

Synthesis, Stability, Spectral and Characterization of Mercury (II) Complexes with a Novel Bis-Schiff base Ligand

M. H. Moustafa*, A. Abd-Elnaeem and O. A. Abbas

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

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. Dissociation constants of the reagent OPTS have been determined by spectrophotometry 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 0.1M. The stability constants of the Hg-OPTS are $\log K_1=6.18\pm 0.04$ and $\log K_2=5.22\pm 0.05$. The reaction of Hg(II) with OPTS gives mononuclear complex in 50% ethanol - water mixture solution with $\lambda_{\max} = 448$ nm at pH 8.5. The effects of foreign ions and masking agents on the determination of Hg(II) with the new reagent were monitored. The mono complex obey the Beer law in the Hg(II) concentration range 5.10–50.17 mg/25ml. Molar absorption coefficients was determined. In this paper, we report the synthesis of the novel Hg(II) complexes with OPTS. The complexes were characterized by UV-vis and IR spectroscopy, elemental analysis, molar conductivity and thermal decomposition.

Keywords: Mercury (II) complexes, Bis (thiosemicarbazone), Synthesis, Physico-chemical characterization and Thermal decomposition.

Antitumor activity of thiosemicarbazone was reported first by Domagk⁽¹⁾. Because of their biological activity and analytical application, thiosemicarbazides and thiosemicarbazones, as well as their metal complexes have been the subject of many studies⁽²⁻⁴⁾. The metal complexes show more activity as compared to the free thiosemicarbazones and semicarbazones. They may have numerous applications, e.g. anticancer^(5,6), fungicides, antibacterial^(7,8), antiviral^(9,10), antifungal⁽¹¹⁻¹²⁾, anti HIV⁽¹³⁾, antitumour activity⁽¹⁴⁾, antimalarial^(15,16) and other biological activities⁽¹⁷⁻¹⁹⁾. This paper describes the synthesis of one of the newer bis (thiosemicarbazone) reagent (2E,2'Z)-2,2'-(3-((E)-(2-hydroxyphenyl) diazenyl) pentane-2,4-diylidene) bis (hydrazinecarbothioamide) (OPTS). The acid-base equilibria of the ligand (OPTS) were investigated. We also describe here the synthesis and some physico-chemical and structural characteristics of its first complexes with Hg(II), as well as two new Hg (II) complexes with OPTS.

*E- mail: mahhassan1959@yahoo.com

The bis-Schiff base ligand, H₂L, was synthesized by condensing *o*-hydroxyphenyl azo acetylacetone with thiosemicarbazide, on refluxing in stoichiometry of 1:2. The first Hg(II) 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 these complexes has the support of IR and UV-vis spectra.

Experimental

Reagents

All chemicals were Analar grade. *O*-aminophenol, acetylacetone and thiosemicarbazide which were used for the preparation of the ligand OPTS was from Sigma-Aldrich Chemicals Co., USA and were used as received. The metal salt mercuric chloride (HgCl₂) was from Merck (Germany) and were used without purification. Perchloric acid (HClO₄), sodium perchlorate (NaClO₄), sodium hydroxide (NaOH), potassium hydrophthalate (KHC₈H₄O₄), borax (Na₂B₄O₇·10H₂O), DMF and ethanol of Analar grade were obtained from Merck (Germany).

Physical measurements

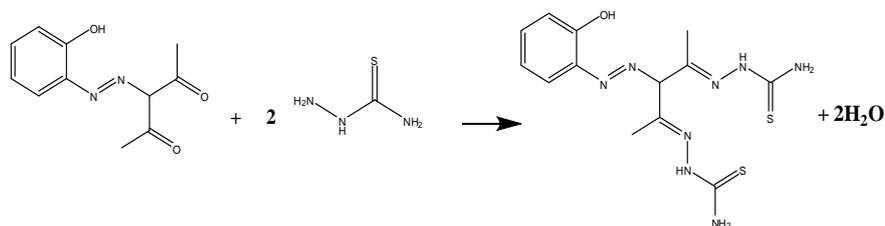
pH measurements were carried out using a Corning 215 pH meter with a combined glass electrode. The glass electrode was calibrated before each titration with two Merck standard buffer solutions, first with the pH 7.0 followed by a pH 4.0 at 25°C by coupling the titration cell with a thermostatic bath set at this temperature.

The electronic spectra of solutions of the ligand OPTS and its mercury complexes were recorded on a Perkin-Elmer (Lambda 35) computerized spectrophotometer equipped with 1 cm matched quartz cells. IR-spectra were recorded using a Fourier transform infrared spectrometer (FT-IR) in the region 400-4000 cm⁻¹ with Jasco 480 spectrometer using the potassium bromide disk technique. Elemental analysis was carried out by the unit of micro analyses on a Perkin-Elmer 240 C instrument. NMR spectra were recorded in DMSO on Varian EM-360 L, 60 MHz NMR spectrometer and JEOL FX 90 Q Fourier transform NMR. Molar conductivities of freshly-prepared 1X10⁻³M solution were measured on a Jenway 4320 conductivity meter. Mass spectra were performed by Shimadzu- GCMS-OP 1000 Ex using direct inlet system. Thermogravimetric analysis TG was carried out with a Shimadzu DTG-60 H. A simultaneous DTA-TG apparatus at a heating rate of 10°C/min in nitrogen atmosphere.

