



## SYNTHESIS, SPECTROSCOPIC AND POTENTIOMETRIC STUDIES ON A SILVER(I) COMPLEX DERIVED FROM A NEW BIS(THIOSEMICARBAZONE)

Mahmoud Hassan Moustafa\*, Ahmed Abd-Elnaeem and Osama Ahmed Abbas

Department of Chemistry, Faculty of Science, Al-Azhar University, Assiut Branch, Assiut, Egypt

\*Author to whom correspondence should be addressed: E- mail: mahhassan1959@yahoo.com

### ABSTRACT:

A new reagent, (2E,2'Z)-2,2'-(3-((E)-(2-hydroxyphenyl)diazenyl)pentane-2,4- diylidene)bis(hydrazinecarbothioamide) (OPTS) was synthesized and studied. Acid-base, spectrophotometric properties of OPTS were studied in 50% ethanol-water mixture solutions at pH 3-11. Ionization constants of the reagent OPTS have been determined by a spectrophotometric and potentiometric titrations:  $pK_1=9.60 \pm 0.02$ ;  $pK_2=10.45 \pm 0.05$  in its computational and graphical versions at an ionic strength 0.1 M NaClO<sub>4</sub>. The stability constants of the Ag-OPTS are  $\log K_1=4.55 \pm 0.04$  and  $\log K_2=3.92 \pm 0.05$ . The reaction of Ag(I) with OPTS gives a mononuclear complex in 50% ethanol - water mixture solution with  $\lambda_{max}=462$  nm at pH=8.1. The effects of foreign ions and masking agents on the determination of Ag(I) with the new reagent are studied. The mono complex obeys the Beer's law in the Ag(I) concentration range 1.1-17 mg/25ml. Molar absorption coefficients were determined. In this paper, we report the synthesis of the novel Ag(I) complexes with OPTS. The complexes were characterized by UV-Vis and IR spectroscopy, elemental analysis, molar conductivity and thermal decomposition.

### INTRODUCTION:

Thiosemicarbazones and their metal complexes have become the subjects of important studies because of their wide ranging biological activities (antibacterial<sup>[1]</sup>, antimalarial<sup>[2,3]</sup>, antiviral<sup>[4]</sup>, analytical applications and interesting chemical and structural properties<sup>[5-7]</sup>. Antitumor activity of thiosemicarbazone were reported first by

Domagk<sup>[8]</sup>. This paper describes the synthesis of one of the newer bis(thiosemicarbazone) reagents (2E,2'Z)-2,2'-(3-((E)-(2-hydroxy phenyl)diazenyl)pentane-2,4-diylidene) bis(hydrazinecarbothioamide) (OPTS). The acid-base equilibria of the ligand (OPTS) have been investigated. We also describe here the synthesis and some physico-chemical and structural characteristics of its first prepared complex with Ag(I). The bis-Schiff base ligand, H<sub>2</sub>L,

synthesized by condensing *o*-hydroxyphenyl azo acetylacetone with thiosemicarbazide, by refluxing in a stoichiometry of 1:2. The first Ag(I) complexes with thiosemicarbazide-based derivatives have raised considerable interest due to their analytical properties. On the basis of elemental analysis, absorption spectra and potentiometry, the metal to ligand stoichiometry of 1:1 has been proposed for these complexes.

The proposed structure for the complex has the support by IR and UV-visible spectra.

## Experimental :

### 1-Reagents:

All chemicals were Analar chemically pure grade. *O*-aminophenol, acetylacetone and thiosemicarbazide used to prepare the ligand OPTS were purchased from Sigma-Aldrich Chemicals Co., USA and were used as received. The metal salt silver nitrate (AgNO<sub>3</sub>) was purchased from Merck (Germany) and was used without purification. Perchloric acid (HClO<sub>4</sub>), sodium perchlorate (NaClO<sub>4</sub>), Sodium hydroxide (NaOH), potassium hydrogen phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O), DMF and pure ethanol of Analar products were obtained from Merck (Germany).

### 2-Physical measurements:

pH measurements were carried out using a Corning 215 pH meter with a combined glass electrode. The glass electrode was calibrated before each titration with two Merck standard buffer solutions, at pH 7.0 followed by a pH 4.0

at 25°C by coupling the titration cell with a thermostatic bath set at this temperature.

The electronic spectra of solutions of the ligand OPTS and its silver complex were recorded on a Perkin-Elmer (Lambda 35) computerized spectrophotometer equipped with 1 cm matched quartz cells. IR-spectra were recorded using a Jasco 480 Fourier transform infrared spectrometer (FT-IR) analysis in the region 400-4000 cm<sup>-1</sup> using the potassium bromide disk technique. Elemental analysis were carried out by the unit of micro analyses on a Perkin-Elmer 240 C instrument. Molar conductivities of freshly-prepared 1x10<sup>-3</sup>M solutions were measured on a Jenway 4320 conductivity meter. NMR spectra were recorded in DMSO on Varian EM-360 L, 60 M<sub>Z</sub> NMR spectrometer and JEOL FX 90 Q Fourier transform NMR. Mass spectra were performed by Shimadzu- GCMS-OP 1000 Ex using direct inlet system. Thermogravimetric analysis TGA were carried out with Shimadzu DTG-60 H Simultaneous DTA-TG apparatus at heating rate of 10°C/min in nitrogen atmosphere.

### 3-Preparations of the ligand:

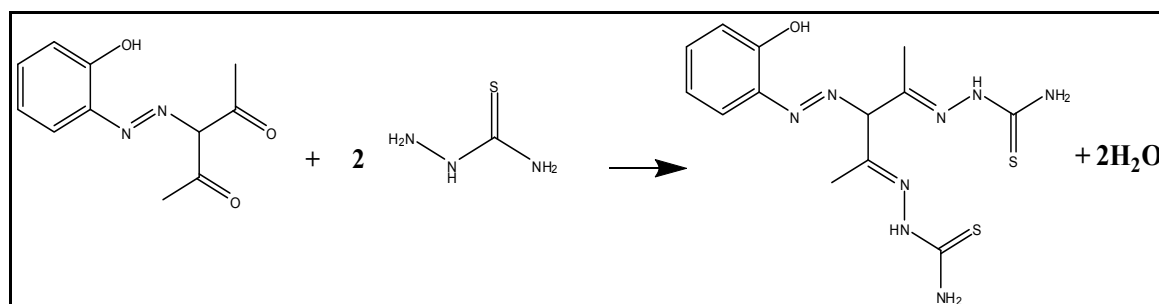
*o*-Hydroxyphenyl azo acetyl acetone (*o*-HPAA) was synthesized by the known procedure<sup>[9]</sup>, adopting a reported earlier procedure<sup>[10]</sup>. The reaction of two molecules of diamines and ketone gives a compound containing two imino groups —CH=N— in each unit. Preparation of the ligand (2*E*,2'*Z*)-2,2'-(3-((*E*)-(2-hydroxyphenyl)diazanyl)pentane-2,4-diyldene) bis(hydrazinecarbothioamide)

