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Complexes of a newly synthesized tetraoxime with silver(I) in acetonitrile: Study with different analytical techniques

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ABSTRACT

We are reporting the study of the complexation of a newly synthesized tetera-oxime derivative (2,5,10,13-Tetraazatricyclo[12,2,2,2]icosa-1(16),6,8,14,17,19-hexene-3,4,11,12,13-tetraone tetraoxime) with Ag(I) in acetonitrile. Analytical techniques (IR and UV-Vis), conductometry and potentiometry showed that the ligand reacts selectively towards Ag(I) ion. In addition, the stoichiometry of resulted complexes was investigated by studying their GC-Mass spectra. The results revealed that the mole ratios of the reactants in the complexes were 2:1 and 1:1 (metal:ligand). The stepwise formation constants (K_1 and K_2) were evaluated (3.2×10^8 and 4.3×10^7, respectively) by using a computerized non-linear curve-fitting program.

KEYWORDS

Complexation;
Silver(I);
Tetraoxime.

INTRODUCTION

The importance of mixed oxygen/nitrogen donor environments is their great potential for important applications in both organic and inorganic chemistry[1]. Mostly, nitrogen, oxygen, and sulfur donor atoms from the complexing reagents dominate the coordination environments of metal ions in all metal complexes.

Oximes have possessed a noted position in the development of coordination chemistry[2,3] by playing important roles as electron transfer[4-6], vitamin B_{12} mimics[7-9] and the biosynthesis of nitric oxide[1,10]. Furthermore, oxime metal complexes have been used for a number of purposes such as coordination of metal ions as neutral dioximes[11,12] oxidazing reagents[11-13] and utilized in medicine[14-18]. However, self-assembling multinuclear metal complexes are of great interest[19-22]. Probably, this is largely due to the discovery of the ability of the oximato group to coordinate additional metal ions *via* the bridging N and O functions.

Recently, we can find a large number of papers in the literature about oxime-containing complexes. Certainly, the ability of oximes to coordinate in different modalities to metals, as well as the easy tunability of their substituents[23-25], is the main reason for the current interest in oxime metal complexes. These important characteristics of oximato complexes have lead to an increased interest in the study of their coordination chemistry.

In this work, we investigated the complexation of the newly synthesized tetera-oxime derivative (2,5,10,13-tetraazatricyclo[12,2,2,2]icosa-1(19),6,8,14,17,19-hexene-3,4,12,13-tetraone tetraoxime) (abbreviated as L, Figure 1) with Ag(I) in acetonitrile.

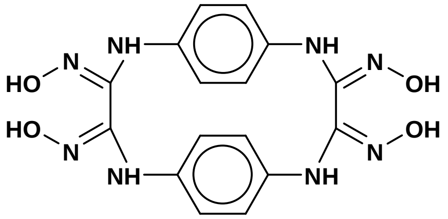

Figure 1 : The chemical structure of the ligand (L).

EXPERIMENTAL

Materials

We purchased reagent-grade acetonitrile (AN) from Fluka chemical company and used it as received. The nitrate salts of the needed cations (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled and deionized water was used throughout. The ligand (L) was synthesized and purified as described elsewhere[26].

Apparatus

All absorbance measurements were carried out on a UV-Vis 1650PC (Shimadzu Japan) spectrophotometer. The mass spectra were recorded on a GC-MS (17A-QP5050, Shimadzu Japan). In order to take IR spectra, an FTIR (8400S, Shimadzu Japan) spectrophotometer was used. Potentiometric studies were preformed by using a Jenway 3020 (UK) pH/mV-meter including an Ag-Ag/AgCl electrode system. Conductance measurements were carried out with a Metrohm 712 conductivity-meter. We used a dip-type conductivity cell that was made of platinum black. The cell constant at the desired temperature were determined by measuring the conductivity of a 0.010 M solution of analytical grade KCl (Merck) in triply distilled and deionized water. The specific conductance of this solution at various temperatures has already been reported in the literature. In all measures, the reaction cell was thermostated at the desired temperature (20.0± 0.1 °C) by using a circulating water-bath system.

