shows the relationship of thermal conductivity with temperature for the legand (Z), from the figure (10) calculating the values of specific heat (C) of the legand (Z) from the relationship the amount of heat (ΔQ) and temperature difference (ΔT) in the temperature range (298-323K) through forms of (S_{17}-S_{22}), respectively. The relationship between each of the specific heat (C) and thermal diffusion (D) with temperature of the legand (Z) shows in the form (11) through two forms (S_{15}) and (S_{16}), respectively.

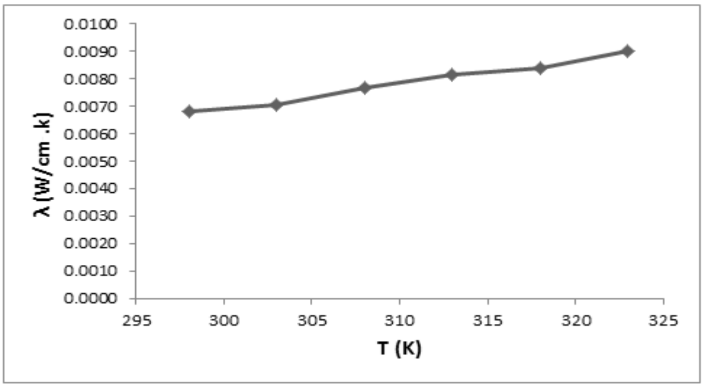
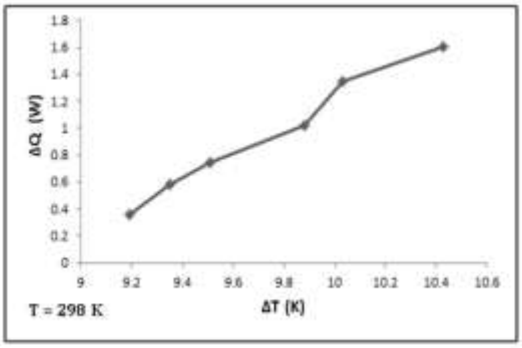
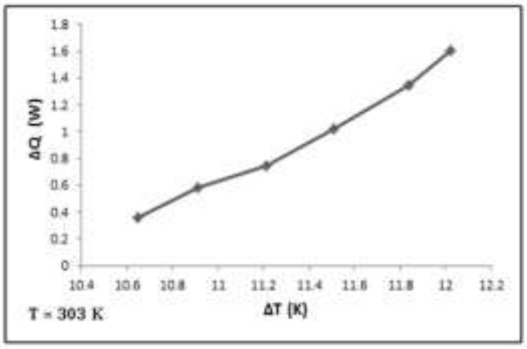


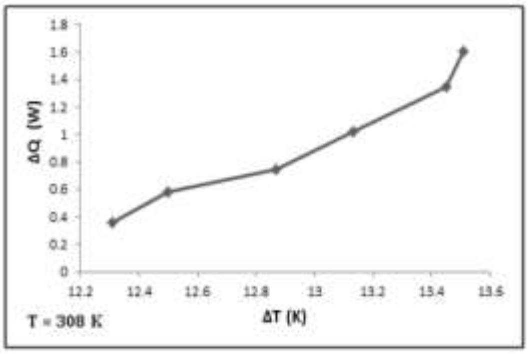
Figure (9): Relationship between thermal conductivity and temperature of complex (CZ2).



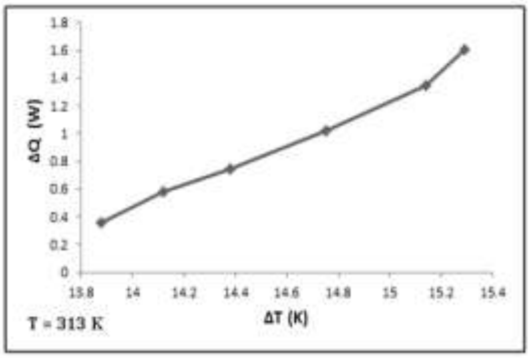
(S_{17})



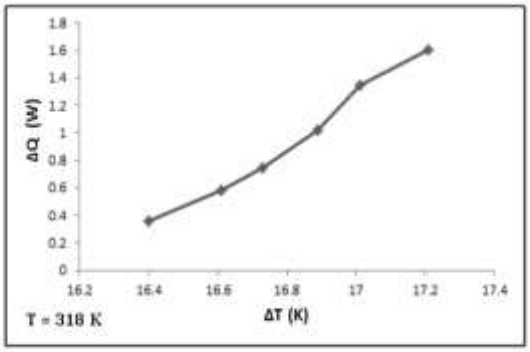
(S_{18})