(OPTS) is depicted in Scheme 1. A solution of o-hydroxyphenyl azo acetyl acetone (0.02 M) in 20 ml of ethanol was continuously stirred with an ethanolic solution of thiosemicarbazide (0.04 M). The reaction mixture was heated under reflux for 6 h on a water bath at 60°C. The resulting solution mixture was kept for one day. After this time, the formed yellowish powder of the bis(thiosemicarbazone) ligand was collected. The solid formed was filtered and washed with cold EtOH and Et<sub>2</sub>O and dried in vacuo. H<sub>2</sub>L: *Anal. Found*: C, 42.82; H, 4.30; N, 29.97; S, 17.47. C<sub>13</sub>H<sub>18</sub>N<sub>8</sub>OS<sub>2</sub> calculate; H, 4.31; N, 29.98; S, 17.48%; mass spectrum: *m/z* 365.77 (Fig. 1), yields 76% m.p 290°C. <sup>1</sup>H NMR spectra of the Schiff base ligand (Fig. 2) were performed in DMSO and the chemical shifts in ppm were recorded as follows: δ=2.4 ppm (s, 3H, CH<sub>3</sub>-C=N), δ=11.35 ppm (s, 1H, (s, 1H, OH), δ=10.45 ppm (s, 2H, NH-C=S), δ=7.66 ppm (s, 2H, NH<sub>2</sub>-C=S), δ=7.27 , 7.25, 7.01 ,6.95 ppm (m, 4H, Ar-H). Fig. 2. <sup>1</sup>H NMR spectra (δ, ppm) in DMSO-

d6 solvent of the (a) Schiff base, H<sub>2</sub>L, ligand (b) Schiff base, H<sub>2</sub>L, ligand after addition of D<sub>2</sub>O (\*)-NH, NH<sub>2</sub> and OH bands which disappeared after the addition of D<sub>2</sub>O solvent. Where (a) NMR for ligand, D<sub>2</sub>O NMR for ligand,) b(notes that the disappearance for (OH) and (NH) in Fig. 2(b).

#### 4-Preparation of silver (I) complexes:

A general procedure was followed: An equimolar amounts of a warm aqueous (20 mL) solution of corresponding metal salt (0.01 mol.) was added to a warm ethanolic solution (20 mL) of the ligand OPTS (0.01 mol). The mixture was heated under reflux with stirring at an adjusted pH value of 8.1 for 6–7 h. On cooling a black complex precipitated out, which was filtered washed with cold ethanol and dried in vacuo over P<sub>4</sub>O<sub>10</sub> (yield 71%). AgL: *Anal. Found*: C, 32.75; H, 3.58; N, 23.64; S, 6.77, C<sub>13</sub>H<sub>17</sub>ON<sub>8</sub>AgS<sub>2</sub> calculate: C, 32.99; H, 3.59; N, 23.68; S, 6.76.



Scheme 1: Preparation of the OPTS (H<sub>2</sub>L) ligand

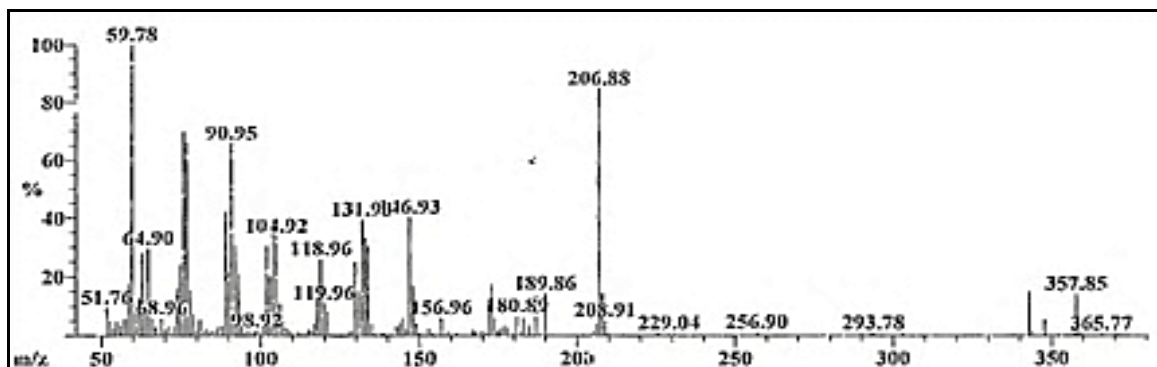


Fig. 1: Mass spectrum of the bis(thiosemicarbazone)(OPTS)

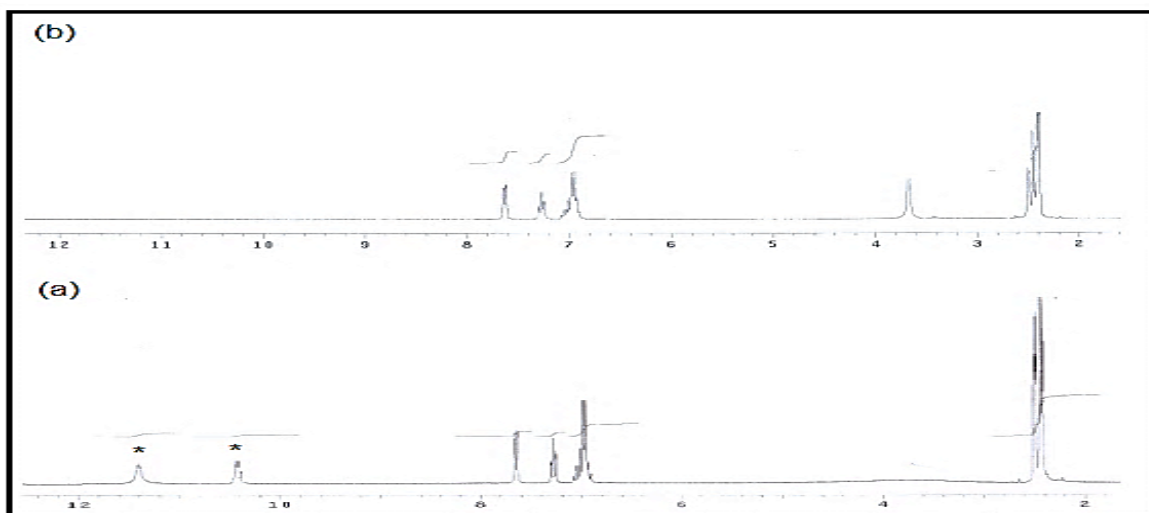


Fig. 2: <sup>1</sup>H NMR spectra of the bis(thiosemicarbazone)(OPTS)