Preparations of the ligand

The compound *o*-hydroxyphenyl azo acetyl acetone (*o*-HPAA) was synthesized by a known procedure⁽²⁰⁾, adopting a reported earlier procedure⁽²¹⁾. The reaction of two molecules of diamines and ketone ensures giving a

compound containing two imino groups —CH=N— in each unit. **Scheme 1**, adopts a procedure of preparing the ligand (2E,2'Z)-2,2'-(3-((E)-2-hydroxyphenyl) diazenyl) pentane-2,4-diylidene) bis (hydrazinecarbothioamide) (OPTS). 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 hr 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 dried in vacuo. H_2L : *Anal.* Found: C, 42.82; H, 4.30; N, 29.97; S, 17.47. $\text{C}_{13}\text{H}_{18}\text{N}_8\text{OS}_2$ requires: 42.84; H, 4.31; N, 29.98; S, 17.48%; mass spectrum: m/z 365.77 (**Fig. 1**), yields 76% m.p 290. ^1H NMR spectra of the Schiff base ligand (**Fig. 2**) were performed in DMSO and the chemical shifts in ppm were recorded as follows: $\delta = 2.4$ ppm (s, 3H, $\text{CH}_3\text{—C=N}$), $\delta = 11.35$ ppm (s, 1H, (s, 1H, OH), $\delta = 10.45$ ppm (s, 2H, NH—C=S), $\delta = 7.66$ ppm (s, 2H, $\text{NH}_2\text{—C=S}$), $\delta = 7.27$, 7.25, 7.01, 6.95 ppm (m, 4H, Ar—H) . (**Fig. 2**). ^1H NMR spectra (δ , ppm) in DMSO- d_6 solvent of the (a) Schiff base, H_2L , ligand (b) Schiff base, H_2L , ligand after addition of D_2O (*)-NH, NH_2 and OH bands which disappeared after the addition of D_2O solvent, where (a) NMR for ligand, D_2O NMR for ligand, (b) Notes that the disappearance for (OH) and (NH) in **Fig. 2(b)**.



Scheme 1. Synthesis strategy for the preparation of OPTS (H_2L).

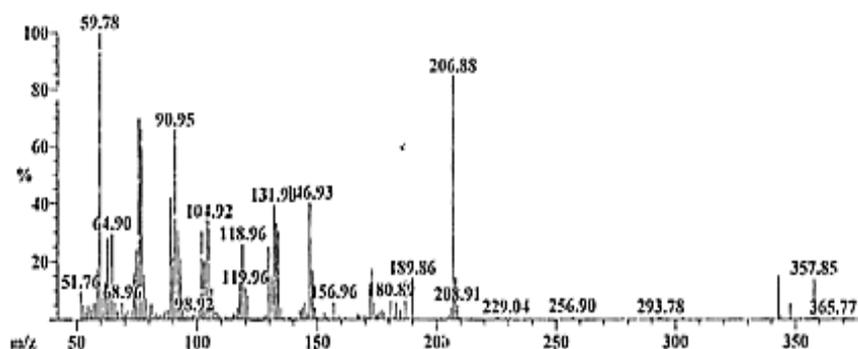


Fig. 1. Mass spectra of bis(thiosemicarbazone)(OPTS).

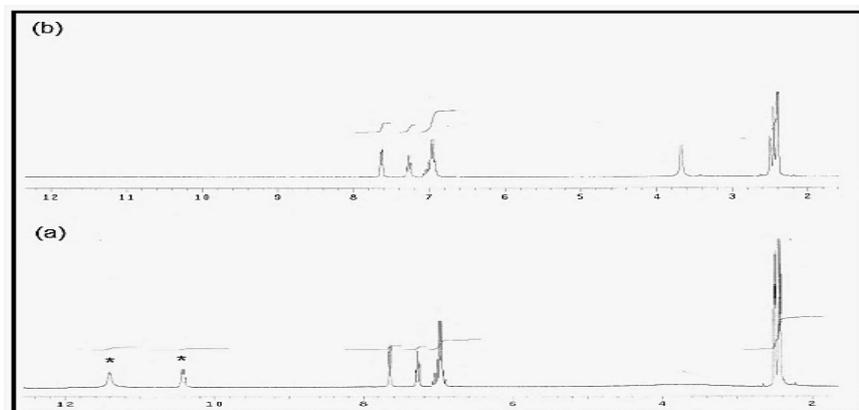


Fig. 2. ^1H NMR spectra of bis(thiosemicarbazone) (OPTS).

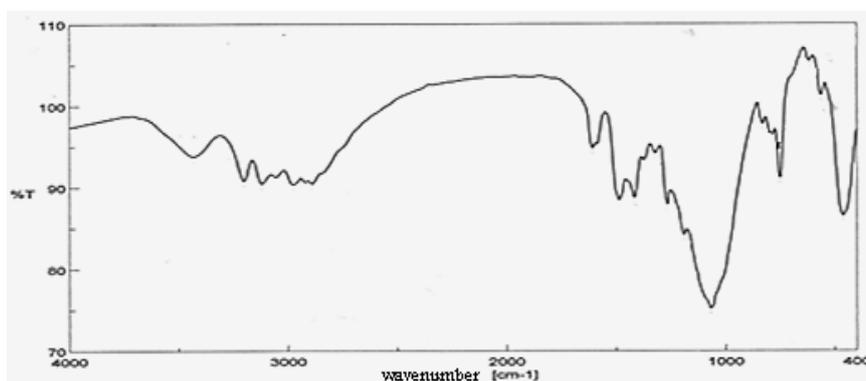


Fig. 3. FT-IR spectra of bis(thiosemicarbazone) (OPTS).

