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Methylene bis(p-chlorobezodithioate): Synthesis, characterization and its use as analytical reagent for Silver ion

Yasser N. Mutter AL-Guraby, Ahmed A. S. Alwaaly and Hassan T. Abdul sahib
Department of Chemistry, College of Science, University of Basrah, Iraq.

Abstract

The study included the preparation and diagnosis of disulfur ligands (Dithiols) and the preparation of their complex with monovalent (Silver), which included the the following steps: First: preparation of the sulfur compound through the reaction of Grignard reagent (CPhMgX), with carbon disulfide (CS₂), this step form [CPhCS₂]⁻, an acidic liquid sulfur compound which was converted into a dimer compound by second step :- reacting with (Benzene tetra methyl ammonium hydroxyl) which produce a negatively charged compound [CPhCS₂]⁻, which is a viscous, hydrated compound with a strong sulfur smell. The product [CPhCS₂]⁻ react with dichloromethane (DCM) which produce (methylene-bis (p-Chlorodithiobenzoate). Which is characterized with (IR,UV-VIS, ¹H-NMR, ¹³C spectroscopy , mass spectrometry) then followed by Analytical study for the prepared compound were investigated by preparation of their complex with Monovalent (Silver), where the stability constants of the prepared complex were studied, which showed the stability of the complex at room temperature and at pH (PH = 8). The absorbance of the complex for UV-Vis. light was studied and the mole ratio (M: L) was studied. From the study of spectroscopic methods.

KEY WORDS: *Dithiols, Silver, Reagents*

1. INTRODUCTION: -

The importance of sulfur compounds lies in that they are organic compounds with sulfur substitutes ending in (-SH) or (= S)⁽¹⁾, and they are of several types, including aliphatic compounds and aromatic compounds of all kinds^(2,3) and they have physical and chemical properties⁽⁴⁾ and biological activity⁽⁵⁾ distinctive⁽⁶⁻⁸⁾ Thiols are called alcohols or thiols because they are similar to alcohol and phenol compounds, where the difference lies in replacing oxygen with a sulfur atom. Goods are derivatives of sulfides H₂S in the same way that alcohols are derivatives of water H₂O and very volatile aniolates have an unpleasant smell more than the smell of sulfide hydrogen itself. Compared to oxygen, sulfur has a larger atomic size, and its atomic orbitals are more diffuse electronic orbitals. The energy of the oxygen-hydrogen bond is (100

kcal mol^{-1}), so thiols are more acidic than the corresponding alcohols and the hydrogen bond in them is weaker than that of alcohol compounds, and this results in lower relative boiling points and solubility in aqueous solutions. For example, methanethiol (MeSH) is a gas, while methanol (MeOH) is a liquid that boils at 65°C , and ethanethiol (EtSH) is a liquid that boils at 37°C , while ethanol, EtOH, boils at 78°C . The weakness of hydrogen bond in thiols is clearly notice at the frequency of the IR. Compared with alcohols, the thiol hydrogen bond S-H absorbs at a frequency of $(2600\text{-}2550\text{ cm}^{-1})$, while the O-H bond is absorbed in alcohols at a higher frequency of 3350 cm^{-1} , and the absorbance of the thiol band is S-H does not change significantly with a change in concentration, solvent, or physical state, as it definitely indicates a weak hydrogen bond for thiols ^(9, 10). Some thiols are natural, such as skunk secretion containing the compound (3-methyl-butanethiol) and the smell of onions containing the compound (1-propanethiol) as well as the thiol group in the amino acid cysteine. Environmental pollution and human contact with dust storms and wastewater containing heavy metals, have become a crucial ecological and health problem worldwide. Continuous exposure by man to silver sources leads to the occurrence of a number of diseases, including, for example, hemorrhagic disease, damage to vital tissues of the bone marrow, liver, and kidneys, enlargement of the heart, delayed growth and changes in the liver ^(11, 12). Silver is found in nature in free form or in the form of compounds such as ores (Ag_2S , AgCl). Therefore, current study was conducted to synthesize new important chemical compounds, methylene dibenzodithioate derivatives. In addition, the chemical structures of their metal complexes were studied indetails

2.MATERIALS AND METHODS

2.1. Materials

All chemicals used in the preparation of thiol ligand and metal complexes are products from BDH and Merck.

2.2. Measurements

Melting points were determined by open capillary tube method by using melting point model BUCI 510. FTIR spectra were recorded on a Shimadzu 8400S FTIR spectrophotometer in the $(4000\text{-}400)\text{ cm}^{-1}$ range using KBr discs. Electronic spectra were obtained by (CO.LTD(UK)-UV-9200 spectrophotometer) using THF as solvent in the $(200\text{-}800)\text{ nm}$ range at College of science, university of Basra, Chemistry Department. Mass Spectra were recorded on Agilent Technologies 5975C 110 . ^1H NMR & ^{13}C were recorded on MHZ500 Bruker using DMSO as solvent in college of science university of Tehran Islamic R. of Iran, the concentration of the solutions was $(10^{-3}\text{ mol L}^{-1})$.

2.3. Synthesis of (methylen-bis(p-Chlorobenzodithioate)

(methylene-bis(p-Chlorobenzodithioate) ligand is prepared according to the general procedure by (Ahmed Alwaaly, William Clegg)⁽¹³⁾

1- (110 ml, 10 M) was withdrawn from Grignard (p-Chlorobenzene magnesium bromide) reagent is placed in a circular flask of (500 ml) volume, then a (6.04 ml) of CS₂ compound slowly added to the beaker wick containing the reagent while maintaining a temperature of 20 °C and dissolve the mixture with 40 ml of THF Anhydrous solvent. leave the mixture react for an (90 min.)^(14,15) with continuous stirring. After the end of the reaction, 2/3 volume of the solvent was removed by evaporation by rotating at a temperature of 25 °C, then the remainder after evaporation of the solvent was added to a mixture consisting of (100 gm of ice non ionic water , 50 ml of 10 N HCl and 80 ml of n-hexane) mixed with product and shaken for 10 minutes, the resulting compound was extracted by separating funnel and using 100 ml of hexane for two successive times (50 ml each time) where the viscous sulfur compound with a dark red color. It has a distinctive, puffy odor, which is (p-Chlorobezodithioic acid) (Fig.1).

