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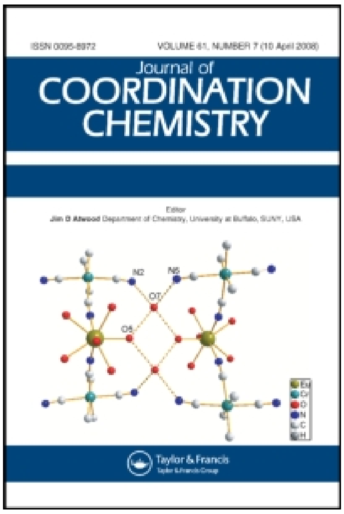

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Spectrophotometric and theoretical studies on complexation of a newly synthesized *vic*-dioxime derivative with nickel(II) in dimethylformamide

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Spectrophotometric and theoretical studies on complexation of a newly synthesized *vic*-dioxime derivative with nickel(II) in dimethylformamide

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The complexation of a recently synthesized *vic*-dioxime derivative, 1-({2-[(2-aminoethyl) amino]ethyl}amino)-6-methyl-9H-xanthen-9-one with Ni(II) in N,N-dimethylformamide, was investigated by spectrophotometric and conductometric methods. The possible molecular geometries, binding, and spectroscopic properties for the formed complexes were theoretically studied in detail by the Hyperchem program. The stoichiometry of the complex species was determined from spectrophotometric molar ratio methods at 25°C. The spectral data were further treated by KINFIT to calculate the formation constants of the 1 : 1 and 1 : 2 complexes and their molar absorptivities. Program DATAN was used to calculate the spectral behavior of the complexes in the wavelength range ~380 – ~550 nm for different mole ratio solutions.

Keywords: Dioxime; Nickel(II); Spectrophotometry; Stability constant

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1. Introduction

There has been a great deal of interest in coordination compounds containing vicinal dioximes ligands. Dioxime ligands are known to coordinate metal ions as dioximates and neutral dioximes [1, 2]. The chemistry of the bis-dioximate complexes of transition metal ions attracts continuous attention because of their importance to dioxygen carriers [3], catalysis in chemical transformations [4–6], intramolecular hydrogen bonding and metal–metal interactions [7–9]. In addition, stable complexes prepared with *vic*-dioxime ligands have been used extensively for different purposes such as analytical and medicinal chemistry, pigments, and biochemistry [10]. In 1905, Tschugaeff discovered the *vic*-dioxime metal complex bis-dimethylgloximatonickel(II) [11], initiating an area of coordination chemistry which has been widely explored during the past century. In the literature, the numerous *vic*-dioximes and their transition metal complexes have been investigated for a long period of time [2, 12–15]. However, spectrophotometric characterizations of their complexation and stability constants have rarely been investigated.

Computational chemistry is a multidisciplinary area of science. Since theory can be very helpful to rationalize experimental observations, provide information not

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amenable to direct observation, and even make predictions concerning the outcome of possible investigations, it is becoming more widely accepted by experimental scientists as a valuable complement to their current studies and interpretations of data. In particular, molecular modeling has been warmly embraced by the chemical community [16].

The purpose of this work is to investigate the complexation and stability constants of a recently synthesized *vic*-dioxime, 1-({2-[(2-aminoethyl)amino]ethyl}amino)-6-methyl-9H-xanthen-9-one (H_2L), and complexes with Ni^{2+} spectrophotometrically using suitable theoretical computer aided programs.

2. Experimental

2.1. *Materials*

Analytical grade nitrate salt of nickel(II), and tetraethylammonium perchlorate (TEAP) (from Merck), used in the solution studies, were of the highest purity available and were used without further purification except for vacuum drying. Reagent grade N,N-dimethylformamide (DMF) (Merck) was used as received.

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2.2. *Apparatus*

All calculations of the quantum chemistry and of formation constants were performed on a Pentium IV 1994 (256 MB, 80 GB) computer. Absorption spectra were recorded on a Shimadzu (Japan) double beam spectrophotometer 1650PC, equipped with a water-thermostatic system and two 1-cm optical path quartz-cells. Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type conductivity cell made of platinum black was used. In all measurements, the temperature was kept at 25.0°C.