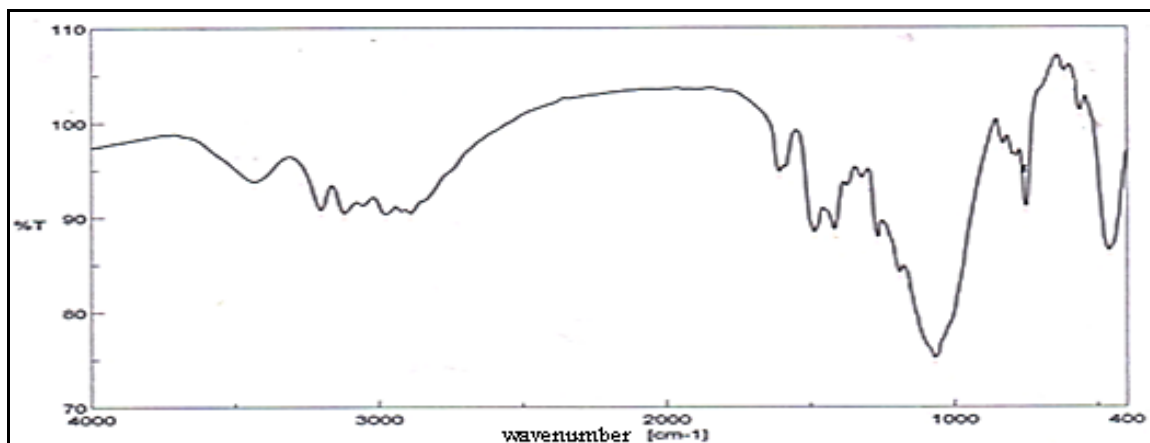
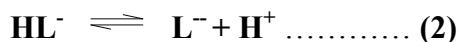
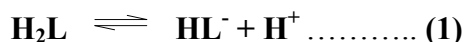


Fig. 3: FT-IR spectrum of the bis(thiosemicarbazone)(OPTS)

## RESULTS AND DISCUSSION:

### 1- pH metric studies:

The acid-base properties of the bis-Schiff base ligand (2E,2'Z)-2,2'-(3-((E)-(2-hydroxyphenyl) diazenyl)pentane-2,4-diylidene) bis (hydrazinecarbothioamide) OPTS (H<sub>2</sub>L) in 50% ethanol-water mixture solution indicated that the predominant form of the ligand is the neutral species, which undergoes stepwise ionization on increasing the pH of solution. The protonation equilibria of ligand (H<sub>2</sub>L) can be represented by equations (1) and (2):



The  $\bar{n}_A$ ,  $\bar{n}$  and pL values were calculated at different pH values using the known equations<sup>[11]</sup>. The proton dissociation constants were determined by plotting  $\bar{n}_A$  against the pH values giving the proton ligand formation curve. The ionization constants of the ligand (logK<sub>1</sub> and or logK<sub>2</sub>) are calculated at  $\bar{n}_A$  values of 0.5 and 1.5. The values of dissociation constants of OPTS were found by potentiometry: pK<sub>1</sub>=9.60±0.02 and pK<sub>2</sub>=10.45±0.05 in NaClO<sub>4</sub> as supporting electrolyte [I=0.1M]. The reagent OPTS is considered as H<sub>2</sub>L ligand and the following species are involved in the acid-base forms H<sub>2</sub>L, HL<sup>-</sup>, L<sup>2-</sup> (Scheme 2). The central NH group can deprotonate rapidly and delocalise with the terminal C=S groups, forming an enamic form in the conjugate anionic ligand. As a consequence there are several resonance structures for the N-substituted

thiosemicarbazides anion in which the sulfur atom is anionic<sup>[12,13]</sup>. The dianionic form results from deprotonation of the two mercapto groups. The potentiometric titration curve for OPTS (Fig. 4) in the form H<sub>2</sub>L shows two inflections at m=1 followed by a moderate inflection at m=2 (m=moles of base added per mole of ligand) corresponding the stepwise dissociation constants of the ligand. The titration curve for a system containing 1:1 molar ratio of Ag(I) and OPTS exhibits one inflections at m=1 (m= moles of base added per mole of metal ion) indicating the formation of mono-binary complex.

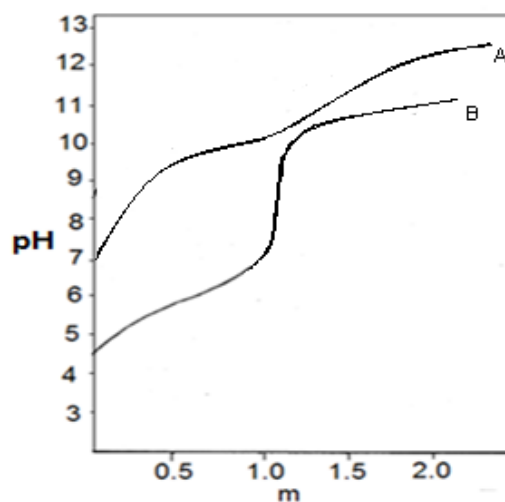


Fig. 4. Potentiometric titration curves of: A) deprotonated ligand OPTS, and B) Ag(I)- OPTS binary systems. The abscissa represents the moles of alkali added per mole of ligand

The formation and stability of binary complex with OPTS in 1:1 molar ratio were studied by potentiometric pH titration in 50% (v/v) ethanol-water medium, ionic strength I=0.1M (NaClO<sub>4</sub>), temp.=25°C. The metal-ligand stability constants were obtained from

the curves drawn between  $\bar{n}$  and pL using half method. The  $\bar{n}$  and pL values were calculated at different points in the pH range of study. Potentiometric determination of stoichiometry of the binary complexes proved that the ligand (OPTS) form 1:1 (M:L) binary complex. The stability constant for the binary Ag-OPTS complexes were calculated from titration curves

in which the metal to ligand ratio was 1:2 and the concentration of each metal ion was  $8 \times 10^{-5}$  M. From the formation curves the stepwise stability constants of binary chelates were determined and are listed in Table (1). The complexed species found in this work for OPTS and the studied metal ions can be represented by the following Eqs. 3.