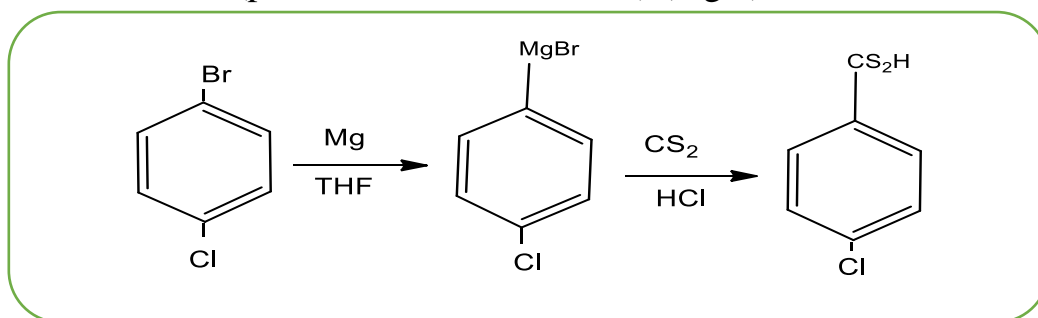


Fig. 1: Synthesis of (p-Chlorobezodithioic acid)

2 -(10 ml) of Benzyltrimethylammonium hydroxide was added to the reaction product from the first step and leave the mixture to react, then after completing the reaction, the mixture was evaporated under vacuum pressure and crystals of a dark violet precipitate were obtained with chemical structure as shown fig. (2).

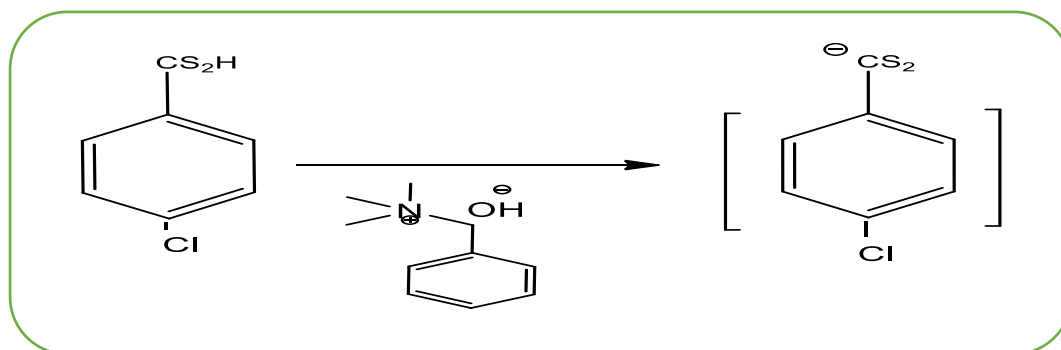


Fig. 2: Synthesis of (p-Chlorobezodithioate)

3- (3.03 g) of the Benzyltrimethylammonium Benzodithioate salt prepared in step 2 was weighed and a stoichiometric amount of halogen compound (DCM) was added to it , the mixture was left to react for (2hrs) to form a bright red precipitate, then the precipitate was separated by filtering and then added to it

10 ml of hexane, then put into a chromatographic tube of silicon oxide SiO_2 with specification (~15 g in a 0.5-in.-diameter column) using (THF and Hexane) to rinse the column, then a red precipitate was isolated and recrystallization was performed With hexane and DCM, this precipitate is the compound Methylene bis(p-chlorobezodithioate) (Fig.3).

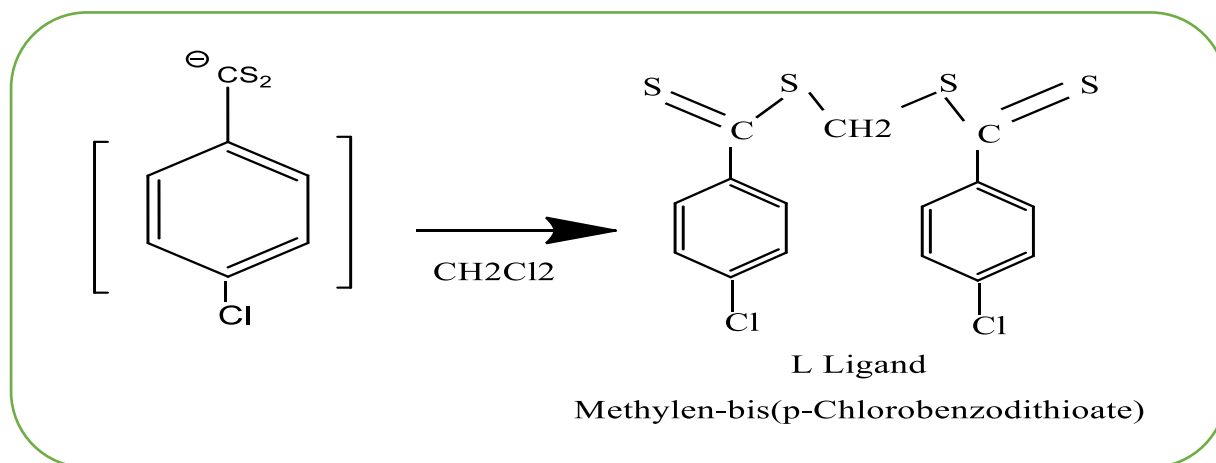


Fig. 3: Synthesis of Methylene bis(p-chlorobezodithioate) = L

Table (1) the physical properties of compound(L)

M.WT. ⁽¹⁶⁾	λ_{\max}	M.point	Crystal shape	color	Molecular formula	Yield%
389.414	320,502	125	regular radial	bright red precipitate	$\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{S}_4$	85

2.4. A- Preparing the organic solution for Ligand:

The organic reagent solution was prepared with a concentration of (0.001 M) for organic compounds (L) by dissolving (0.038 g), respectively, in an appropriate volume of THF organic solvent. It was kept as a stock solution.

B- Preparation of metal solutions of (Ag^{+1}):

Solutions of (0.001 M) Silver was prepared by dissolving (0.1698g) of Silver nitrate AgNO_3 in 100 ml of deionized water.

C - Synthesis of metal complexes

The metal solution with the ligand was prepared Roughly by mixing and shaking for only two minutes.

D - Preparation of the universal buffer solution:

A series of buffer solutions with pH range (2 to 12) were prepared by Britton-Robinson⁽¹⁷⁾ method by continuous skewing of 100 ml of mixture (0.1 M of acetic acid, boric acid and phosphoric acid) with 0.5 M of NaOH to the desired pH. And

using distilled water to keep the ionic strength constant, using a PH-Meter to adjust the PH.

Absorption spectra in different polar organic solvents:-

The absorption spectrum of L was studied by preparing a solution with a concentration of (0.0001M) by withdrawing an appropriate volume of its buffer solution using organic solvents of different polarity as follows:

(H₂O+Aceton, DMS, DMF, Methanol, Ethanol, Isopropane, Acetone, Ethyl acetate, CHCl₃, THF, DCM, Diethyl ether, Toluene, Hexane)

The spectrum was recorded in the region (200-800 nm) at room temperature and using the solvent as a reference solution (Blank).