2.3. *Synthesis of Ligand H_2L*

Ligand H_2L (figure 1) was synthesized and purified as described elsewhere [17]. To a stirring solution of 2-aminothiophenol (1.25 g, 10 mmol) in 20 mL of MeOH (65% aqueous) a solution of dichloroglyoxime (1.56 g, 10 mmol) in 15 mL MeOH (35% aqueous) was added at room temperature. The solution was stirred for 10 min, then 0.15 g $NaHCO_3$ was added. After 3 h stirring at room temperature, the mixture was filtered and the precipitate was washed with cold CH_3CN to give 1.97 g (94.25% yield) of product, m.p., 217–219°C. The yellow precipitate was washed with hot distilled

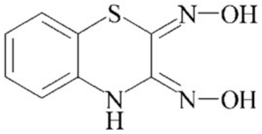

Figure 1. The chemical structure of the *vic*-dioxime, H_2L.

water to give 1.73 g (82.77%, yield) of yellow crystals of H_2L with melting point at 219.0–219.3°C. Some selected spectral data: IR (KBr) cm^{-1}: 3400(NH), 2800–3200(OH), 1600, 1635(C=N). ^1H-NMR, ppm: 12.35(2H, OH), 10.76(2H, OH), 9.35(bs, 2H, NH), 6.82–7.37(8H, CH_{Ar}). Upon addition of D_2O to the NMR sample, the NH and OH signals disappeared. ^{13}C-NMR, ppm: 137.50, 137.24, 133.64, 126.97, 125.89, 120.97, 116.62, 112.81. The mass spectrum showed, *m*/*z* (rel. intensity): 418(m^+, 1.2), 335(1.3), 209(41.25), 193(100), 150 (93.75). Elemental analysis for $C_{16}H_{14}N_6O_4S_2$ Calcd: C, 45.93; H, 3.35; N, 20.10; S, 15.31. Found: C, 45.91; H, 3.37; N, 20.12; S, 15.30.

2.4. *Spectrophotometric data collection*

To study the formation of Ni(II)–H_2L complexes in DMF, in a typical experiment, 3.5 mL of the ligand solution (6.8×10^{-6} M) in the given solvent was placed in a 1-cm optical path quartz cell. The ionic strength of the solution was stabilized with 0.04 M TEAP. The absorbance of the solution, at λ_{max} of the new band (420 nm), was measured. Then known amounts of nickel(II) solution $(0.0 - 1.0) \times 10^{-5}$ M were added in a stepwise manner (with 1.7×10^{-6} M steps) using a pre-calibrated micro-syringe and the absorbance of the solution was measured after each addition. Addition of the metal solution was continued until the desired metal to ligand ratio was achieved.

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3. Results and discussion

3.1. *Solution studies*

The absorption spectra of H_2L showed a maximum centered at 305 nm and no absorption band at wavelengths higher than 380 nm (figure 2). As it can be seen in figure 2, the titration with increasing amounts of Ni^{2+} into the ligand solution produced spectra with well-defined isosbestic points at 310 and 330 nm, and a shift of the absorption band of the ligand to longer wavelengths, from 305 to 320–570 nm region, including a sharp and clear peak about 420 nm. Simply, the existence of these new bands must be associated with the formation of donor–acceptor molecular complexes between the ligand and nickel(II) in solution. Therefore, the subsequent data collection wavelength was set at $\lambda_{max} = 420$ nm.

The absorbance of H_2L in DMF solution was monitored as a function of $[Ni^{2+}]/[H_2L]$ molar ratio. The resulting absorbance/molar ratio plot is shown in figure 3. Addition of Ni^{2+} to the H_2L solution causes a rather sharp and linear increase in the absorbance of the solution until a molar ratio of 1/2 (metal-to-ligand) is reached. After this metal-to-ligand molar ratio, further addition of the Ni^{2+} concentrations resulted in a minor change in the absorbance of the system about the molar ratio of 1. Such inflection points are indicative of the formation of 1 : 2 and 1 : 1 (metal : ligand) complexes in solution. Experimentally, the color of the solution went from initially yellow purple into red during the titration. These changes could be attributed to complexation between H_2L and Ni^{2+}.

In addition, to further investigate the stoichiometry of the complex species formed during the spectrophotometric titrations, the molar conductance of a DMF solution