Preparation of mercury(II) complexes

A general procedure was followed: 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 for 6–7 hr. On cooling a black coloured complex precipitated, which was filtered, washed with cold ethanol and dried in vacuo over P_4O_{10} (yield 62%). HgL ; *Anal.* Found: C, 27.51; H, 2.80; N, 19.64, $\text{C}_{13}\text{H}_{16}\text{ON}_8\text{HgS}_2$, requires: C, 27.52; H, 2.82; N, 19.76; S, 11.18

Results and Discussion

pH metric studies

The acid-base properties of the bis-Schiff base ligand 2E,2'Z)-2,2'-(3-((E)-(2-hydroxyphenyl)diazanyl)pentane-2,4-diylidene)bis(hydrazinecarbothioamide) OPTS (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_2L) can be represented by Eq. (1) and (2):



The \bar{n}_A , \bar{n} and pL values were calculated at different pH values using the known equations of Irving and Rossotti⁽²²⁾. The protons dissociation constants were determined by plotting \bar{n}_A against the pH giving the proton ligand formation curve. The ionization constants of the ligand ($\log K_1$ and or $\log K_2$) were calculated at \bar{n}_A values of 0.5 or 1.5. The following values of dissociation constants of OPTS were found by potentiometry: $pK_1=9.60\pm 0.02$ and $pK_2=10.45\pm 0.05$ in $NaClO_4$ as supporting electrolyte [$I=0.1M$]. The reagent OPTS is considered as H_2L ligand and the following species are involved in the acid-base forms H_2L , HL^- , L^{2-} (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 thiosemicarbazide anion in which the sulphur atom is anionic^(23,24). The dianionic form resulting from deprotonation of the two mercapto groups. The potentiometric titration curve for OPTS (Fig. 4) in the form H_2L shows two inflections at $a = 1$, followed by a moderate inflection at $a = 2$ ($a =$ moles of base added per mole of ligand) corresponding to the stepwise dissociation constants of the ligand. The titration curve for a system containing 1:1 molar ratio of Hg(II) and OPTS exhibits one inflections at $m = 1$ ($m =$ moles of base added per mole of metal ion) indicating the formation of mono-binary complexes. The formation and stability of binary complexes with OPTS in 1:1 molar ratio were studied by potentiometric pH titration in 50% (v/v) ethanol-water medium, ionic strength $I=0.1M$ ($NaClO_4$), temp. = 25 °C. The \bar{n} and pL values were calculated at different points in the pH range of study. The metal-ligand stability constants were obtained from the curves drawn between \bar{n} and pL.

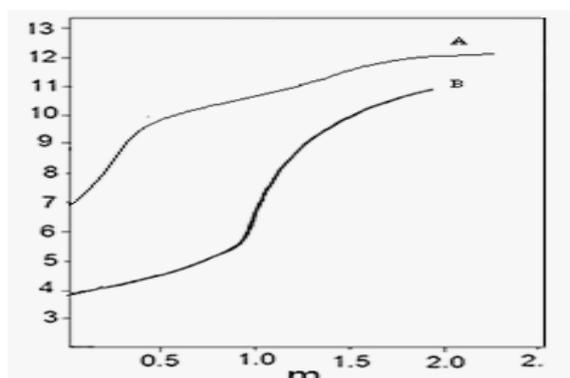
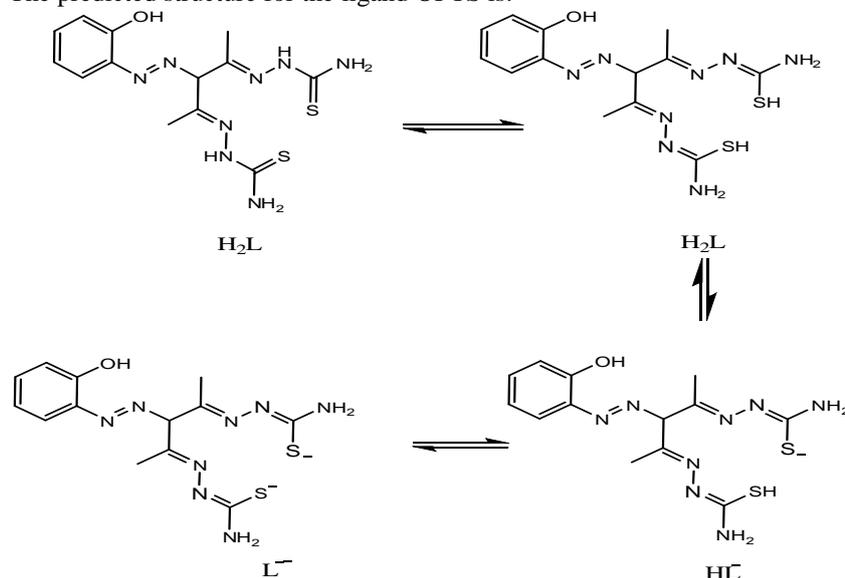


Fig. 4. Potentiometric titration curves of: A) diprotonated ligand OPTS, and B) Hg(II)- OPTS binary systems [$m =$ moles of alkali per mole of metal ion]. The abscissa represents the moles of alkali added per mole of ligand.