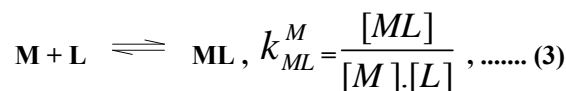
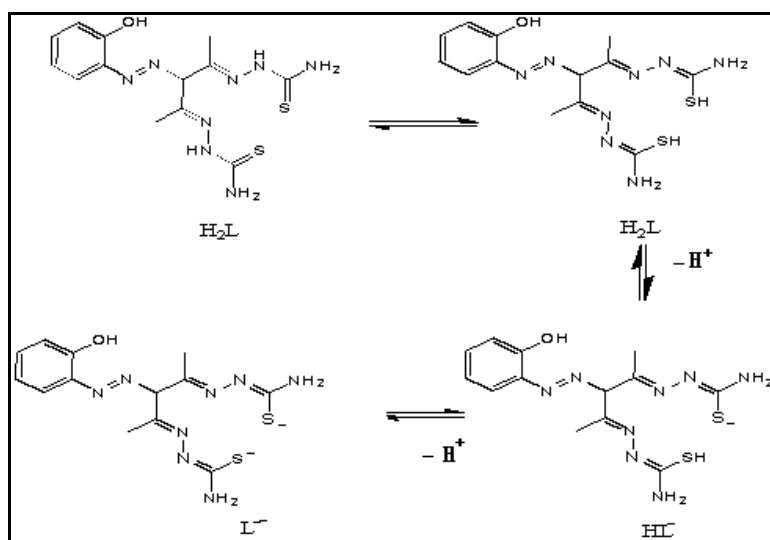


Table 1: The ionization constants of the ligand OPTS and the formation constants of their Ag(I) complexes

Compound	$H^+$		Ag(I) complex		
	$pK_1$	$pK_2$	$\log k_{ML}^M$	$\log k_{ML_2}^{ML}$	$\log \beta_{ML_2}^{ML}$
OPTS	10.45	9.60	4.55	3.92	8.47

$\beta_a$  is the overall stability constant.

The predicted species for the ligand OPTS in the pH range studied are depicted in Scheme 2.



Scheme 2: structural representations of  $H_2L$ ,  $HL^-$  and  $L^{2-}$

## 2-Electronic spectra:

The spectra of the neutral forms of the ligand OPTS were recorded over the available region in 50% (v/v) ethanol-water medium, from 270 to 800 nm, as well in the presence of NaClO<sub>4</sub> [I=0.1 M] as supporting electrolyte. The absorption spectra of 2.5X10<sup>-4</sup>M solution of the reagent (OPTS) were recorded as A=F(λ) for various pH's in the presence of 50% ethanol. The spectra showed an absorption band with the pH range 5–9. The strong broad band observed between (300-700 nm). The spectra of the ligand are characterized by a band at 340 nm (Fig. 5). The absorbance versus pH graphs were interpreted according to the relationship reported in literature<sup>[14]</sup>. The dissociation constants of OPTS were also determined spectrophotometrically beside the above study in water-ethanol and I=0.1 M NaClO<sub>4</sub>. The pK values were calculated from the variation of the absorbance with pH according to Phillips and Merrit<sup>[15]</sup> and Sommer<sup>[16]</sup>. The data obtained for each method to estimate of the acidity constants of OPTS and the complex formation constants were calculated using the SUPERQUAD program<sup>[17]</sup>. The program has been used to calculate acidity constants in systems previously studied<sup>[18-20]</sup>. The final results for pK values are the average of six pairs of independent titrations. Molar absorption coefficient of the spectra of the complexes were also recorded under similar conditions (2880 l mol<sup>-1</sup> cm<sup>-1</sup>). The prominent strong bands of the reagent OPTS with the highest absorbance gives molar absorption coefficient equal to 14800 l mol<sup>-1</sup> cm<sup>-1</sup>

(Fig. 6) in the range 300–400 nm and is assigned to a combination of intraligand and LMCT absorptions<sup>[21]</sup>. It can be seen in Fig. 6 that the absorption maxima at 462 nm of silver mono complex exhibit bathochromic shifts relative to the absorption maximum of the reagent. The solution spectra were recorded in equimolar solutions and in solutions containing an excess of the reagent or the metal ions. The absorption spectra reflect the formation of one complex species and the existence of chelate equilibrium in the studying pH range. The absorption spectra for equimolar solutions and those containing an excess of Ag<sup>I</sup> are analogous and exhibit an absorption band at 462 nm. The absorption bands are observed in the pH range 4–9.9. The absorption bands characterizing the Ag<sup>I</sup> complex species in the pH studied range are shown in Fig. 6. The absorbance versus pH graphs for Ag-OPTS were interpreted using relations derived by Sommer *et al.*<sup>[22,23]</sup>. The absorbance vs. pH graphs were analyzed graphically as described previously<sup>[24]</sup> and one complexation equilibria was established in solutions of the complex Ag-OPTS species within the pH range studied. The acidity constants and stability constants of the complex were determined and are a most the same as calculated using potentiometry. The titrations were carried out at four OPTS/Ag<sup>I</sup> ratios. The ligand/metal ratio was varried from 4:1 to 1:1. The absorption spectrum (Fig. 6) shows the maximum absorbance of the reaction of an aqueous Ag(I) solution with an ethanolic solution of OPTS at pH 8.1. The absorbance

versus pH graph for solution (Eq. 4) were determined under the same conditions as used in the experiments for those containing Ag-OPTS complex indicating the presence of one system only of complex equilibria at wavelength 462 nm. The effect of pH absorption spectra of

the binary complexes under investigation limited the optimal reaction conditions for synthesis of the solid complex. The formation constant for the following equilibria in binary systems containing Ag-OPTS:



were calculated considering the relevant data or the acid dissociation constants and the cumulative binary constants.

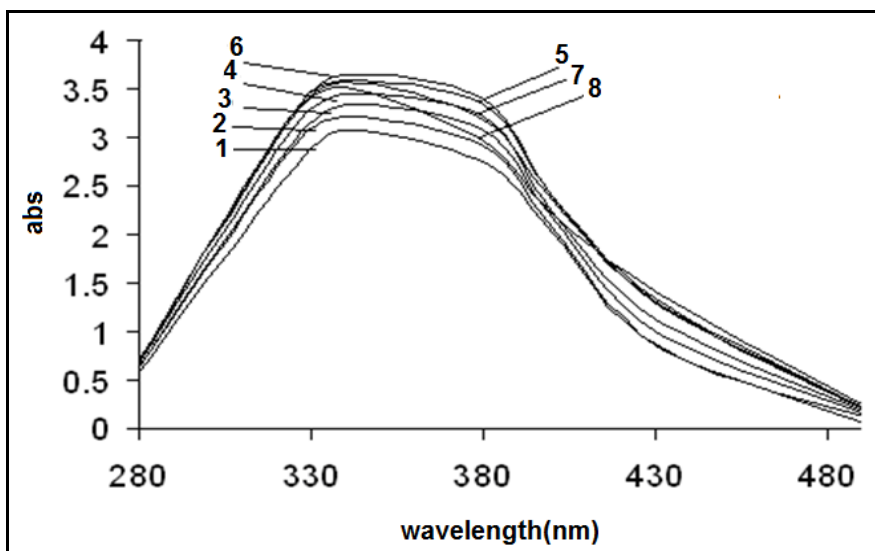


Fig. 5: Absorption spectra of Ligand (OPTS) pH: 1(3), 2(4), 3(5), 4(6), 5(7), 6(8), 7(8.5), 8(9) .