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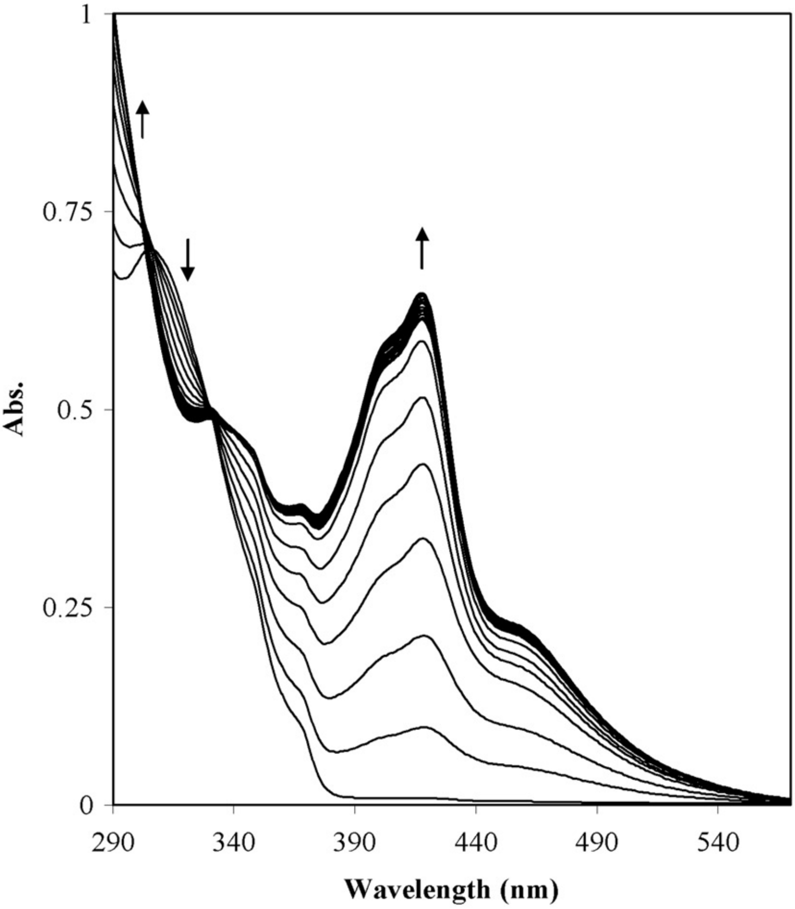

Figure 2. Electronic spectra of the titration of H_2L (6.8×10^{-6} M) with increasing amounts of Ni^{2+} ion (1.0×10^{-3} M) in DMF, at a fixed ionic strength ($I = 0.04$ M, TEAP) and 25.0°C.

of Ni^{2+} was monitored at 25.0°C while adding increasing amounts of the ligand. The resulting molar ratio plot for $[H_2L]/[Ni^{2+}]$ system (figure 4) was in good agreement with that of the photometric study both from the position of inflection points and the values for stability constants evaluated from conductance molar ratio plots, which are not given here. Two distinct inflection points show both 1 : 1 and 2 : 1 ($[H_2L] : [Ni^{2+}]$) molar ratio for the resulted complexes between nickel(II) and H_2L molecules in solution. In contrast to the spectrophotometric experiment due to high concentration of the metal ions, at the beginning of the titration, the 1 : 1 complex formed first followed by forming a 1 : 2 complex. This behavior tells us that the formation constants for the resulted complexes are approximately the same order of magnitude.

3.2. *Theoretical studies on the spectrophotometric data*

It is reported that *vic*-dioximes have *syn*, *amphi*, and *anti* isomers, depending on the position of –OH groups in molecule, which the anti-isomer constitutes complex with