The predicted structure for the ligand OPTS is:



Scheme 2. Structural representations of H_2L , HL^- and L^- .

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 Hg- 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 $8 \times 10^{-5} \text{M}$. 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 Eq. 3:

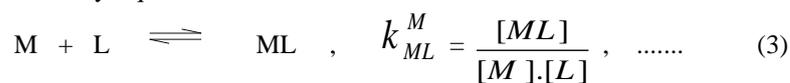


TABLE 1. The ionization constants of the ligand OPTS and the formation constants of their Hg(II) complexes.

Compound	H^+		HgL		
	$\text{p}K_1$	$\text{p}K_2$	$\log k_{\text{ML}}^{\text{M}}$	$\log k_{\text{ML}_2}^{\text{ML}}$	$\log \beta_{\text{ML}_2}^{\text{ML}}$
OPTS	10.45	9.60	6.18	5.22	11.40

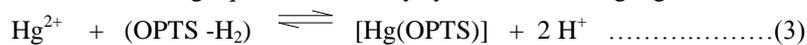
β_a is the overall stability constant.

Egypt. J. Chem. **54**, No.5 (2011)

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 NaClO₄ [I=0.1 M] as supporting electrolyte in the measurements. The absorption spectra of 2.5X10⁻⁴M solution of the reagent (OPTS) were recorded as a function $A = F(\lambda)$ for various pH values in the presence of 50% ethanol. The spectra showed absorption bands with the pH range 5–9. The strong broad bands were 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 which described in literature⁽²⁵⁾. The dissociation constants of OPTS were determined spectrophotometrically beside the above study in water-ethanol and I=0.1 M NaClO₄. The pK values were calculated from the variation of the absorbance with pH according to Phillips and Merrit⁽²⁶⁾ and Sommer⁽²⁷⁾. From the data obtained by each method, estimation of the acidity constants of OPTS and the complex formation constants were determined using the SUPERQUAD program⁽²⁸⁾. The program has been used to calculate acidity constants in systems previously studied⁽²⁹⁻³¹⁾. 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 (1800 l mol⁻¹ cm⁻¹). The prominent strong bands of the reagent OPTS with the highest absorbance gives molar absorption coefficient equal to 14800 l mol⁻¹ cm⁻¹ (Fig. 6). Bands in the range 300–400 nm are assigned to a combination of intraligand and LMCT absorptions⁽³²⁾. It can be seen in Fig. 6 that the absorption maxima at 448 nm of mercury 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 studied pH range. The absorption spectra for equimolar solutions and those containing a preponderance of M^{II} are analogous and exhibit an absorption band at 448 nm for Hg^{II}. The absorption bands are observed in the pH range 4–9.9. The absorption bands characterizing the Hg^{II} complex species in the pH studied range are shown in Fig. 6. The absorbance versus pH graphs for Hg-OPTS were interpreted using relations derived by Sommer *et al.*^(32,33). The absorbance vs. pH graphs were analyzed graphically as described previously⁽³⁴⁾ and once complexation equilibria established, in solutions of the complex Hg-OPTS species within the pH range studied for the complex. The acidity constants and stability constants of the complex were determined and are the same as those calculated by potentiometry. The titrations were carried out at four OPTS/M^{II} ratios. The ligand/metal ratio was varied from 4:1 to 1:1. The absorption spectrum (Fig. 6) shows the maximum absorbance of the reaction of an aqueous Hg(II) solution with an ethanolic solution of OPTS at pH 8.5. The absorbance versus pH graph for solution (Eq. 6-8) were determined under the same conditions as used in the experiments for those containing Hg-OPTS complex indicating the presence of one system only of complex equilibria at wavelength 448 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 Hg-OPTS:



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

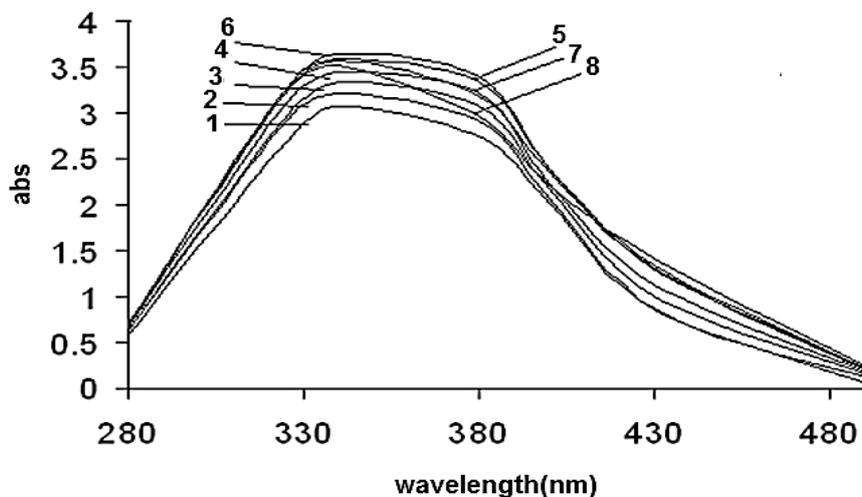


Fig. 5. Absorption spectra of ligand (OPTS) pH: 1(3), 2(4), 3(5), 4(6), 5(7), 6(8), 7(8.5), 8(9).