**A- Stoichiometry of the complexes:**

Job's method of continuous variation<sup>[25,26]</sup> was applied to establish the composition of the complex Ag-OPTS. In solutions with  $C_o=C_M + C_L= 3.6 \times 10^{-3} \text{ mol L}^{-1}$  at pH=8.1, the maximum of Job plot corresponds to a component ratio of 1:1 (metal to ligand). The plot of absorbance versus mole fraction of  $\text{Ag}^+$  shows a maximum at 0.5, suggesting the formation of 1:1 (M:L)

complex. The composition of the complexes was also confirmed by applying the mole ratio method<sup>[27]</sup>.

**B-Calibration graph and reproducibility:**

Under the optimum conditions a linear calibration graph for Ag-OPTS complex was obtained up to a concentration of 22.62  $\mu\text{g}/25 \text{ ml}$  silver with a molar absorptivity of  $2600 \text{ l mol}^{-1}$



$\text{cm}^{-1}$  at 462 nm. A Ringbom plot showed that the optimum concentration range for the determination of Ag(I) was 1.35 - 19.98  $\mu\text{g}/25$  ml. Sandell's sensitivity index<sup>[28]</sup> of the reaction was found to be  $6.96 \times 10^{-3}$   $\text{ng cm}^{-1}$ . The relative standard deviation (RSD) was 0.72% for nine determinations, each having a silver concentration 9.75  $\mu\text{g ml}^{-1}$ . The reproducibility of the method was checked by testing two series of solutions having silver concentrations of 3.84 and 8.87  $\mu\text{g ml}^{-1}$ .

### 3- Molar conductivity:

Molar conductivity of the freshly prepared Ag-OPTS complex in DMF solution corresponds to 1:1 molar ratio was 4.97  $\text{ohm cm}^{-1}$ . The data reveal that the complex is nonelectrolyte type.

### 4-IR spectra:

An evidence for the formation of thiosemicarbazone and the metal complex was obtained from the IR spectra. The character of the IR spectra is in accordance with the established structure of tetradentate diprotic Schiff-base ligand OPTS which can be found in the thione or thiol forms (Fig. 3) and its Ag-OPTS complex (Fig. 8). Their prominent feature is the presence of  $\nu_{(\text{OH})}$  stretching vibration frequency at  $3435 \text{ cm}^{-1}$ , this mean that the phenolic group not coordinated. This band may be overlapped with the bands corresponding to the stretching vibrations of  $\text{H}_2\text{O}$ . The IR spectrum of OPTS, shows two bands at 3125

and  $3202 \text{ cm}^{-1}$  which are attributed to asymmetric and symmetric stretching vibration of the  $\text{NH}_2$  functionality. The weak band at  $2977 \text{ cm}^{-1}$  is assigned to vibrations of  $\nu_{(\text{C-H})}$ . Another important band occurs at  $1606 \text{ cm}^{-1}$  in the spectrum of the ligand attributed to  $\nu_{(\text{C=N})}$  stretching mode which is red shifted by  $20 \text{ cm}^{-1}$  in the spectrum of metal complex. This indicates the involvement of the N-atom of the azomethine in coordination. The thioamide [N-HCS] group exhibits a band at  $1189 \text{ cm}^{-1}$  in the spectrum of the ligand which disappeared in complex spectrum due to its coordination through the sulfur atom, in the thione form, of the thioamide groups. The bands at 1486, 1418, 1322 and  $830 \text{ cm}^{-1}$  have contribution from [ $\nu_{(\text{C-H})} + \nu_{(\text{N-H})}$ ], [ $\nu_{(\text{C-S})} + \nu_{(\text{C-N})} + \nu_{(\text{C-H})}$ ], [ $\nu_{(\text{C-N})} + \nu_{(\text{C-S})}$ ] and [ $\nu_{(\text{C=S})}$ ], respectively<sup>[29]</sup>. The IR spectra of the ligand shows an absorption bands at 830 and  $790 \text{ cm}^{-1}$  due to  $\nu_{(\text{C=S})}$  stretching vibrations. The disappearance of the two bands at 1189 and  $790 \text{ cm}^{-1}$  and remaining the band at  $830 \text{ cm}^{-1}$  in complex spectrum indicate that the ligand is coordinated with Ag(I) in its thione form in the solid state. This result proved that the absence of the participation of NH group in the complexation. The band observed at  $458 \text{ cm}^{-1}$  is attributed to Ag-N bonding. Thus, the infrared spectra reveal that OPTS bis(thiosemicarbazone) behave as dibasic, quadridentate ligand coordinating through thione sulphur and azomethine nitrogen. A summary of the analytical, FT-IR spectral data appear on Table 2.

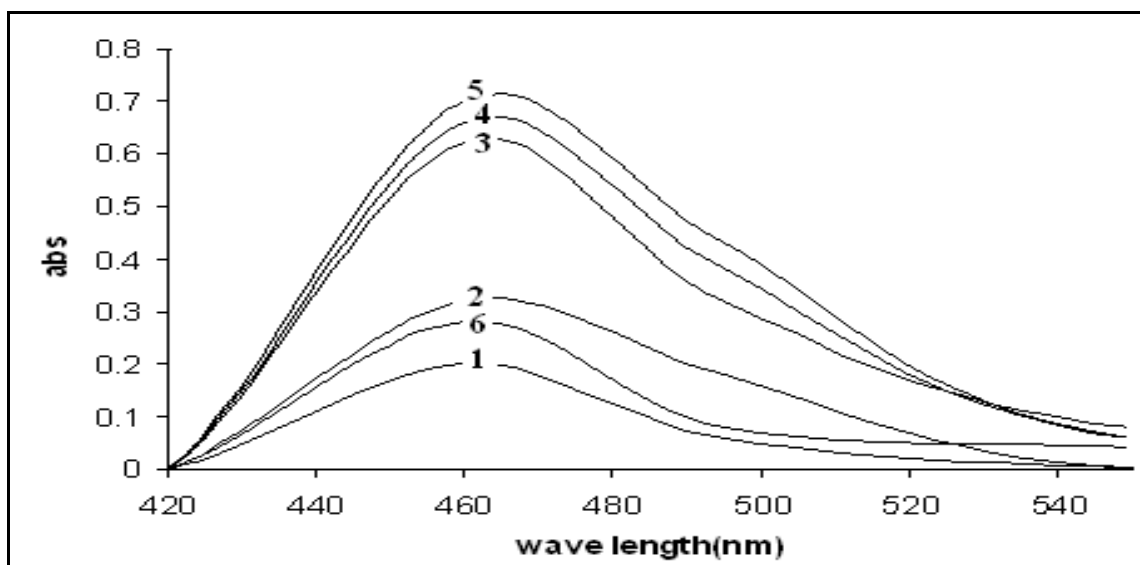


Fig. 6: Absorption spectra of Ag-OPTS complex:  $C_L=C_M=2.5 \times 10^{-4}$  M,  $I=0.10$  M ( $\text{NaClO}_4$ ), pH 1(5), 2(5.5), 3(7.1), 4(7.5), 5(8.1), 6(8.5)