RESULTS AND DISCUSSION

UV-Vis spectrophotometric studies

In order to find a clue about the complexation reaction of the ligand with some common transition and heavy metal ions in AN, we studied the reaction of L with metal cations such as Ag(I), Hg(II), Ni(II), Cd(II), Cu(II), Zn(II) Pb(II), Mg(II), Sr(II), Ba(II), Rh(II), Co(II), Fe(III) and Al(III) by using UV-Vis spectrophotometric technique. We found that the ligand showed a good selectivity toward Ag(I) ion over the other metal cations tested in the solution because the spectral properties of the ligand didn't change in the presence of increasing amounts of mentioned metal ions except for the case of Ni(II), which will be described in the proper place in the text. The electronic spectra for the titration of L (2.5 mL, 1.0×10^{-3} M) with increasing amounts of Ag(I) (0.0 to 2.8×10^{-3} M, with 1.3×10^{-5} M steps) are shown in Figure 2. As can be seen in this figure, the spectral behavior of the ligand undergoes no changes until the molar-ratio of Ag(I)/L riches 1:1 and then the system reveals a distinct increase in the absorption which beyond that there is no changes in the absorption of the system when the molar-ratio of [Ag^+]/[L] passes 2:1 in the solution.

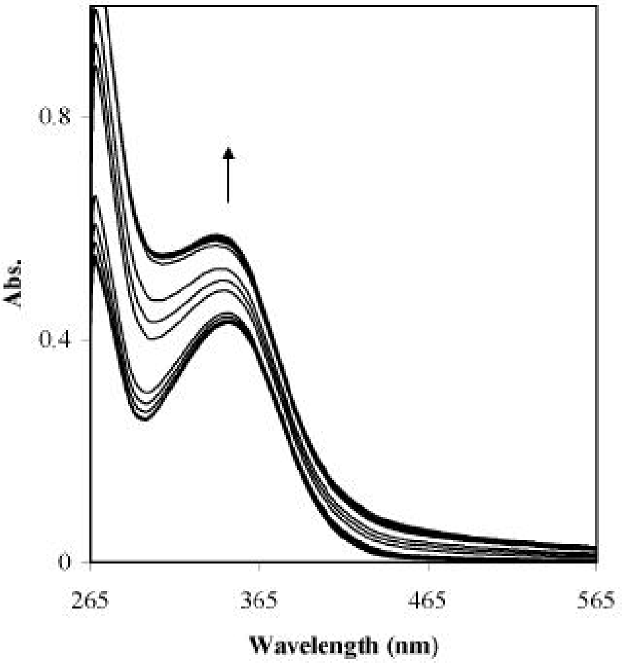

Figure 2 : Electronic spectra of the titration of L (1.0×10^{-3} M) with Ag^+ (1.0×10^{-2} M) in AN.

Determination of stoichiometry and formation constants of the resulted complexes

An absorbance/mole-ratio curve plot was constructed from the spectra in Figure 2 (at $\lambda_{max} = 347$ nm). The results are demonstrated in Figure 3. From this figure, we can see two distinct inflection points at 1 and 2 metal-to-ligand molar ratios that are indicative the formation of two 1:1 and 1:2 (ligand:metal) complexes in the solution. In order to evaluate the stepwise formation constants, a non-linear least-squares curve-fitting program, KINFIT[27], was used. The output of the program comprises the refined parameters, the sum-of-squares and the standard deviation of the data. The evaluation process was carried out based upon the appropriate mass-balanced equations for the ML + M_2L model as described elsewhere[28].

The solid line in Figure 3 shows the corresponding predicted curve plot for this model which reveals a good agreement between the experimental (points) and theoretical (solid line) data. The sum-of-squares of the system was less than 0.0002. According to this fitting procedure the calculated formation constant for the ML and M_2L complexes are 3.2×10^8 and 4.3×10^7, respectively.