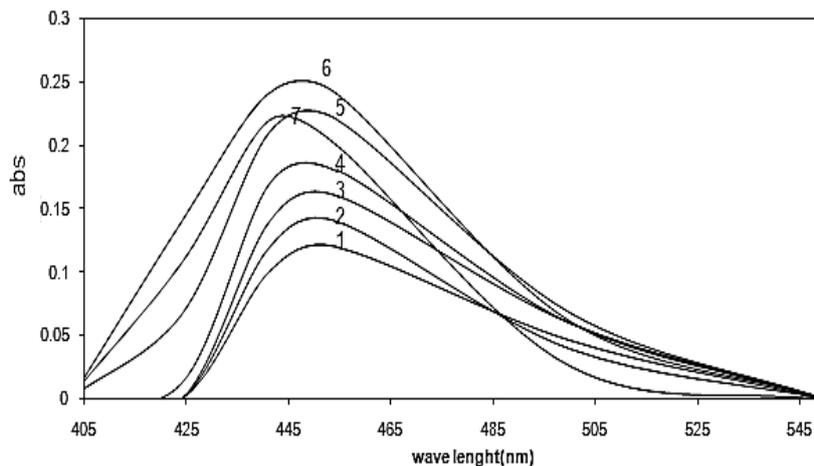


Fig. 6. Absorption spectra of Hg-OPTS complex; $C_L = C_M = 2.5 \times 10^{-4} \text{ M}$, $I = 1.0 \text{ M}$ (NaClO_4), pH 1(5), 2(5.5), 3(6), 4(6.5), 5(7), 6(8.5), 7(9.2).

Stoichiometry of the complexes

Job's method of continuous variation^(35,36) was applied to establish the composition of the complexes $\text{Hg}^{\text{II}} - \text{OPTS}$. In solutions with $C_o = C_M + C_L = 3.6 \times 10^{-3} \text{ mol l}^{-1}$ at pH 8.5, the maximum of Job plot corresponds to a component ratio of 1:1 (metal to ligand). The plot of absorbance versus mole fraction of Hg^{II} shows a maximum at 0.5, suggesting the formation of a 1:1 (M:L) complex. The composition of the complexes was also confirmed by applying the mole ratio method⁽³⁷⁾.

Calibration graph and reproducibility

Under the optimum conditions, a linear calibration graph for Hg-TAR complex was obtained up to a concentration of $45.02 \mu\text{g}/25 \text{ ml}$ mercury with a molar absorptivity of $720 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 448 nm. A Ringbom plot showed that the optimum concentration range for the determination of Hg(II) was $1.35 - 41.98 \mu\text{g}/25 \text{ ml}$. Sandell's sensitivity index⁽³⁸⁾ of the reaction was found to be $4.76 \times 10^{-3} \text{ ng cm}^{-1}$. The relative standard deviation (RSD) was 0.76% for nine determinations, each having a mercury concentration $15.75 \mu\text{g ml}^{-1}$. The reproducibility of the method was determined by testing two series of solutions having mercury concentrations of 7.54 and $17.85 \mu\text{g ml}^{-1}$.

Molar conductivity

The molar conductivity of the freshly prepared Hg-OPTS complex in DNF solution, corresponding to 1:1 molar ratio was 7.8 ohm cm^{-1} . The data reveal that the complex is none-electrolyte type.

IR absorption spectra

The character of the IR spectra is in accordance with the established structure of the ligand (Fig. 3) and Hg-OPTS complex (Fig. 7). Their prominent feature is the presence of $\nu_{(\text{OH})}$ stretching vibration band at 3435 cm^{-1} ; which means that the phenolic group is not coordinated. This band may be overlapping with the bands corresponding to the stretching vibration of $-\text{NH}_2$ group. The IR spectra of OPTS, show two bands at 3202 and 3120 cm^{-1} which are assigned to symmetric and asymmetric vibrations of $\nu_{(\text{NH})}$ and the band at 2977 cm^{-1} assigned to vibrations of $\nu_{(\text{C-H})}$. The band at 2880 cm^{-1} , attributed to $\nu_{(\text{SH})}$ mercapto mode disappears in the spectrum of Hg-OPTS complex. This indicates the presence of thiol-tautomer in the solid state. Another important band occurs at 1606 cm^{-1} in both spectra of the ligand and complex, attributed to $\nu_{(\text{C=N})}$ stretching mode; indicating none involvement of the N-atom of the azomethine in coordination. The thioamide [N-HCS] group has four bands observed in the spectrum of the ligand at 1486 , 1418 , 1322 and 830 cm^{-1} . These bands 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⁽³⁹⁾. These bands are observed at 1499 , 1411 and 834 cm^{-1} in complex spectrum. The absorption bands due to $\nu_{(\text{C=S})}$ stretching are in the region between 1067 and 1267 cm^{-1} . In principle, the ligand can exhibit thione/thiol tautomerism, since it contains a thioamide NH-C=S functional group. In addition, OPTS exhibits characteristic (C=S) band at 790 cm^{-1} , which is red shifted by 20 cm^{-1} in the spectra of metal complex suggesting deprotonation of

the 2 (S–H) proton; thus generating thiolato sulfur which is one of the coordinating sites. This proved that OPTS may bind through thione (C=S), thiol (–C–SH) or both as a consequence of tautomerism. A new band appears at 991 cm^{-1} corresponding to the ring breathing. Thus, the infrared spectra reveal that OPTS bis (thiosemicarbazone) behaves as dibasic, bisbidentate ligand, coordinating through thiol sulphur and azomethine nitrogen. A summary of the FTIR spectral data is given in Table 2.