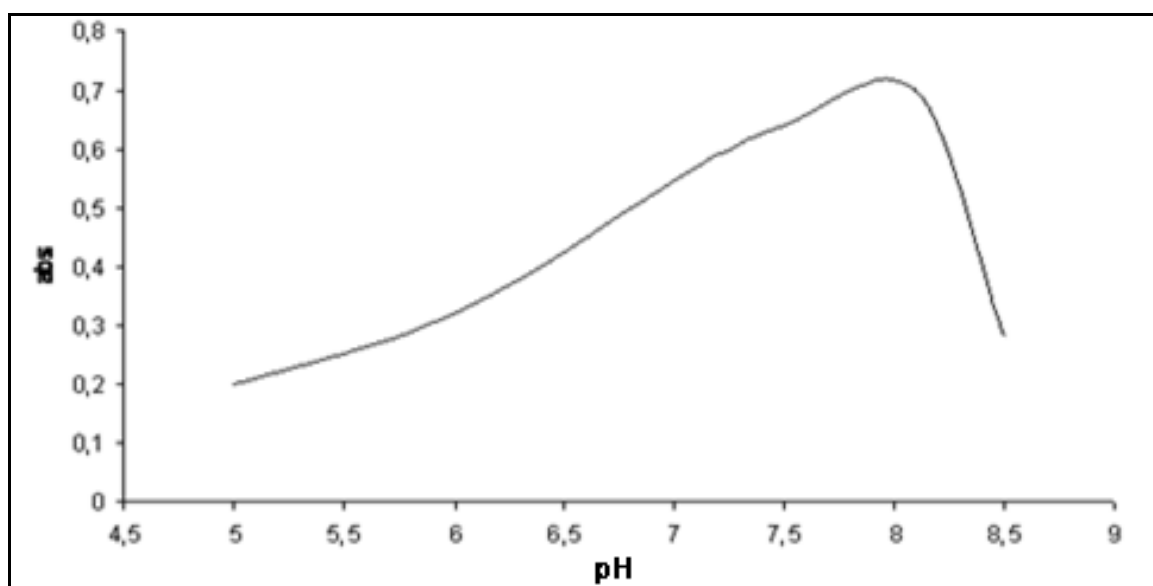


Fig. 7: Absorption spectra of Ag-(OPTS) binary complex:  $C_L=C_M=2.5 \times 10^{-3}$  M,  $I=0.1$  M ( $\text{NaClO}_4$ ),  $\lambda_{\text{max}}=462$  nm

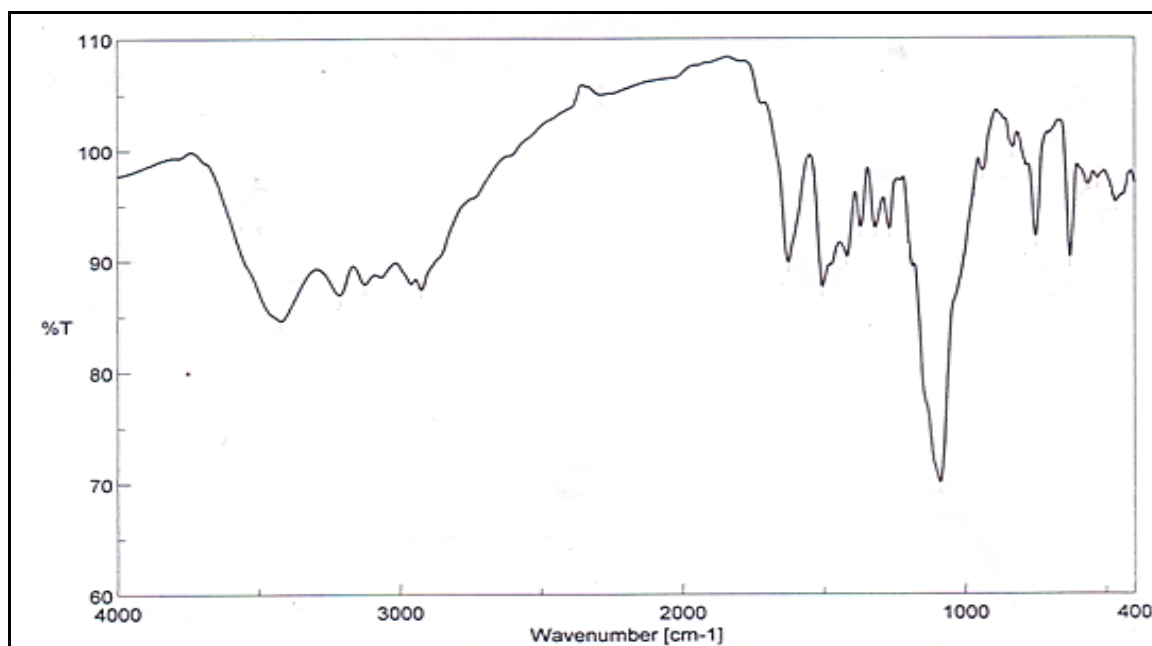


Fig. 8: FT-IR spectrum of complex Ag-OPTS

Table 2: Infrared spectral data for OPTS ligands and its Ag(I) complex (cm<sup>-1</sup>)

Compound	Y (OH)	$\nu$ (NH <sub>2</sub> )	$\nu$ (C=N)	$\nu$ (N=N)	$\nu$ (C=S)	$\nu$ (N-C=N)	$\nu$ (C-S)	$\nu$ (M-N)
OPTS	3435	s3202 as3120	1608	1486	1189 790	1418	1067	-
Ag-OPTS	3445	-	1628	1506	750	1419	1088	458

### 5-Thermal analysis:

The thermal behaviour of Ag-OPTS complex was started in the temperature range from room temperature up to 800°C under nitrogen flow. The corresponding TG and DTG curves are presented in Fig. (9), showing three stages of mass loss. The first mass loss started from room temperature with the removal of 2(HNCSNHNH) ended at 70°C<sup>[30]</sup> and is associated with an endothermic heat effect. The

second mass loss in the temperature range 73 up to 236 °C corresponding 22% weight loss is associated with an endothermic heat effect. The observed mass loss (20%) corresponding exothermic heat effect is connected with thermolysis of the complex remaining<sup>[31]</sup>. The last step starts immediately after second step and continue until complete decomposition of the ligand and formation of the end product as silver metal. The decomposition of the complex was completed at  $\geq 600^\circ\text{C}$ .