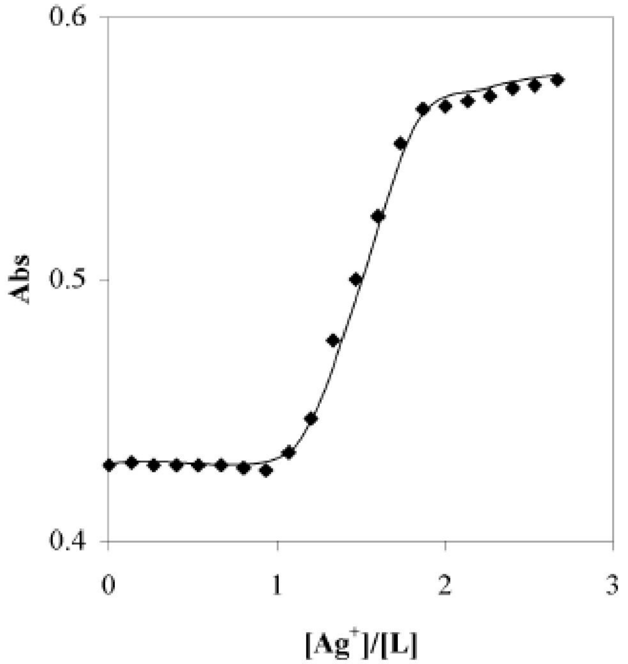

Figure 3 : Absorbance/molar ratio plot from the absorbance values (points) of the spectra in Figure 1, at λ_{max} = 347 nm. The solid line indicates the predicted curve plot for the theoretical complexation models.

Potentiometric studies

We also studied the complex formation between the ligand (L) and Ag(I) ion by using potentiometric titration method. The titration of 50 mL of a standard solution of Ag^+ (8.0×10^{-5} M) was carried out with a solution of L (1.0×10^{-2} M). The data collection followed by potential (E, mV) measurements of the solution in the presence of increasing amounts (0.0 to 2.0×10^{-3} M) of L (with 6.4×10^{-5} M steps). The potentiometric curve plot, which was formed by plotting the measured E(mV) values versus the $[L]/[Ag^+]$ ratio in the solution, is shown in Figure 4 (points). From this figure, we see that the potentiometric method isn't able to differentiate the Ag(I) ion potentials when they are involved in the two new situations in the formed complexes. This fact is come into view by the unclear inflection point of the system's response around 1:1 $[L]/[Ag^+]$ ratio. We constructed a predicted E(mV)/($[L]/[Ag^+]$) curve plot for a 1:1 model, based upon the Nernst's potential equation[29], by using Microsoft Excel® (solid line in Figure 4). Figure 4 shows that there is good agreement between the data from the proposed model and the experimental data. The best fit was obtained for the case in which the suggested formation constant was 5.2×10^8, which is very close to the value calculated by the former photometric method.

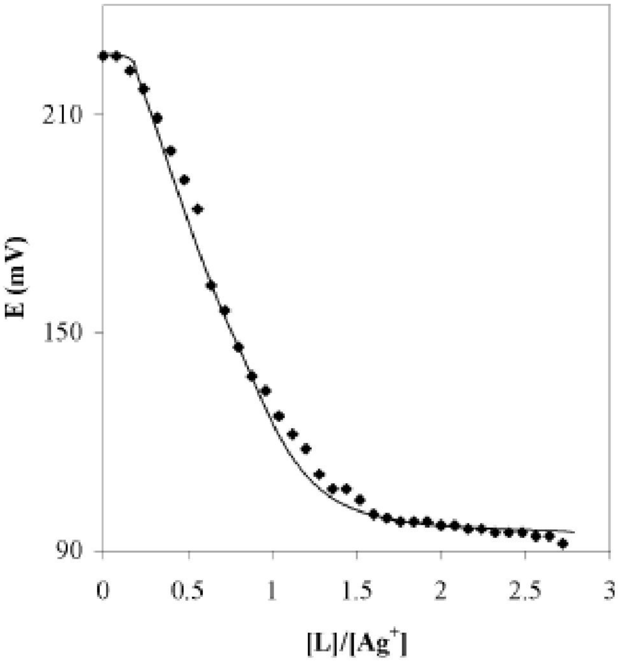

Figure 4 : Potential/molar ratio plot for the potentiometric titration of Ag^+ (8.0×10^{-5} M) with L (1.0×10^{-2} M) in AN (points). The solid line indicates the predicted curve plot for the theoretical complexation model.