2.5. Study of optimal conditions for complex formation:

The optimal conditions (maximum wavelength, reaction time, pH and sequence of addition) ^(18,19) were studied to form complexes for L with the element Ag as follows:

A- the wavelength:-

The appropriate wavelength was selected at room temperature, following the following steps:

*- Solutions of L was prepared at a concentration of (0.001M) and the absorption of the solution was recorded in the region (200-800 nm) using THF as Planck's solution.

*- Solutions of complexe with (Ag) was prepared for L at a concentration of (0.0001M) and the absorption spectrum of the solution was recorded within (200-800 nm) using THF as Planck's solution.

B - Effect of reaction time:-

The effect of the reaction time on the formation and stability of complex was studied by measuring the absorbance of complex solutions at a concentration of (0.0001M) for L Compound and metal ions (Ag⁺) at the maximum wavelength λ_{Max} , in the period of time from (1 min. to 1440 minutes).

C- PH effect:

The effect of (pH) on the formation and stability of complex was studied by preparing a series of solutions by mixing (0.5 ml) of metal and ligand (L) in a volumetric bottle of (5ml) and then completing the volume with buffer solution to the mark and for several variable values of PH and the absorbance was recorded. In the region (200-800 nm) and using the buffer solution as plank solution.

D -Effect of addition sequence on the formation and stability of complexes:

Three successive additions were studied through the following sequence:
Metal + Buffer + Ligand

Metal + Ligand + Buffer

Ligand + Buffer + Metal

The absorbance of these successions was recorded at the greatest wavelength and using the pH regulator as Planck's solution.

Molecular ratio of the complex:

The following spectroscopic methods were used to estimate the molar ratio of the complex:

a- molar ratio method:

A series of solutions has been prepared in which a fixed concentration of metal solution (0.6×10^{-4} M) and the concentration of the ligand solution vary with a range (0.2×10^{-4} - 2.4×10^{-4} M), and the absorbance of these solutions was measured at λ_{max} of the complex using the ligand solution and a solution of The optimum pH for each as plank, complex is also called the Yoe and Jones ⁽²⁰⁾ method.

Photometric method for the determination of a metal ion according to Beer's law:

series of solutions were prepared in each of them having a fixed concentration of the ligand 1.8×10^{-5} M, while the concentration of the metal ion is regularly variable and with a range (0.2×10^{-4} - 4×10^{-4} M). The absorbance of the solutions was measured at λ_{max} of the complex and using a volume of Non-reactive ligand as a plank solution.

3. RESULTS AND DISCUSSION:

ligand L was a crystal, but the chelate complex of this ligand vary in color depending on metal ion. The metal complex was characterized by, molar conductivities, FT-IR, UV-Vis, ¹HMNR & ¹³C spectra. The elemental analyses of complexes indicated that the metal-ligand ratio was 1:1 in the [M: L], M = Ag⁺¹, metal complex. The ligand and its complex were quite air-stable, insoluble in water but soluble in organic solvents such as CHCl₃, THF, DCM, DMSO giving stable solutions at room temperature.

3.1. Infrared [IR] spectra of the Ligand

The FT-IR spectra⁽²¹⁾ provided valuable information regarding the nature of functional group. There are similarities in IR spectra of the ligands and their corresponding metal complexes to each other, except for some changes in the shifts and intensities caused by different metal ions. The infrared spectra of L compound under study display a band at a range of (1176 cm^{-1}) indicates the presence of C=S And the band (826.14 cm^{-1}) indicates the presence of C-S the two bands indicates to the thiols compounds, the band (3414 cm^{-1}) indicate the aromatic C-H, while the band (1527.27 cm^{-1}) indicate to aromatic C=C and the

band (2912 cm^{-1}) indicate to $-\text{CH}_2-$ aliphatic between the two thiols molecules so the compound is a Dimer (Fig.4) .

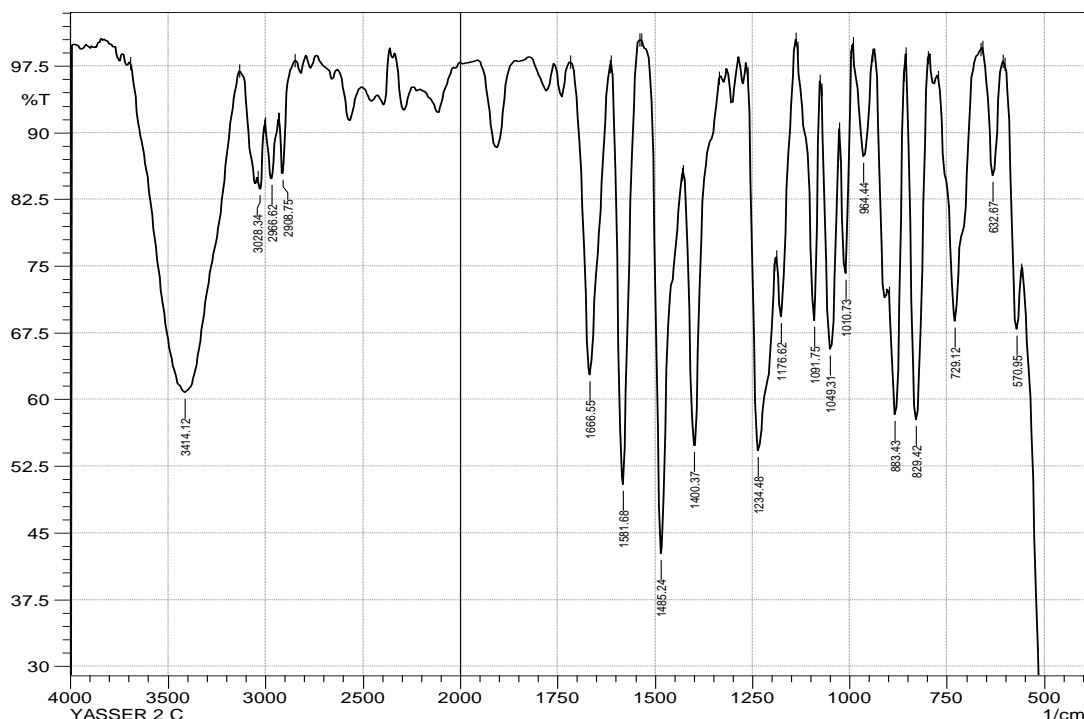


Fig. (4) FTIR Spectrum of ligand L

3.2. NMR spectra of the H^1 -NMR proton of Ligand

The prepared compound L was diagnosed by H-NMR proton spectroscopy using DMSO as solvent and TMS as standard reference using a frequency of 500 MHz. The results showed the nuclear magnetic resonance spectrum of the compound L shown in Figure (5), a single signal at the position ($\delta = 7- 8.5\text{ ppm}$), and the integration indicates that it corresponds to ten protons and belongs to the phenyl ring. While a broad signal appeared at the site ($\delta = 3\text{ ppm}$), the integration indicates that it corresponds to two protons attributed to the (CH_2) group. while the sign at ($\delta = 2.5\text{ ppm}$) belongs to the hydrogen atoms of the solvent DMSO ⁽²²⁾.