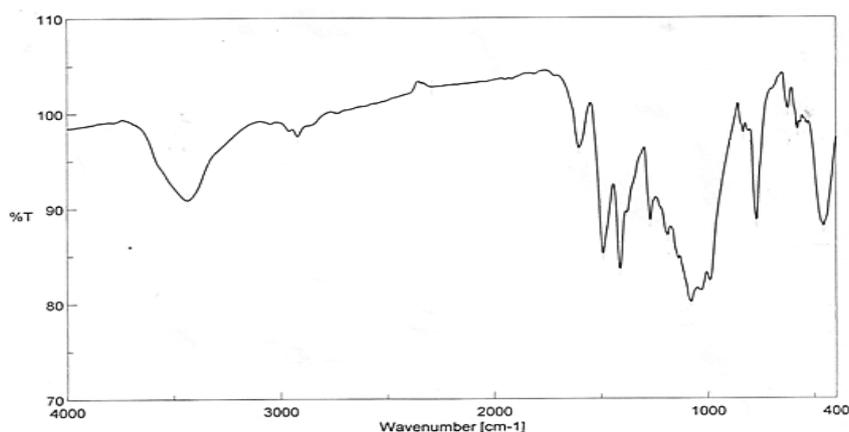


Fig. 7. FTIR absorption spectrum of complex Hg-OPTS.

TABLE 2. Infrared spectral data for OPTS ligands and their Hg(II) complex (cm^{-1}).

Compound	$\nu(\text{OH})$ and $\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{N}-\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$
OPTS	3435, 3202	3120	1608	1486	1486	1418	1067, 790	-
Hg-OPTS	3435	-	1606	1491	1491	-	1078, 771	458

Thermal analysis

Heating of Hg-OPTS complex in the temperature range from room temperature up to 800 $^{\circ}\text{C}$ under nitrogen and the resulting TG and DTA curves are presented in Fig. 8. It is accompanied by two stages of mass loss. The first loss in the temperature range from room temperature up to 250 $^{\circ}\text{C}$ started with the removal of 2(HNCSNHNH) and ending at 70 $^{\circ}\text{C}$ ⁽⁴⁰⁾, was followed by the complete decomposition of the ligand. The observed second mass loss was connected with thermolysis of the complex remaining ⁽⁴¹⁾. The second step starts

immediately after first step and continues until complete decomposition of the ligand. Although decomposed fragments of the ligands could not be approximated due to continuous weight loss, the total % weight loss corresponds to the loss of the respective ligand after considering the transfer of the oxygen atom to the mercury and residue corresponds to the respective metal and the formation of the end product as mercuric oxide HgO. The decomposition of the complex was completed at ≥ 750 °C.

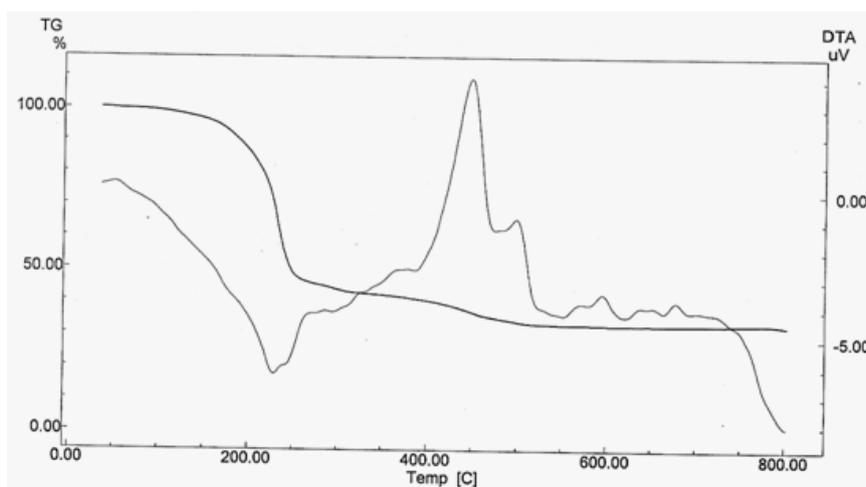


Fig. 8. Thermal analysis data and DTG of the Hg-OPTS complex.

Conclusion

The straight forward condensation of *o*-hydroxyphenyl azo acetyl acetone and thiosemicarbazide in 1:2 molar ratio to yield the novel bis(Schiff base) (2E,2'Z)-2,2'-(3-((E)-(2-hydroxyphenyl) diazenyl) pentane-2,4- diylidene) bis (hydrazinecarbothioamide) was reported. 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 important for studying its coordination behaviour with metal ions (Fig. 9). The compound presents in thione/thiol or both the tautomers forms. The interaction of OPTS with mercury (II) leads to the formation of a different type of complex. In this work, the dissociation constants of the reagent and the stability constants of their mercury complex were determined by pH-metric and spectrometric titrations. The spectral data indicate that when equimolar amounts of ligand and mercury are used, the ligand can behave as a neutral tetradentate ligand to coordinate with a single metal ion through the C= N and C-SH groups. The coordinating behavior of bis(thiosemicarbazone) ligand establishes that it is the azomethine nitrogen and thiol sulphur which function as the donor sites toward the metal ion.

