Mercury Determination by New Asymmetric Triazene Ligand, 1-(2-Ethoxyphenyl)-3-(4-Nitrophenyl)Triazene (ENT) with Partial Least-Squares Calibration Method (PLS) Method

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Abstract
Synthesis, characterization, spectrophotometric studies of three mercury (II) complexes of 1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triazene (ENT) are reported in this article and it was characterized by means of NMR, FT-IR, UV spectroscopy and CHN analysis, then determination of Hg(II) was performed by spectrophotometric determination using chemometric techniques and new triazen ligand which was prepared by us. The calibration graphs of individual components were linear in the ranges of 1 - 5.25 mg·L⁻¹. The root means square errors of prediction (RMSEP) were 4.4 х10⁻³. The proposed method are simple, fast, inexpensive and do not need to any separation or preparation method.

Keywords
Synthesis, Triazen Ligand, Spectrophotometric Determinatio, Chemo Metric Techniques, Mercury

1. Introduction

The first extensive investigation of the coordination chemistry of a triazene derivative (1,3-diphenyltriazene) was carried out in 1887 by Meldola [1]. The study of transition metal complexes 1, 3-diaryl triazenide ligands has increased greatly in the past few years, because of their potential reactivity in relation to their coordination modes [2-4].

Over the last three decades there has been increasing global concern over the public health impacts attributed to environmental pollution, in particular, the global burden of disease [5].

Mercury is one of the most toxic elements and a threat to wild life [5], therefore determining and analyzing this element is so critical.

Several methods have been proposed for the individual or simultaneous determination of some heavy metals [6, 7]. Several techniques such as atomic absorption [8-12], inductively coupled plasma [13, 14], solid and liquid extraction [15, 16] have been used for mercury determination in different samples.

Spectrophotometry[8]1-(2-Ethoxyphenyl)-3-(4-nitrophenyl) triazene (ENT) reacts with several metal ions to form colored metal complexes. This chelating agent has been used to determine several metal ions by ultraviolet-visible (UV-Vis) spectrophotometry.

In this study a new asymmetric triazene ligand was synthesized and characterized with several different methods then chelating agents of the ligand with three kinds of mercury salts were examined then PLS was employed as a simple method for determination of mercury.

2. Experimental

2.1. Reagents

Reagent grade mercury (II) nitrate, acetate and chloride, acetonitril and all other reagents used were supplied by Merck chemical company. 1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triazene (ENT) ligand (L) was prepared which will be discussed in next section.

2.2. Synthesis and Characterization of ENT

The 1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triazene (ENT) used as ligand and its structure is shown in Fig. 1. It was synthesized as follows: A 100 ml flask was charged with 10 g of ice and 15 ml of water and then cooled to 0 °C in an ice-bath. After that, 0.69 g (5 mmol) of para nitroaniline and 3.61 g (0.1 mol) of hydrochloric acid (d=1.18 g mL⁻¹) were added to the mixture, and then a solution of NaNO₂
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containing 0.35 g (5 mmol) in 10 ml of water was added during 15 min under stirring solution. Afterwards, 0.68 ml (5 mmol) of 2-ethoxyaniline (1.06 g mL\(^{-1}\)) was added drop wise with vigorous stirring for a period of 30 min to this mixture. Finally, a solution containing 14.76 g (0.18 mol) of sodium acetate in 45 ml of water was added and stirred for 45 min. The orange-colored product was filtered and dissolved in diethyl ether. After the evaporation of diethyl ether, a purified sharp pale orange powder, which has a melting point of 101–102 °C, was produced (yield, 72%).

Infrared and \(^1\)H NMR spectra and CHN analysis, were confirmed the ENT structure. IR (KBr): 3389, 3325, 2984, 1600, 1519, 1468, 1343, 1253, 1209, 1113, 1045, 894, 739 cm\(^{-1}\).

\(^1\)H NMR (DMSO): \(\delta\) 1.37 (CH\(_3\), 3), 4.13 (CH\(_2\), 2), 6.94-8.06 (phenyl protons, 8), 12.89 (NH, 1).

CHN: (C\(_{14}\)H\(_{14}\)N\(_4\)O\(_3\)) C: 58.66%, H: 4.82%, N: 19.52%.

Figure 1. 1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triazene (ENT)

2.3 Physical Measurements

Elemental (C, H, N and O) analyses were made on a Perkin-Elmer Model automatic analyzer.

Infrared (IR) spectra were recorded on Perkin-Elmer Model 843.

NMR spectra were recorded on a Bruker Avance 300 spectrometer, and all chemical shifts are reported in \(\delta\) units downfield from Me\(_4\)Si.

UV–vis absorption spectra were recorded using the double-beam in-time spectrophotometer (Perkin-Elmer model Lambda 25, U.S.A.) with a 1 cm quartz cell, a scan rate of 400 nm/min and slit width of 2 mm and the temperature of the cell holder was maintained at 25 °C. FT-IR spectrum of ENT is shown in figure 2.