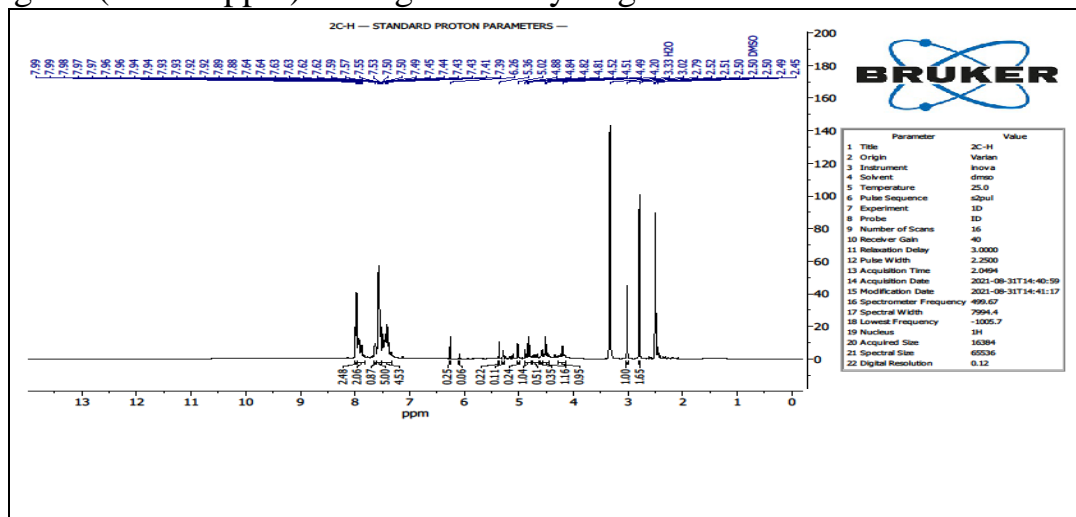
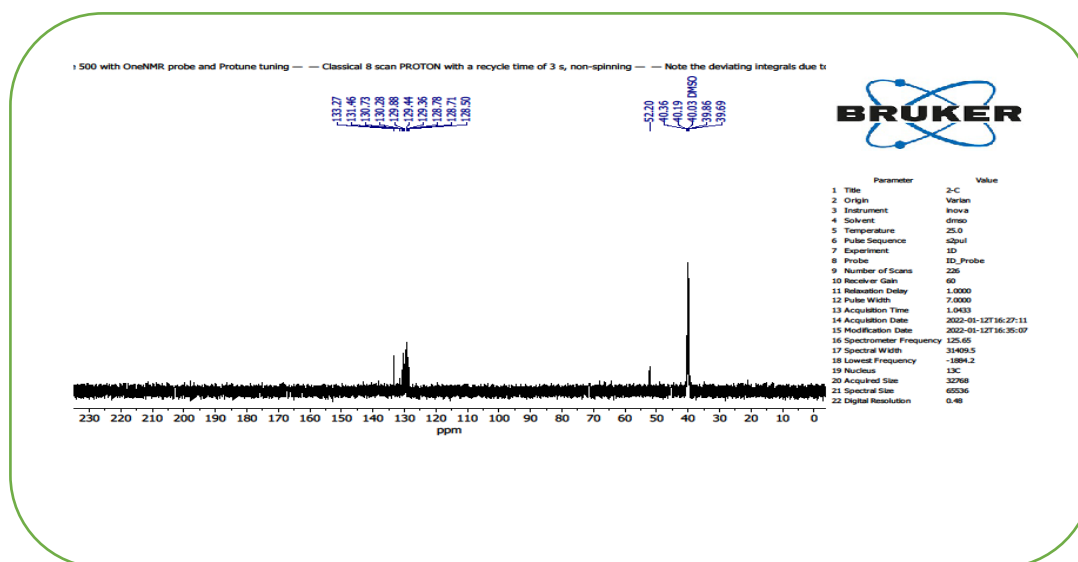


Fig. 5: ^1H -NMR spectrum of ligand

3.3. ^{13}C NMR spectrum of Ligand:-

The ^{13}C NMR spectrum of Ligand was measured at room temperature in DMSO. The ligand displayed characteristic signals at The ^{13}C -NMR spectrum of the compound L shown in Figure (6) showed multiple signals at different chemical shift sites, where the signal appears at the site ($\delta=40.6$ ppm), which is attributed to the carbon atom directly attached to the sulfur atom. As for the signal at the position ($\delta = 52$ ppm) it goes back to the carbon atom in the homologous group (CH_2) bonding between the two sulfur atoms in the two molecules of dithiobenzoate, moreover, in the benzene ring system, several signals appeared at ($\delta=135$, 133, 130, 125 ppm) refer to the carbon atoms in the two benzene rings⁽²²⁾

Figure (6) ^{13}C NMR spectrum of Ligand

3.4. Mass spectrum of ligand:-

The mass spectra of synthesized ligand were recorded at room temperature. This spectrum confirms the proposed formula by showing a molecular ion peak (m/z). Figure (7) and schematic (1) show the fragmentation of ions. It is noted from the mass spectrum of the compound L that the molecular ion is at (389.8 m/z) with relative abundance (0.35%) and the base peak at (154.9 m/z) (100%). Molecular ion indicates agreement with the molecular weight of the proposed structure of compound $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{S}_4$ ⁽²¹⁾.