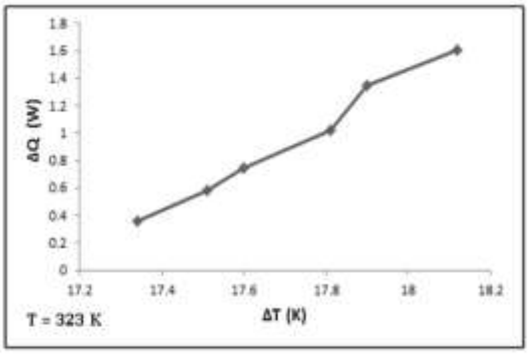
(S19)



(S20)

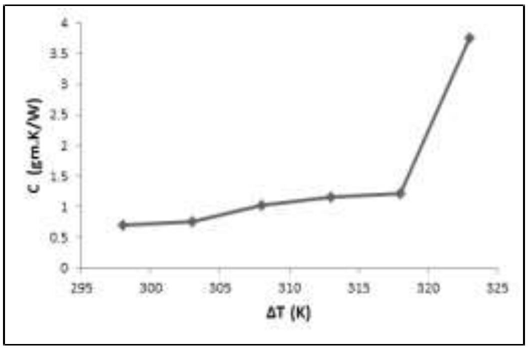


(S21)

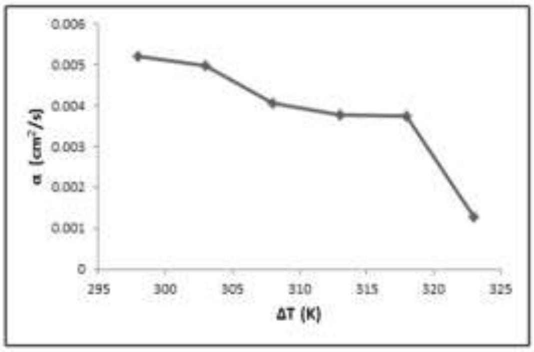


(S22)

Figure(10): Relationship between thermal quantity ΔQ(W) and temperature difference ΔT(K) for complex (CZ2) at temperature range T=(298-323K).



(S23)



(S24)

Figure(11): Relationship between specific heat , diffusion heat and temperature for complex (CZ2).

From observe the relationship between the thermal conductivity and temperature of legand in Figure (3), we found that the thermal conductivity values slightly increase with a high degree of temperature, because the high temperature leads to increased kinetic energy of the metal electrons (ligand), which in turn leads to increased thermal conductivity, while the values of the thermal conductivity decreases with increasing temperature for the complexes as shown in Figures (6 and 9) because the difference in effective set of complex than in legand, and the presence of succession electronic for bonds of complex rings.By observing the Figures (5,8,11) we found that the specific heat values slightly increase with a high degree of temperature, and it is due to the extent of thermocouples sensing because of the increased amount of heat flowing through the sample. It is well known that the value of the thermal conductivity and specific heat of the element chromium free is greater than the value of the thermal conductivity and specific heat of the element cobalt free, and when see the Figs (6,8,9,11) noticed that the value of the thermal conductivity and specific heat of the complex chromium remained greater than the value of the thermal conductivity and specific heat of the complex cobalt, this means that the metal remained conservative on the thermal qualities after complex, in general all the results of thermal measurements agree with the source [11].

Note by the results we found the thermal diffusion for the legand and the complexes behaves differently from the behavior of specific heat with high temperatures and the reason is due to the inverse relationship between the two, as in equation (4). In general, the results gave me all of the specific heat and thermal diffusion consistent with the results of experiments conducted on this type of compound [12].

Conclusions:

1- The study of thermal conductivity as a function of temperature for prepared compounds, it was Found that the values of thermal conductivity for the ligandincreases slightly with increased temperatures, while decreases for the complex at the temperature range (298-323) K.
2- The study of thermal quantity of the prepared compounds, it was found that the value increases with temperature within the temperature range is confined between (398-323) K.
3- A study of the thermal diffusion and specific heat of the prepared compounds under study, found that the valueof thermaldiffusionincreases slightly with rising temperatures at the same temperature range,whilespecificheat decreasesslightly with rising temperatures at the same temperaturerange.

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