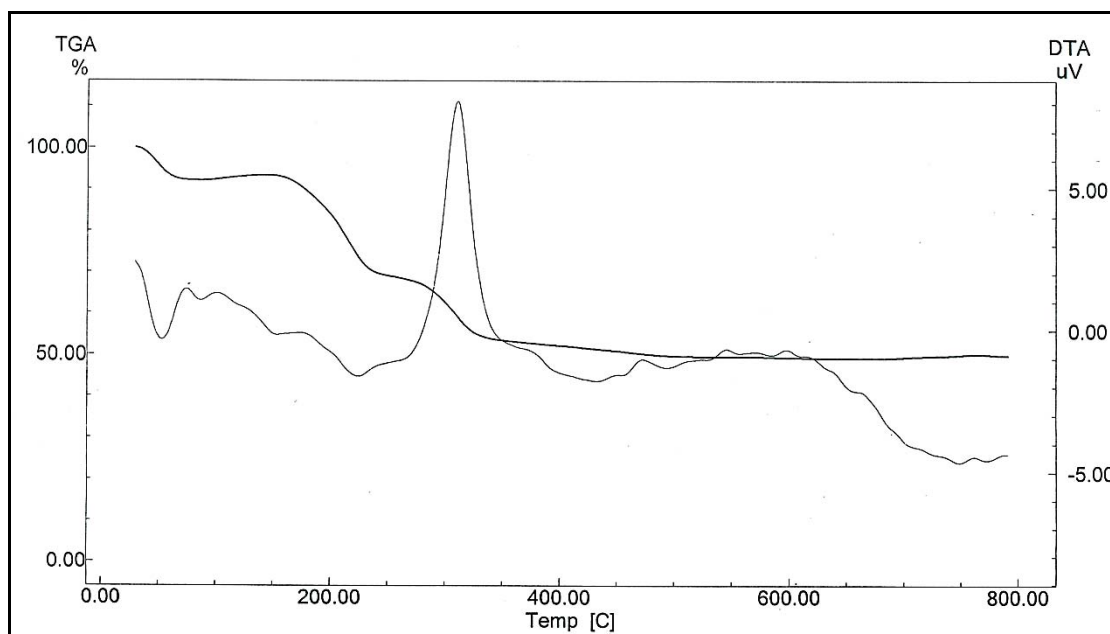


Fig. 9: Thermal analysis data and DTA of the Ag-OPTS complex

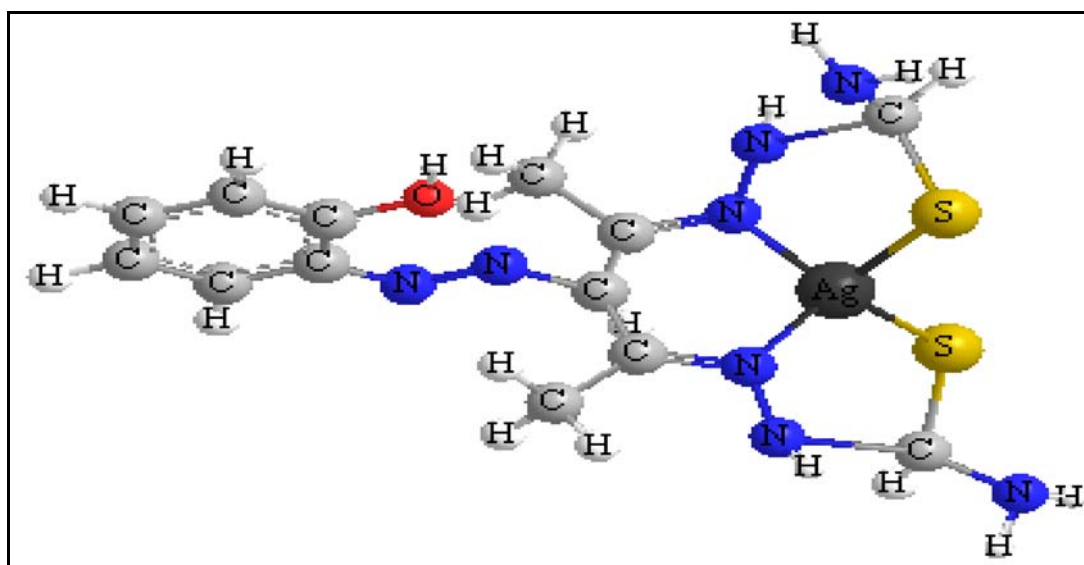


Fig. 10: ORTEP drawing of Ag-OPTS binary complex, showing their molecular structure and the labeling schemes used

## CONCLUSION:

The straight forward condensation of *o*-hydroxyphenyl azo acetyl acetone and thiosemicarbazide in 1:2 molar ratio yield the

novel bis(Schiff base) (2*E*,2'*Z*)-2,2'-(3-((*E*)-(2-hydroxyphenyl)diazanyl)pentane-2,4- diylidene) bis(hydrazinecarbothioamide), the compound is interesting in analytical chemistry and biology.

Its composition and structure were determined by elemental analysis and IR spectrometry. Its flexible back bone, with the presence of N and S donor atoms, renders this compound interesting for studying its coordination behavior with metal ions (Fig. 10). The compound presents in thione/thiol or both the tautomers forms. The interaction of OPTS with silver(I) leads to formation of one different type of complex. In this work, the dissociation constants of the reagent and the stability constants of their silver complex were determined by pH metric and spectrometric titrations. The spectral data indicate that when equimolar amounts of ligand and silver are used, the ligand can behave as a neutral tetradentate ligand to coordinate a single metal ion through the C=N and C-SH groups. The coordinating behaviour of bis(thiosemicarbazone) ligand establishes that it is the azomethine nitrogen and thiol sulphur which functions as the donor sites toward metal ion.