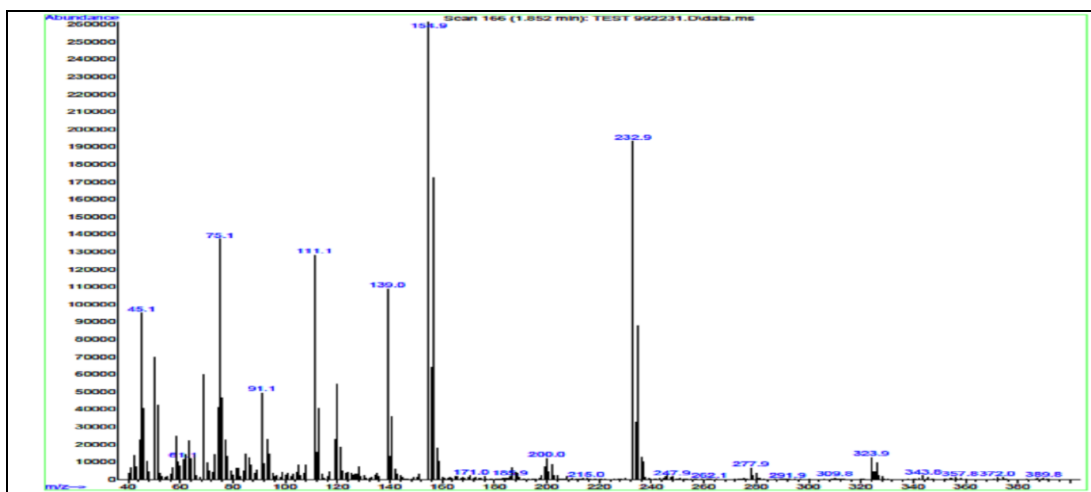
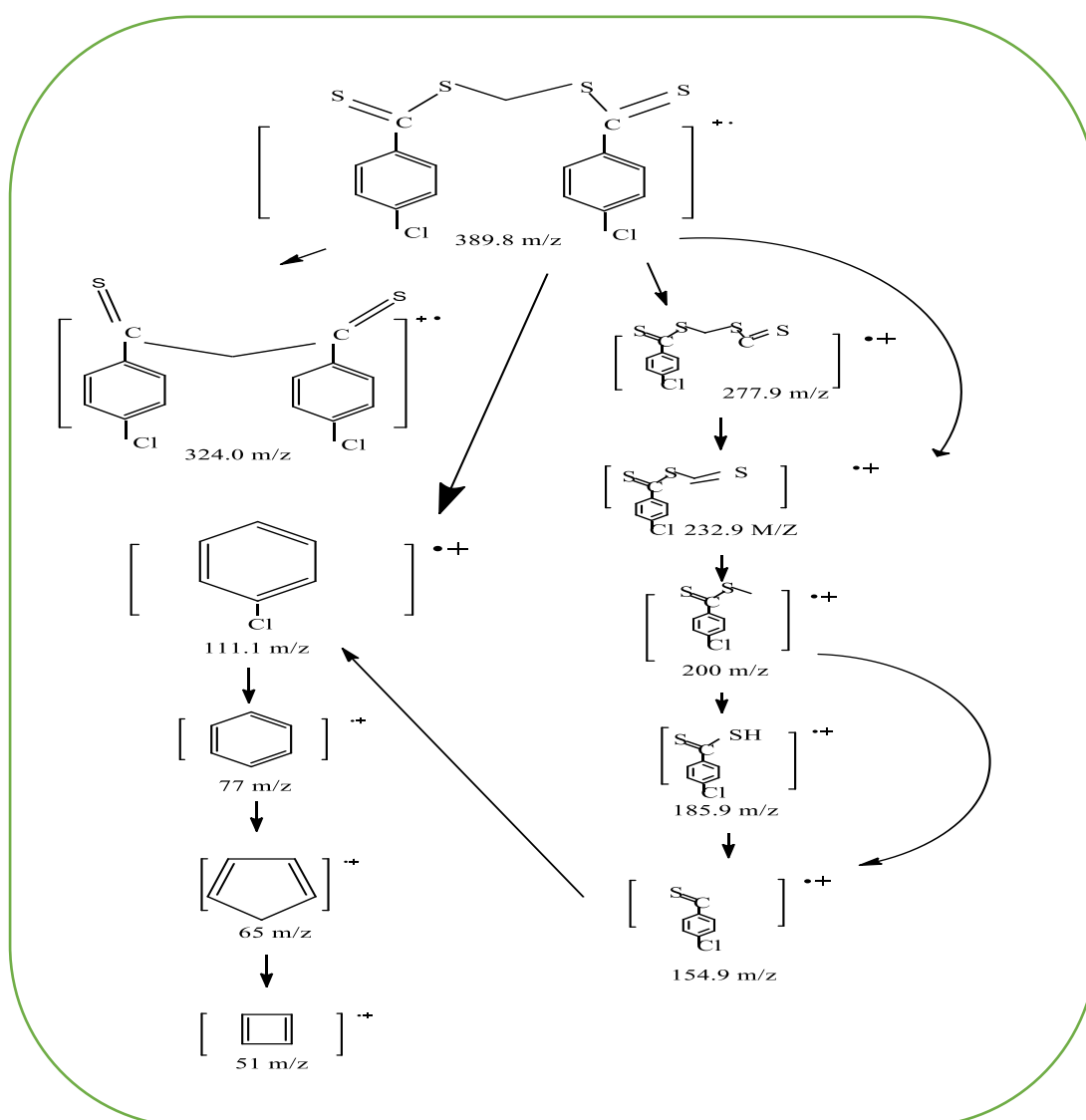


Fig. (7) Mass spectrum of L ligand



Scheme (1) Mass spectrum of ligand

4. Analytical application of (Ligand+ metal) complex :

4.1. Spot test

The spot test was conducted to show the ability of the prepared compound L to form complexes with some important metals such as Na(I), K(I), Ag(I), Mg(II), Co(II), Ni(II), Cu(II), Hg(II), Pb(II), Al(III), Cr(II), Fe(III), Cd(II), Li(I), after preparing a solutions with a concentration of 0.001M for each of the compound and elements. L ligand gives a positive test with element (Ag^{+1}).

4.2. Solvent Effect

The solubility of the prepared compound L was studied using the following solvents ⁽²³⁾: (H_2O , Acetone, DMSO, DMF, Methanol, Ethanol, isopropane, Acetone, Ethyl acetate CHCl_3 , THF, DCM, Diethyl ether, Toluene, Hexane) In order to be able to prepare for the process of preparing ligand and their metal

complexes during the election process. It was observed that it was not soluble in most solvents, while it gave a high solubility at laboratory temperature in the organic solvents: CHCl_3 , THF, DCM, DMSO. The study of (UV-VIS) radiation for Ligand L with a concentration of 0.001M at room temperature the visible spectrum of the Complex showed the effect of the solvent on the maximum absorption (λ_{max}) of Complex were shown in fig. (8)

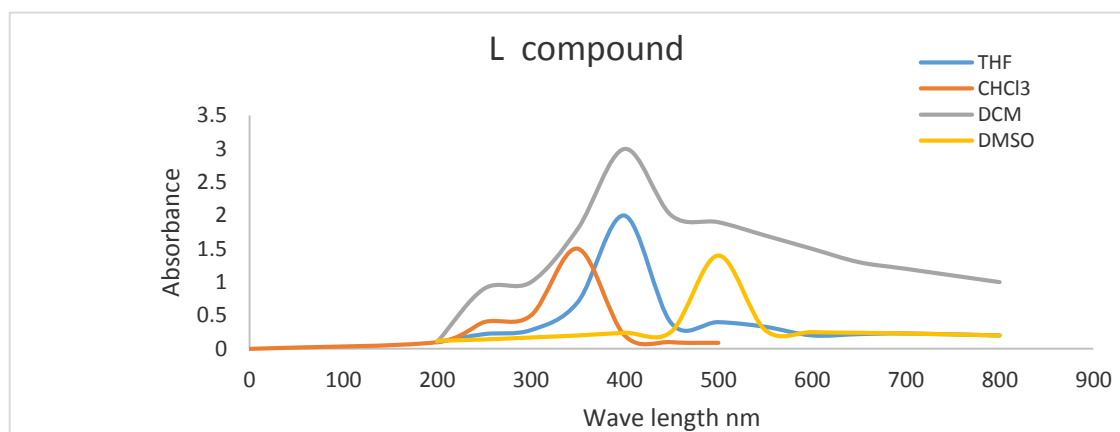


Fig.(8)(UV-Vis)spectrum of compound L:M Complex with different polar solvents

4.3. Optimum conditions for complex formation:

The process of affinity of disulfur ligand with various elements from the periodic table and the optimum conditions for the preparation of complex and the behavior of this ligand with metal element in its aqueous or non-aqueous solutions are of interest. We will discuss the optimal conditions for the concentrations and molar