3. Results and Discussion

3.1. Solution Studies

The electronic absorption spectra of the ligand L in the presence of the increasing concentration of mercury (II) ions in acetonitril at room temperature are shown in Fig.2. Fig3 and Fig4. In a typical procedure, 2.0 ml of ligand solution (5.0 × 10\(^{-5}\) M) in acetonitrile was placed in the spectrophotometer cell and the absorbance of the solution was measured. Then a known amount of the concentrated solution of Hg (II) nitrate, Hg(II) acetate and Hg(II) chloride in acetonitrile (5.0 × 10\(^{-3}\) M) were added in a stepwise manner using a 5µl Hamilton syringe separately. The absorbance spectrum of the solution was recorded after each addition. Fig.3. shows that, the absorbance band of ENT at wavelength 393 nm decreases and at 402 nm increases by increasing in metal ion concentration and it reveals distinct inflection points at a metal-to-ligand molar ratio of about 1 emphasizing the formation of a 1:1 complexes. The conditional formation constants was evaluated as log K =4.88 ± 0.003 by using a non-linear least-squares curve fitting program KINFIT.

Figure 2. FT-IR spectrum of 1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triazene (ENT)
Figure 3. (a) Electronic absorption spectra of ligand [ENT] in acetonitril (5.0 × 10^{-5} M) in the presence of increasing concentration of Hg (II) acetate at room temperature. (b) Corresponding mole ratio plot at 450 nm.

Figure 4. (a) Electronic absorption spectra of ligand [ENT] in acetonitril (5.0 × 10^{-5} M) in the presence of increasing concentration of Hg(II) nitrate at room temperature. (b) Corresponding mole ratio plot at 438 nm.

Figure 5. (A) Electronic absorption spectra of ligand [CNT] in acetonitril (5.0 × 10^{-5} M) in the presence of increasing concentration of Hg (II) chlorid at room temperature. (B) Corresponding mole ratio plot at 426 nm.
Fig. 4 shows that, the absorbance band of ENT at wavelength 344 nm decreases and at 350 nm increases by increasing in metal ion concentration of Hg (II) nitrate and it reveals distinct inflection points at a metal-to-ligand molar ratio of about 0.5 emphasizing the formation of a 1:2 complex. The conditional formation constants was evaluated as log \( K =4.93 \pm 0.003 \) by using a non-linear least-squares curve fitting program KINFIT.

Fig. 5 shows that, the absorbance band of ENT at wavelength 270 nm decreases and at 290 nm increases by increasing in metal ion concentration of Hg (II) chloride and it reveals distinct inflection points at a metal-to-ligand molar ratio of about 0.5 emphasizing the formation of a 1:2 complex. The conditional formation constants was evaluated as log \( K =4.56 \pm 0.001 \) by using a non-linear least-squares curve fitting program KINFIT.

Solution studies show that our ligand chelated to mercury nitrate better than the other mercury salts, therefore mercury nitrate was selected for further studies.

### 3.2. Extraction Procedure

Thirty mixtures with different mercury concentration and triazene ligand were selected as the calibration set. Their composition was randomly designed for obtaining more information from calibration procedure. Under this condition, the Calibration model was obtained. The calibration model was validated with 5 synthetic mixtures containing the metal ion in different concentrations. The results obtained are given in Tables 1 and 2. Each solution was prepared to contain combinations of the concentration levels 0.5-10 mg/L of mercury. Twenty seven of these solutions were used as a calibration set for PLS model development. Another 5 calibration mixtures, not included in the previous set were employed as an independent test set called the prediction set.

To select the number of factors in the PLS algorithm, the leave one out cross-validation method, was used [20]. The prediction error was calculated for each component in the prediction set. The optimum number of factors (latent variables) was determined by computing the prediction error sum of squares (PRESS) for different numbers of latent variables (1-10 latent variables).

| Sample | Actual concentration(mg/L) | Prediction concentration(mg/L) |
|--------|----------------------------|-------------------------------|
| 1      | 0.910                      | 0.912                         |
| 2      | 1.245                      | 1.244                         |
| 3      | 1.700                      | 1.668                         |
| 4      | 2.010                      | 2.010                         |
| 5      | 4.341                      | 4.335                         |

Table 3. Absolute and relative errors by PLS model.

| Sample | Absolute error | Relative errors |
|--------|----------------|-----------------|
| 1      | 2 x 10^{-3}    | 2.1 x 10^{-3}   |
| 2      | 1 x 10^{-3}    | 8.03 x 10^{-4}  |
| 3      | 3.2 x 10^{-2}  | 1.8 x 10^{-2}   |
| 4      | 0              | 0               |
| 5      | 6 x 10^{-3}    | 1.38 x 10^{-3}  |

Figure 7 is shown the relativity between actual concentration and the predicted one by the model.

**Figure 7.** Predicted concentration versus real concentration for Hg (II) ion in the prediction set

### 4. Conclusion

PLS method is a simple, fast and inexpensive method for mercury determination. The results show there’s a good
reaction between triazen ligand and mercury ions, in comparison of three different formation constants of three mercury salts we can conclude that mercury nitrate has the highest interaction with our triazen ligand because of its highest formation constant, mercury nitrate and chloride gave us the ML2 complexes but mercury acetate gave us ML complex.

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