## REFERENCES:

- 1-N. N. Gulerman, S. Rollas, H. Erdeniz, M. Kiraj, *J. Pharm. Sci.*, 26 (2001) 1.
- 2-D. L. Klayman, J. F. Bartosevich, T. S. Griffin, C. J. Mason, J. P. Scovill, *J. Med. Chem.*, 22 (1979) 855.
- 3-D. L. Klayman, J. P. Scovill, J. F. Bartosevich, C. J. Mason, *J. Med. Chem.*, 22 (1979) 1367.
- 4-P. Tarasconi, S. Capacchi, G. Pelosi, M. Cornia, R. Albertini, A. Bonati, P.P. Dall, P. Luunghi, S. Pinelli, *Bioorg., Med. Chem.*, 8 (2000) 154.
- 5-M. J. M. Campbell, *Coord. Chem. Rev.*, 15 (1975) 279.
- 6-J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.*, 209 (2000) 197.
- 7-F. J. Giles, P. M. Fracasso, H. M. Kantarjian, J. E. Cortes, R. A. Brown, S. Verstovsek, Y. Alvarado, D. A. Thomas, S. Faderl, G. Garcia-Manero, et al., *Leukemia Res.* 27 (2003) 1077.
- 8-G. Domagk, R. Behnisch, F. Mietzsch, H. Smidt, *Naturwissenschaften*, 33 (1946) 315.
- 9-A. I. Vogel (*Practical Organic Chemistry*) 3<sup>rd</sup> edn., p. 998, Longmans London (1974).
- 10-M. H. Moustafa; M. Abd-Almottaleb, T. A. Seaf El-Naser, R. M. Issa and A. M. A. Awad; *Al-Azhar Bull. Sci.*, 15(1) (2004) 243.
- 11-H. Irving and H. S. Rossotti; *J. Chem. Soc.*; (1954) 2904.
- 12-M.B. Ferrari, S. Capacchi, F. Bisceglie, G. Pelosi, P. Tarasconi, *Inorg. Chim. Acta*, 312 (2001) 81.
- 13-A. Castineiras, E. Bermejo, J. Valdes-Martinez, G. Espinosa-Perez, D. X. West, J. *Mol. Struct.* 522 (2000) 271.
- 14-V. Kuban and J. Havel; *Acta Chem. Scand.*, 27 (1973) 528.
- 15-J. P. Phillips and L. L. Merrit, *J. Am. Chem. Soc.* 70 (1948) 410.
- 16-L. Sommer, *Folia Fac. Sci. Nat. Uni. Purk., Brno*, 5 (1964) 1.
- 17-P. Gans., A. Sabatini. and A. Vacca.; *J. Chem. Soc., Dalton Trans.*, (1985) 1195.
- 18-M. H. Moustafa, *Al-Azhar Bull. Sci. (AISC'08)*, (March, (2008), 71.

- 19-M. H. Moustafa, Ass. Univ. Bull. Environ. Res.; 13, No. 2 (2010) 77.
- 20-M. H. Moustafa, Al-Azhar Bull. Sci., 12(2) (2010) 295.
- 21-A. I. Matesanz, J. M. Pe´rez, P. Navarro, J. M. Moreno, E. Colacio and P. Souza , J. Inorg. Biochem., 76 (1999) 29.
- 22-L. Sommer, V. Kuban and J. Havel; Folia Fac. Sci. Univer. Brno, Vol, XI, (1970) pt. 1, 33.
- 23-P. Vozinca, J. Havel and L. Sommer; Collec. Czech. Chem. Comm., 45 (1980) 54.
- 24-M. S. Abu-Baker, H. M. Rageh, E.Y. Hashem and M. H. Moustafa; Monatsh. Chemi., 125 (1994) 1197.
- 25- P. Job; Ann. Chem., 9 (1928) 113.
- 26-F. G. Shirif and A. M. Awad, Inorg. Nucl. Chem., 24 (1962) 79.
- 27-J. H. Yoe and H. L. Jones, Indian Eng. Chem., Anal. Ed., 16 (1944) 111.
- 28-E. P. Sandell; Colorimetric Determination of trace metals, Vol. 3, Wiley, New York, (1959) p. 97.
- 29-M. K. Das, M. Nath, J. J. Zuckerman, Inorg. Chem. Acta, 21 (1983) 49.
- 30-N. M. El-Metwally, R.M. El-Shazly, I.M. Gabr, A.A. El-Asmy, Spectrochim. Acta Part A, 61 (2005) 1113.
- 31-K.-K. Du, S.-X. Liu, J. Mol. Struct., 874 (2008) 138.

تحضير ودراسات جهدية وطيفية على مركب بيس (ثيوسيميكاربازون) الجديد ومترابكه مع أيون الفضة

محمود حسن مصطفى، أحمد عبد النعيم، أسامة أحمد عباس

قسم الكيمياء - كلية العلوم للبنين - جامعة الأزهر بأسويوط

تم في هذا البحث تحضير قاعدة شيف الجديدة (E<sub>2</sub> و Z<sub>2</sub>)-٢،٢-(E)-٣-(٢-هيدروكسي فينيل) داي ازينيل بيتان-٤،٢-داي يلدين) بس (هيدرازين كربوثيواميد) المشتقة من الثيوسيميكرابازيد. وذلك بتفاعل جزيئين ثيوسيميكرابازيد مع مركب أرثو هيدروكسي فنيل أزو اسيتيل أسيتون، وتم اثبات التركيب الجزيئي لليجند بواسطة التحليل العنصرى وطيف الكتلة وطيف الرنين النووي المغناطيسى والأشعة تحت الحمراء، واستخدم هذه الليجند لتحضير مترابك أيون الفضة. وتمت دراسة الخواص الحامضية والقاعدية للكاشف المحضر، وكذلك مترابك الفضة المحضر منه بواسطة الطرق الجهدية والطيفية المختلفة، وذلك بهدف تحديد حالات اتزان التراكب الممكن تواجدها بالمحلول ونسب تكوينها وتدرج ثبات نظم التراكب المختلفة على ضوء طبيعة الكاشف الداخلى فى التفاعل، وحسب ثوابت ثبات هذه النظم التركيبية المختلفة فى المعايير عند تغير درجة تركيز أيون الهيدروجين بالمحلول وذلك لمعرفة الظروف المثلى لتكوين المترابكات موضع الدراسة وكذلك استخدمت فى هذه الدراسات قياس أطيايف الامتصاص المرئى والفرق بنفسجية خلال معايير تتبع تغير درجة تركيز أيون الهيدروجين بالمحلول عند ظروف تجريبية محددة. وأمكن حساب ثوابت التآين لليجند وتحديد النسب التكوينية للمترابك موضع الدراسة ووجدت بنسبة ١:١. وقد أمكن تحضير المترابك الصلب للفضة، وتم دراسة وتحديد مواضع الترابط مع أيون الفضة وتم التعرف على شكل وتركيب المترابك.