ratios that have been determined for the preparation of metal ion complexes. Salts of a high degree of purity were chosen to prepare solutions of metal ions with ligand with the choice of negative ion in order to prevent the occurrence of spectral interference, as these solutions had to be clear and free from sediments or suspended particles that lead to light reflection, absorption or scattering during Spectrophotometry.

4.3.1. the wavelength: -

The absorption spectra of the prepared compound and its complex with the element under study was recorded in a solution of (THF + H₂O) at a concentration (4×10^{-5} M) in a quartz cell (1 cm wide) in the (UV-VIS) region within the wavelength range (200 -800 nm), The complex of the compound (L) and (Ag^+) consist a complex ($\text{L} + \text{Ag}^+$) recorded the maximum absorption λ_{max} at wavelength (390 nm), When comparing with the absorption spectrum of the compound (L) which is the maximum absorption at (300 nm). we notice that the shift of the peak depends on the transition $\pi \rightarrow \pi^*$ towards higher wavelength (redshift) due to the formation of the complex ($\text{L} + \text{Ag}^+$) as shown in Fig. (9).

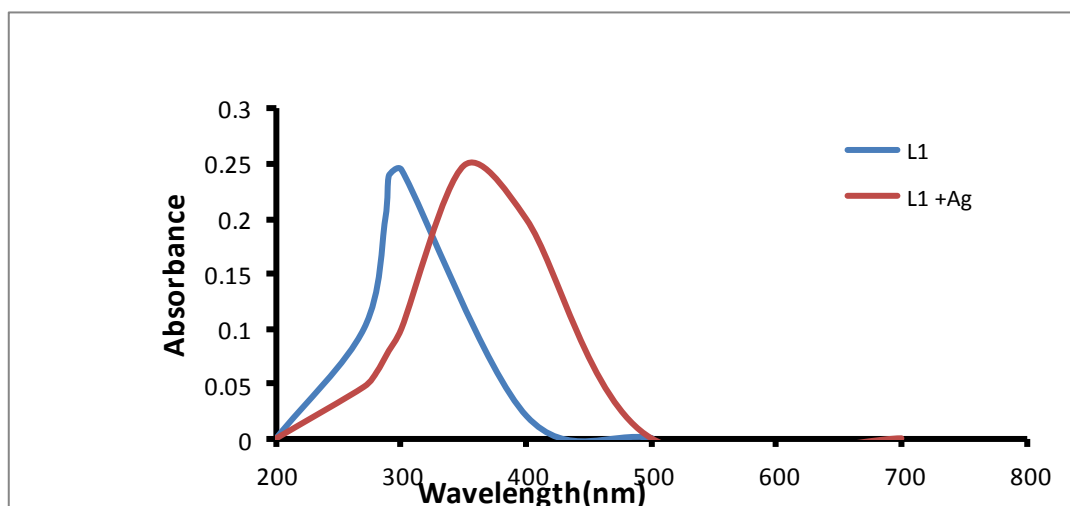


Fig. (9) Absorption spectrum of L and $\text{L} + \text{Ag}^+$, $[\text{M}] = [\text{L}] = 4 \times 10^{-5}$ M

4.3.2. The effect of pH:

The acidity of solutions of mixing metal ions and ligand is important in the coordination process, and this importance lies in the displacement of protons in the active groups (in the alkaline medium) or the fixation of the protons on the active groups (in the acidic medium) in the ligand molecule. The ligand in a particular acidic function differ from the acidic function of another metal ion, and this is called the optimum acidity function for preparing the complex of that metal ion with the ligand in question. As for the ionic complexes (Ag^+) with the compound L, the $\text{L} + \text{Ag}^+$ complex gave the greatest absorption at the acidic

function (PH=8), i.e. in the alkaline medium. Figure (10) shows the absorption spectrum of the $L+Ag^+$ complex at the optimal pH function.

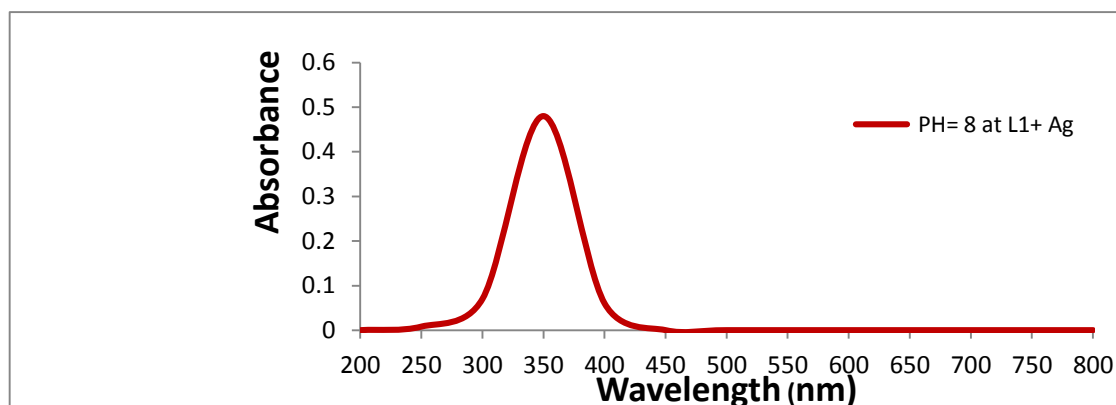


Fig.(10) absorption spectrum of the $L+Ag^+$ at PH =8 of complex

4.3.3. Effect of reaction time:

The time required for the complex to reach its maximum stability and for the complex to remain stable for the maximum period of time is extremely important, especially for the worker in the field of analytical chemistry, so that the necessary spectroscopic measurements can be carried out without any changes in the absorption values that lead to errors and in order to reach the time period that maintains in which the complex is stable and also shows the stability of the prepared metal complexes under study. The effect of the reaction time on the complexes under study was studied at the greatest wavelength (λ_{max}) for each complex, and the changes in the absorption values of the solutions of the complexes were studied for a period of time that ranged from the moment of mixing the solutions of the complexes up to (24 hours). Fig. (11) shows the effect of the reaction time on the $L+Ag^+$ complex.