Conductometric studies

The procedure was carried out as the same as preformed in potentiometric titration except the measured signal here was molar conductance of the Ag(I) solution (5.0×10^{-5} M) in the presence of various concentrations of L. The results are shown in Figure 5 (points). The curve-fitting program, KINFIT, was developed to evaluate the conductometric data. The corresponding predicted curve plot was obtained (solid line in Figure 5) by solving the appropriate mass-balanced equations of the proposed $ML+M_2L$ model. As can be seen from this figure, there is a very good agreement between the theoretical model and the experimental values (sum-of-squares of 0.00001), from which the evaluated values of K_1 and K_2 were 2.7×10^8 and 3.7×10^7, respectively.

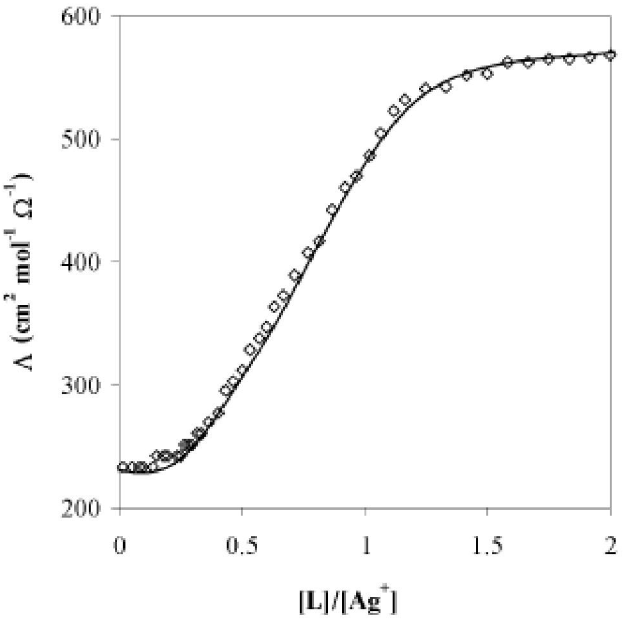

Figure 5 : Molar conduction/molar ratio curve plot (points) for the conductometric titration of Ag^+ (5.0×10^{-5} M) wit L (1.0×10^{-2} M) in AN. Here, the solid line indicates the predicted curve plot for the theoretical complexation models.