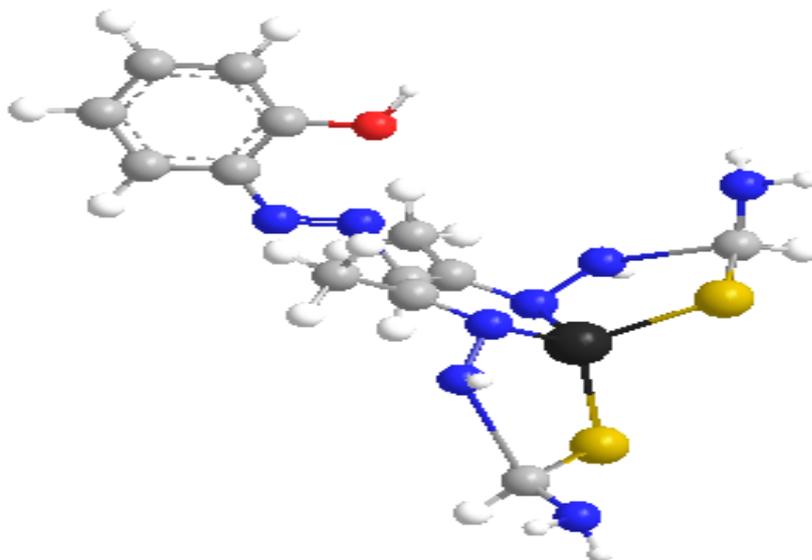


Fig. 9. ORTEP drawing of Hg-OPTS binary complex, showing their molecular structure and the labeling schemes used.

References

1. Domagk, G., Behnisch, R., Mietzsch, F. and Smidt, H., *Naturwissenschaften*, **33**, 315(1946).
2. Zhong, X., Yi, J., Sun, J., Wei, H.-L., Liu, W.S. and Yu, K.B., *Euro. J. Med. Chem.* **41** 1090(2006).
3. Klayman, D. L., Bartosevich, J. F., Griffin, T. S., Mason, C. J. and Scovill, J. P., *J. Med. Chem.* **22**, 855(1979).
4. Beraldo, H. and Gambino, D., *Mini. Rev. Med. Chem.* **4**, 31(2004).
5. Wang, M. and Wang, L. F., *Trans. Met. Chem.* **26**, 307(2001).
6. Clarke, C., Cowley, A.R., Dilworth, J.R. and Donnelly, P.S., *J. Chem. Soc. Dalton Trans.* 2402(2004).
7. Dhumwad, S.D., Gudasi, K.B. and Goudar, T. R., *Indian J. Chem. A* **33**, 320 (1994).
8. Gulerman, N. N., Rollas, S., Erdeniz, H. and Kiraj, M. *J. Pharm. Sci.* **26**, 1(2001).
9. Reddy, K.H., Reddy, P. S. and Babu, P. R., *Trans. Met. Chem.* **25**, 154(2000).
10. Tarasconi, P., Capacchi, S., Pelosi, G., Cornia, M., Albertini, R., Bonati, A., Dall, P. P., Lunghi, P. and Pinelli, S., *Bioorg. Med. Chem.* **8**, 154(2000).
11. Singh, H., Yadav, L.D.S. and Mishra, S.B.S., *J. Inorg. Nucl. Chem.* **43**, 1701(1981).
Egypt. J. Chem. **54**, No.5 (2011)

12. West, D.X., Dietrich, S.L., Thiantanavanich, I., Brown, C.A. and Liberta, A. E., *Trans. Met. Chem.* **19**, 320(1994).
13. Chandra, S. and Sangeetika, *Spectrochim. Acta: Part A* **60**, 147(2004) .
14. Akbar, M.A., Mirza, H.A., Monsur, A. and M. Nazimuddin, M., *Polyhedron*, **20**, 1045(2001).
15. Klayman, D.L., Bartosevich, J.F., Griffin, T.S., Mason, C.J. and Scovill, J.P. *J. Med. Chem.* **22**, 855(1979) .
16. Klayman, D. L., Scovill, J. P., Bartosevich, J. F. and Mason, C. J., *J. Med. Chem.* **22**, 1367(1979).
17. Singh, N. K. and Singh, S. B., *Indian J. Chem. A* **40**, 1070(2001).
18. Mishra, V., Pandeya, S. N. and Anathan, S., *Acta Pharm. Turc.* **42**, 139(2000) .
19. Singh, N. K. and Srivastava, A., *Trans. Met. Chem.* **25**, 133(2000).
20. Vogel, A.I., "*Practical Organic Chemistry*" 3rd ed., p. 998, Longmans London (1974).
21. Moustafa, M. H. , Abd-Almottaleb, M. , Seaf El-Naser, T. A., Issa, R. M. and Awad, A. M. A., *Al-Azhar Bull. Sci.* **15** (1), 243(2004).
22. Irving, H. and Rossotti, H.S., *J. Chem. Soc.* 2904(1954).
23. Ferrari, M. B., Capacchi, S., Bisceglie, F., Pelosi, G. and Tarasconi P., *Inorg. Chim. Acta*, **312**, 81(2001).
24. Castineiras, A., Bermejo, E., Valdes-Martinez, J., Espinosa-Perez, G. and West, D. X., *J. Mol. Struct.* **522**, 271(2000).
25. Kuban, V. and Havel, J., *Acta Chem. Scand.* **27**, 528 (1973).
26. Phillips, J. P. and Merrit, L. L. , *J. Am. Chem. Soc.* **70**, 410 (1948).
27. Sommer, L., *Folia Fac. Sci. Nat. Uni. Purk., Brno*, **5**, 1(1964).
28. Gans, P., Sabatini, A. and Vacca, A., *J. Chem. Soc., Dalton Trans.* **1195**(1985) .
29. Moustafa, M. H. , *Al-Azhar Bull. Sci.* (AISC'08), **71**, March (2008).
30. Moustafa, M. H., *Ass. Univ. Bull. Environ. Res.* **13** (2), 77(2010).
31. Moustafa, M.H., *Al-Azhar Bull. Sci.* **12** (2), 295(2010).
32. Sommer, L., Kuban, V. and Havel, J., *Folia Fac. Sci. Uni. Brno*, Vol, XI, pt. **1**, 33(1970).
33. Vozinca, P., Havel, J. and Sommer, L., *Collec. Czech. Chem. Comm.* **45** ,54 (1980).