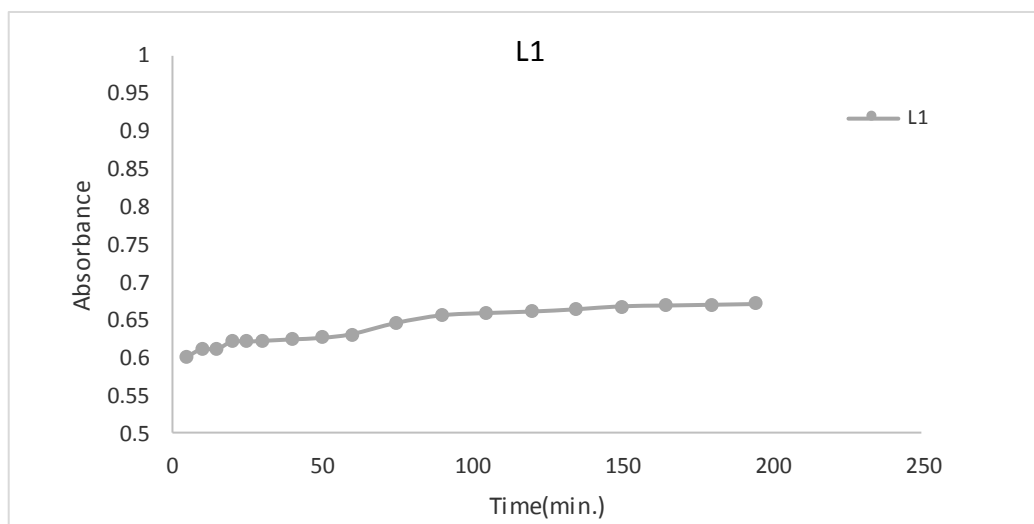


Fig. (11) Effect of reaction time on the complexes L+Ag

4.3.4. Sequence of Additions:

The sequence of additions of the compound, the element and the buffer solution is very important to show the best sequence of addition that leads to the preparation of the active sites in the compound for the purpose of union with the element and the formation of the stable complex. And the best succession is at the optimal acidic function (PH) for each complex. Regarding the effect of the successive additions of the Silver ion (Ag^+) to the compound L at an appropriate wavelength, as shown in Table (2), where it is noted that the succession of the addition showed an effect on the absorption values of the complex $\text{L}+\text{Ag}^+$, the addition sequence gave Ligand+Metal+Buffer) The highest absorption values at the optimal acidity function ((PH = 8 for the bonding of the compound L with the Silver ion Ag^+). The best sequence of addition for $\text{Ag}^+ + \text{L}$ is (1.52) .

Table (2) Effect of Sequence Addition of Silver Ion (Ag^+) to L

PH	Metal+Buffer+Ligand	Ligand+Metal+Buffer	Buffer+Ligand+Metal
	λ_{max} 425 nm	λ_{max} 425 nm	λ_{max} 425 nm
	L1Ag	L1Ag	L1Ag
2	0.42	0.043	0.706
4	0.532	0.521	0.505
6	0.191	0.795	0.254
8	0.235	1.52	0.381
10	0.261	0.141	0.11
11	0.350	0.309	0.09

4.3.5. Molecular Ratio of the Complex:

The spectroscopic method is one of the important methods by which the possible structural formulas of complexes can be found, especially solutions of colored complexes. Ultraviolet-visible spectra are widely used in this field. The process includes determining the ratios of the complex components of the metal ion and ligand. method) is one of the important methods used in determining the ratio of (metal: Ligand), which was presented by (Jones, Yoe). In it, the absorption of a series of solutions containing a fixed amount of metal ion with increasing and proportional amounts of ligand is measured at (λ_{\max}), with no absorption of either the ligand or the metal ion in that region where the complex is absorbed. This method includes drawing the relationship between the absorption on the y-axis and the (metal: ligand) concentration ratio of the mixing solutions on the x-axis, and then the straight lines are drawn until they intersect, and the point of intersection is the ratio of (metal: ligand) in the complex. It is noticeable that the solutions of the complexes when prepared, the intensity of their colors increases as they approach the points of intersection indicating the ratio of (metal: ligand), and the color remains constant when passing this point, which indicates that the complex formed is stable in its solution. From the fig.(12) the ratio of the ion under study with the prepared compounds L is in the ratio of (1:1) (L:M), i.e. one mole of the metal ion with one mole of the compound⁽²⁴⁾ for (Ag^+) complex because it is monovalent.

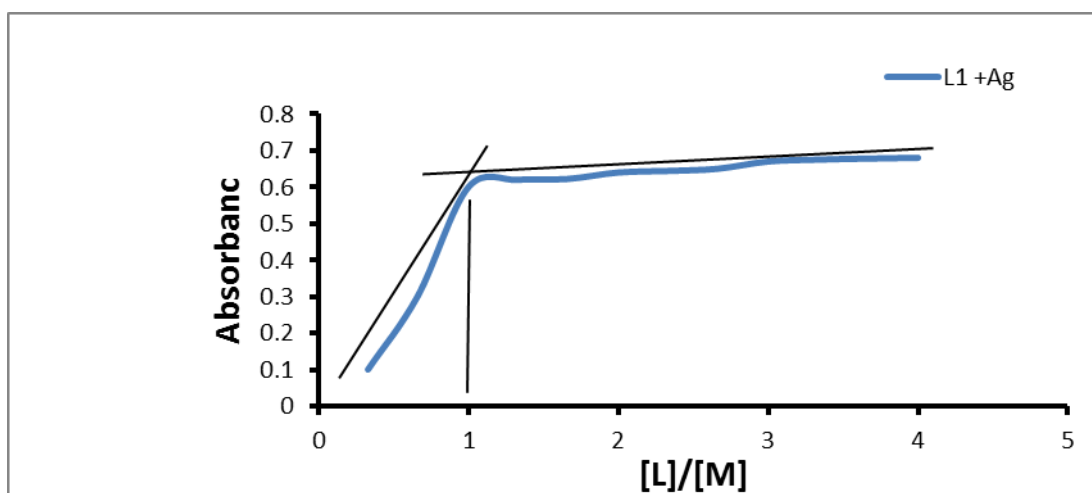


Fig. (12) The method of the molar ratio of the complex ($\text{L}+\text{Ag}^{+1}$)

4.3.6. Obeyence of Beer's Law

For the purpose of constructing standard titration curves⁽²⁵⁾, a series of solutions were prepared, in which the compound concentration was constant (1.8×10^{-4} M), while the element ion concentration was variable and with a range