GC-mass spectrometric studies

Here, in order to find more clue about the stiochiometry of the resulted complexes, from the interaction between the ligand L ($C_{16}N_8O_4H_{16}$, fw= 384 g/mol) and Ag^+ ion, we studied the mass spectra of mixed reactions in the presence of different mixture of reactants in the solution. Various proper mixtures of metal:ligand ratios of 0:1, 1:1 and 2:1 were prepared in 10 mL flasks (including 0:60, 60:60 and 60:30 μL, of Ag^+ 1.0×10^{-2} M and L 1.0×10^{-2} M, respectively). Then a portion of each solution injected into the GC-Mass inlet system. The mass spectra in Figure 6 demonstrate the case in which the mixture is only included the ligand (0:1). The peak at 354 (m/z) reveals the leaving out of two NH groups of the molecule and rearrangement of C-N-OH groups as C=O in the left. Apparently, the ion molecule was sufficiently unstable to be detected at the conditions applied on the ionization chamber of the GC-Mass instrument so the corresponding peak has been missed in the spectra. The other peaks of the mass-spectra can be attributed to the other fragments resulted from the fragmentation process. The mass spectra for the second mixture solution are shown in Figure 7. As we can see, an ML complex has formed in this solution. The main evidence for this fact is the peak at 461 (m/z). This new peak can be related to the existence of the former fragment (354 m/z, Figure 6) including a silver atom in its molecular structure so we can see a peak at 107+354= 461 (m/z). This figure confirms the formation of a 1:1 (Ag:L) complex in the solution, in which the ligand probably embraces a silver ion by one of its barb-like oximic arms to form an ML complex. Furthermore, the spectra in this figure are simpler than the first spectra in Figure 6 indicative the engagement of the side branches of the molecule in complexation, which reduces the fragmentation probability of the system. The mass spectra for the third mixture solution are shown in Figure 8. The major peak at 569 (m/z), 215+354= 569 (215, the total mass for two silver atoms), reveals that two silver atoms have now participated in the complexation. These spectra clearly elucidate that two metal cation are involved to form an M_2L type complex which is a more compacted and much heavier molecule than the former cases. So it can not be affected by the fragmentation process under the same condition for the former mass spectra. Here also, the more simplicity of the spectra in Figure 8 tells us that the fragmentation is much simpler than those we described before.

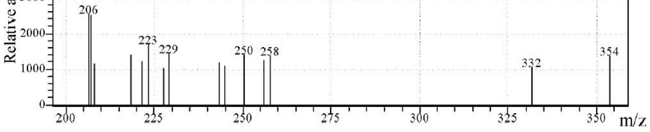

Figure 6 : The mass spectra for the case in which the mixture of Ag(I) and L was only included the ligand (0:1, metal:ligand ratio).

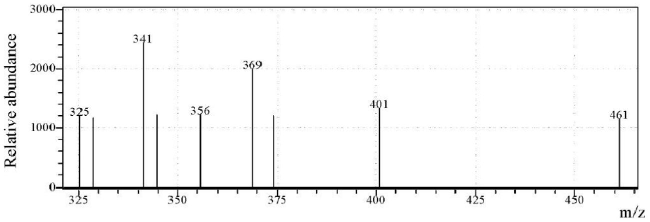

Figure 7 : The mass spectra for the case in which the mixture of Ag(I) and L was included the 1:1 (metal:ligand) ratio.

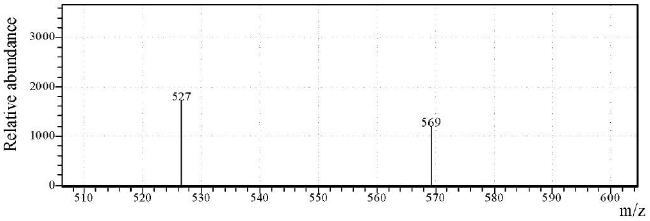

Figure 8 : The mass spectra for the case in which the mixture of Ag(I) and L was included the 2:1 (metal:ligand) ratio.

IR spectroscopic studies

Finally, the complexation between the ligand L and Ag(I) was investigated by using Infra-Red (IR) spectroscopy technique. For this purpose, we prepared two stock solution (1.0×10^{-2} M) of L and Ag(I). Then, four different 10 mL mixture solutions of L and Ag^+ including 0:1, 1:1, 2:1 and 1:2 ratios (the ratios were obtained by using of 30 or 60 μL of each stock solution) were constructed and then one droplet of each solution dropped onto four similar and freshly prepared KBr tablets. After evaporation of the solvent in ambient atmosphere, the dried tablets were mounted on the IR cell to take the related spectra. The resulted spectra are demonstrated in Figures 9-12, respectively. In the first figure (Figure 9), the peaks at 1600, 2900 and 3600 cm^{-1} can be attributed to the C=C, C–N and O–H stretching frequencies of L. Figures 10 and 11, the corresponding spectra for the 1:1 and 1:2 ratios of metal:ligand, are very similar. Comparison of these two figures shows that the excess amounts of the ligand cannot form new types of complexes in the solution. On the other hand, the peak at 3600 cm^{-1} has been changed to a more simpler and sharper one showing less hydrogen bond making in the presence of Ag(I) ion. This fact confirms that the interaction of L toward Ag(I) ion can be occurred from the oximic sides of the ligand. The last figure (Figure 12) shows that the C=C peak at 1600 and the O–H peak at 3600 cm^{-1} have become more weaker than the cases in which the ligand did or didn't form any complexes in the solution (former cases). These evidences confirm the engagement of both two oximic parts of the ligand in complexation with Ag(I) ions. In addition, the decrease in intensity of the peak at 1600 cm^{-1} can be related to the influence of the involvement of oximic nitrogens, which are connected to the carbons in the aromatic ring, on formation of a M_2L complex.