34. **Abu-Baker, M.S., Rageh, H.M., Hashem, E.Y. and Moustafa, M. H.,** *Monatsh. Chemi.* **125**, 1197(1994).
35. **Job, P.,** *Ann. Chem.* **9**, 113(1928).
36. **Shirif, F. G. and Awad, A.M.,** *Inorg. Nucl. Chem.* **24**, 79(1962).
37. **Yoe, J. H. and Jones, H. L.,** *Indian Eng. Chem., Anal. Ed.*, **16**, 111(1944).
38. **Sandell, E.P.,** "*Colorimetric Determination of Trace Metals*", Vol. 3, Wiley, New York, p. 97(1959).
39. **Das, M. K. , Nath, M. and Zuckerman, J. J.,** *Inorg. Chem. Acta*, **21**, 49(1983).
40. **El-Metwally, N.M., El-Shazly, R.M., Gabr, I.M. and El-Asmy, A.A.,** *Spectrochim. Acta Part A*, **61**, 1113 (2005).
41. **Du, K.K. and Liu, S.X.,** *J. Mol. Struct.* **874**, 138(2008).

(Received 15/8/2011;
accepted 10/4/2012)

تحضير وثبات وطيف وتوصيف متراكبات أيونات الزئبق الثنائي مع قاعدة شيف الجديدة

محمود حسن مصطفى ، أحمد عبد النعيم وأسامة أحمد عباس
قسم الكيمياء – كلية العلوم للبنين – جامعة الأزهر – فرع أسيوط – مصر.

تم في هذا البحث تحضير قاعدة شيف الجديدة (E 2 و Z '2)-2,2-(E)-3-(E)-2- هيدروكسي فينيل) داي ازينيل) بينان-4,2-داي يلدين) بس (هيدرازين كربوثيواميد) المشتقة من الثيوسيميكر بازيد. وذلك بتفاعل جزئين ثيوسيميكر بازيد مع جزئ أرثو هيدروكسي فينيل أزو اسيتيل أسيتون وتم اثبات التركيب الجزيئي لليجند بواسطة التحليل العنصرى وطيف الكتلة وطيف الرنين النووي المغناطيسى و الأشعة تحت الحمراء واستخدم هذه الليجند لتحضير متراكبات أيون الزئبق الثنائي. وتمت دراسة الخواص الحامضية والقاعدية للكاشف المحضر وكذلك متراكبات الزئبق المحضر منه بواسطة الطرق الجهدية والطيفية المختلفة وذلك بهدف تحديد حالات اتزان التراكبات الممكن تواجدها بالمحلول ونسب تكوينها وتدرج ثبات نظم التراكبات المختلفة على ضوء طبيعة الكاشف الداخلى فى التفاعل وحسب ثوابت ثبات هذه النظم التركيبية المختلفة فى المعايير عند تغير درجة تركيز أيون الهيدروجين بالمحلول و ذلك لمعرفة الظروف المثلى لتكوين المتراكبات موضع الدراسة و كذلك استخدمت فى هذه الدراسات قياس أطراف الامتصاص المرئى و الفوق بنفسجية خلال معايير تتبع تغير درجة تركيز أيون الهيدروجين بالمحلول عند ظروف تجريبية محددة. وأمكن حساب ثوابت التآين لليجند وتحديد النسب التكوينية للمتراكبات موضع الدراسة ووجدت بنسبة 1:1. وقد أمكن تحضير المتراكبات الصلبة فى الظروف التجريبية المناسبة والمحددة ليتم التعرف على شكل وتركيب هذه المتراكبات بالتحليل العنصرى و طيف الأشعة تحت الحمراء وطيف الامتصاص الإلكتروني وقياسات التوصيل الجزيئية والتحليل الحرارى الوزنى. وتم دراسة وتحديد مواضع الترابط مع أيون الزئبق الثنائي وتم التعرف على شكل وتركيب المتراكبات.