(M 0.2×10^{-4} - 4×10^{-4}) and the absorbance of the resulting solution was measured At λ_{\max} for each complex and by using an unreacted part ⁽²⁶⁾ of the compound solution as Planck's solution, it was observed that the high concentrations that exceeded (6.3 - 8.3 ppm) were invalid due to the appearance of sediments when mixing the two components solutions, which hinders the measurement process or does not comply with Beer's law even when these concentrations do not comply with Beer's law They are free of plankton and sediments, and low concentrations below (0.4 ppm) were excluded due to their low absorbances and weak beams indicating complex formation. From what was mentioned, standard calibration curves were built using concentrations corresponding to Beer's law. The sensitivity of the photometric method was compared with the specific absorbance (a) ⁽²⁷⁾, which is calculated from the equation: $(a = \epsilon / (\text{At. wt of } [M] \times 1000))$ Where ⁽²⁸⁾ (At.wt) is the atomic weight of the element at a concentration of 1 ppm) in a (cuvette) cell with a light path of 1 cm. The photometric sensitivity is usually expressed in terms of the Sandell sensitivity (s), which represents the amount of micrograms per 1 ml of the solution of the element with an absorbance up to (0.001) and a trajectory of 1 cm and is expressed in ($\mu\text{g} \cdot \text{cm}^{-2}$) and is calculated by the relationship: $(S) = \llbracket 10 \rrbracket^{(-3)/a}$ The deviation of the readings ⁽²⁹⁾ was calculated by according to the following statistical relationship: $S.D = [\sum(X_i - X)^2 / N - 1]^{1/2}$ Where X is the average reading of the absorbance values at a constant concentration. And N is the number of laboratory readings. The X_i is the value of each laboratory reading. The detection limit ⁽³⁰⁾ for the items that were used was calculated through the following relationship: $DL = 2 S.D \times \text{Conc. of Metal} / \text{Mean of Abs.}$

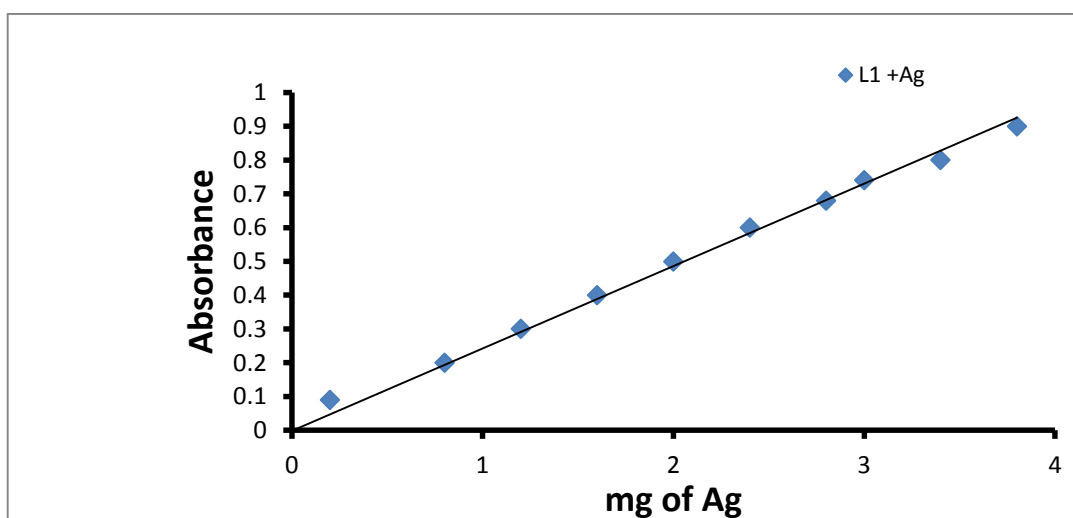


Fig. (13) Calibration curve for the Silver ion in the complex L+Ag⁺

4.3.7. Suggested structural formulas for complexes:

The stereotypes of the complexes differ according to the different coordination centers available in the ligand as well as the nature of the metal ions involved in the complex's composition. Therefore, stereotyped forms were suggested based on the data of the above measurements of the diagnostic chelatic complex prepared in the current study and based on the conclusion that the prepared compound took bidentate ligand, as It is coordinated through two donating sulfur atoms containing the non-binding electron pair. From all of the above, the proposed formulas for the complex under study and their spatial forms can be developed as shown in Fig (14)

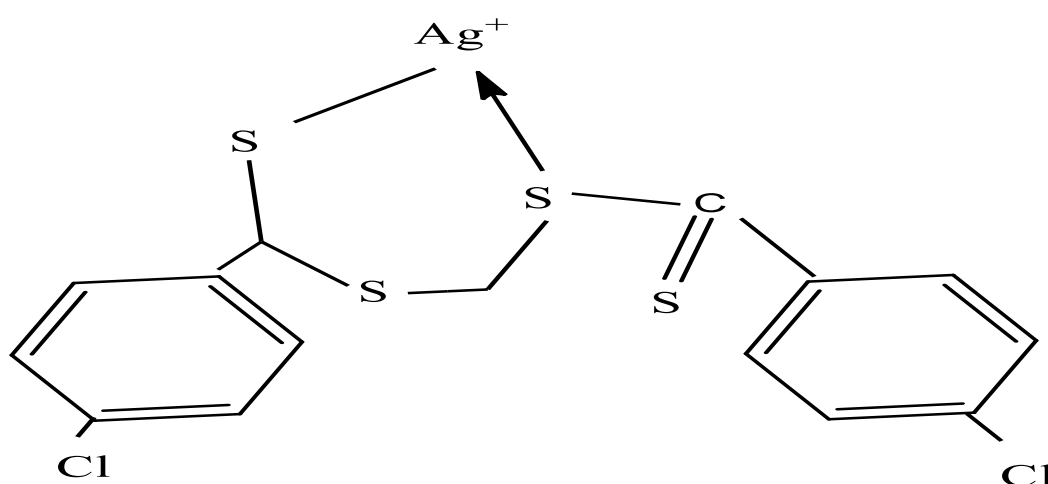


Fig. (14) geometrical shape of complex of Ag^+ ion with the ligand

5.CONCLUSIONS

It can be concluded from the results that we obtained in the current study that:

Through nucleophilic addition, it is easy to prepare two-molecular sulfur reagents and use them spectroscopically in estimating microgram quantities of Silver, as it have colored complexes with Ag. The method for the determination of silver, ions using the prepared two-molecular sulfur reagents is a quick and feasible method from a technical and practical point of view for a wide range of concentrations after stabilizing the best conditions of acidity function, PH, complex stability time, addition succession, temperature, ionic strength and obeyance with Lambert-Beers law. The results of determining the equivalence of (metal: ligand) for the two-molecular sulfur reagents prepared by the molar ratio method showed that the ratios of the reagent to the (1:1) for Silver Complex by studying the effect of positive interferences on the spectral estimation process of Silver ion under study using the prepared two-molecular sulfur reagents, it was found that there is no significant effect of these positive ion on the estimation process.

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