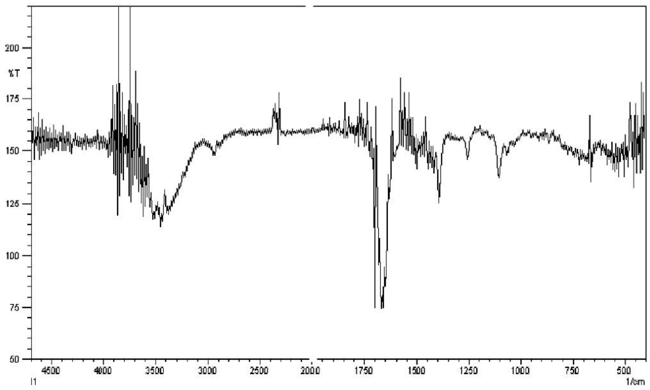

Figure 9 : The IR (%T) spectra for the case in which the mixture of Ag(I) and L was only included the ligand (0:1, metal:ligand ratio).

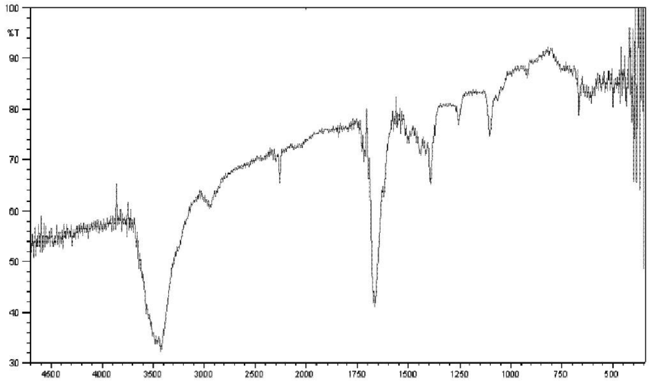

Figure 10 : The IR (%T) spectra for the case in which the mixture of Ag(I) and L was included the 1:1 (metal:ligand) ratio.

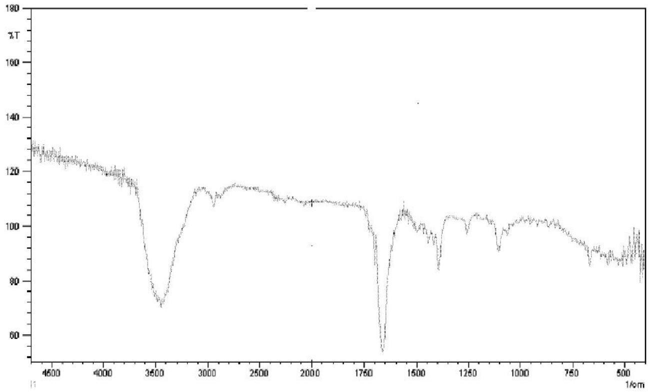

Figure 11 : The IR (%T) spectra for the case in which the mixture of Ag(I) and L was included the 1:2 (metal:ligand) ratio.

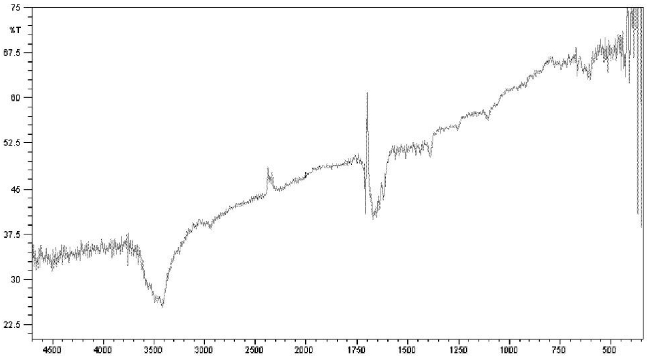

Figure 12 : The IR (%T) spectra for the case in which the mixture of Ag(I) and L was included the 2:1 (metal:ligand) ratio.

The study of the complexation of L with Ni(II)

As we have already mentioned, the ligand L also can react to Ni^{2+} ion in AN solution. A spectrophotometric titration was carried out by proper amounts of L with a standard solution of Ni^{2+} (1.0×10^{-2} M) followed by photometric measurements at $\lambda_{Max} = 420$ nm (Figure 13). The absorbance measurements versus $[Ni^{2+}]/[L]$ resulted in construction a curve plot (points) which is shown in the inset of Figure 13. Here again, by using KINFIT, the solid line demonstrates the predicted absorbance/molar ratio plot for a proposed $ML+M_2L$ model with 1.7×10^4 and 3.2×10^3 for K_1 and K_2, respectively. These formation constant values tell us that L can form complexes with Ni(II) ion that are too weaker than those with Ag(I) in AN.

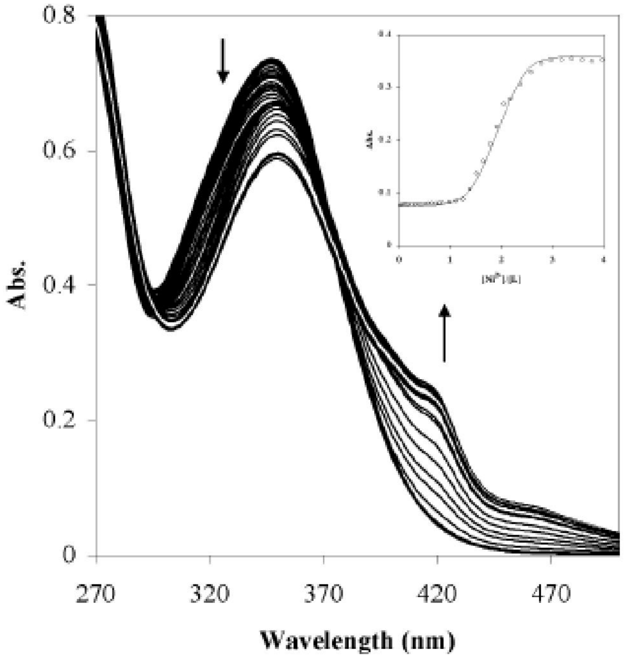

Figure 13 : Electronic spectra of the titration of L (1.0×10^{-2} M) with Ni(II) (1.0×10^{-2} M) in AN. In the inset, the absorbance/molar ratio plot, from the absorbance 13 values (points) at $\lambda_{max} = 420$ nm, has been constructed and the solid line indicates the predicted curve plot for the theoretical complexation models.

CONCLUSIONS

The ligand belongs to a very important class of organic compound, oximes, which are very interesting for chemists because of their attractive behaviors in the chemical reactions. From the results have been obtained in the described studies, we can say that the tetraoxime derivative ligand can selectively complexes the Ag(I) ion in acetonitrile. Based on these observations, the coordination mode of this tetraoxime may be an important indicator in the predictability of coordination behavior of tetraoxime-functionalized ligands. So the proposed ligand can be used as a selective chemosensor toward the Ag(I) ion. Now our co-workers are working to utilize this ligand as a sensing element in construction of an optical sensor to determine Ag^+ ion.

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