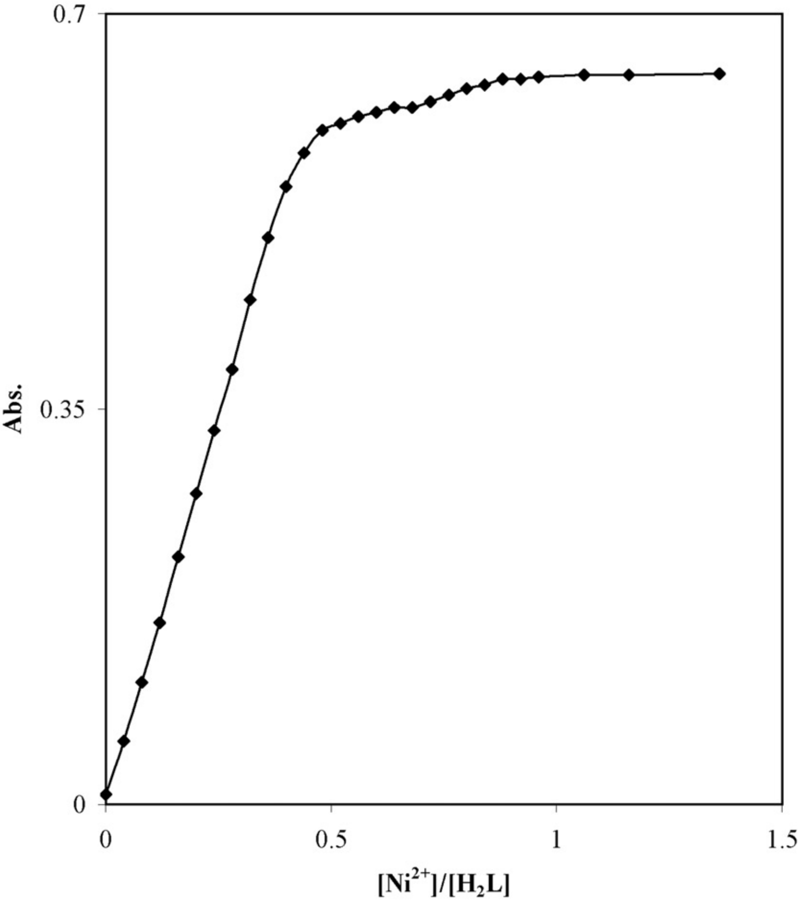

Figure 3. Absorbance/molar ratio plot of titration of H_2L (6.8×10^{-6} M) with Ni^{2+} (1.0×10^{-3} M) in DMF, at $\lambda_{max} = 420$ nm and $I = 0.04$ M TEAP.

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metal ions [18–20]. The transition metal complexes of anti-dioximes are essentially square-planar structures with the four nitrogen atoms of two *vic*-dioxime molecules coordinating to the metal ion [21].

3.2.1. Hyperchem program. To obtain more information about the optimized structures of H_2L and its 1 : 1 and 2 : 1 complexes with nickel(II), the molecular structures of the uncomplexed ligand and its complexes with nickel(II) were built with the Hyperchem program (Release 7 for Windows), a molecular visualization and simulation program package [22]. The structure of free ligand was optimized using the 6.31-G* basis set at the restricted Hartree–Fock (RHF) level of theory. The optimized structure of the ligand was then used to find the initial structures of its complexes with nickel ion. Finally, the structures of the resulting 1 : 1 and 1 : 2 complexes were optimized using the Lan12mb basis set at the RHF level of theory. The optimized structures of the resulting complexes are shown in figure 5. As shown in figure 5, in the

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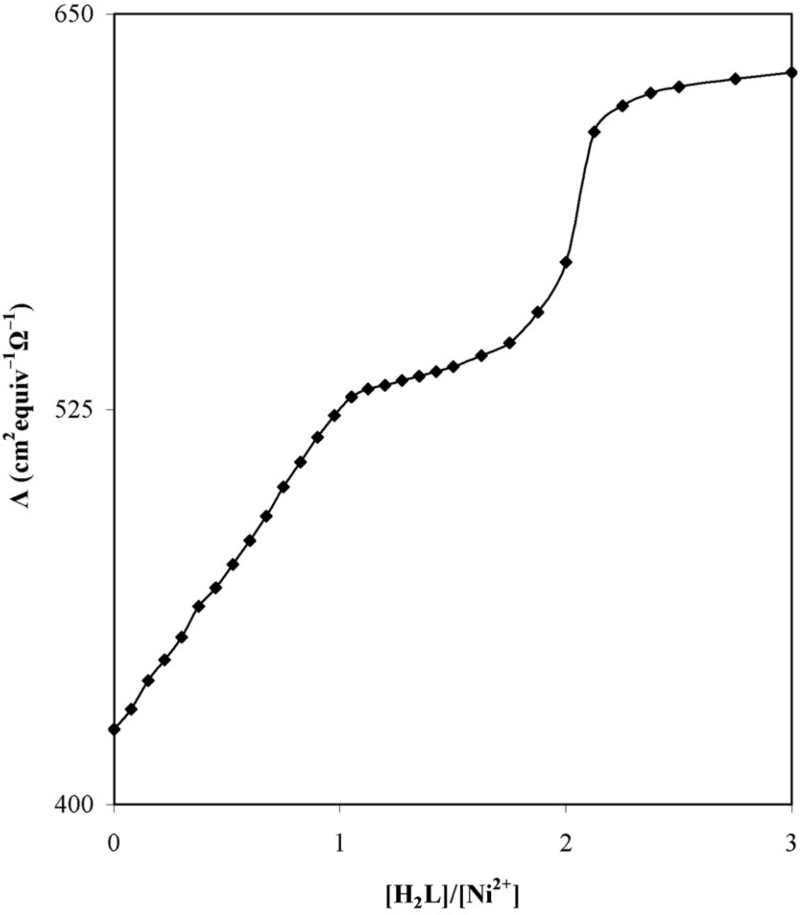

Figure 4. Conductometric curve plot for the titration of a 50 mL DMF solution of Ni^{2+} (1.0×10^{-6} M) with increasing amounts of H_2L (1.0×10^{-3} M), at 25.0°C.

case of the 1 : 1 complex, the presence of nickel ion resulted in the formation of a tetrahedral molecule [23], in which the cation is involved in bond formation with the two donating nitrogen atoms of the oximic portion of the ligand as well as the oxygen atoms of the nitrate counter ions. In addition, in the 1 : 2 complex, the nickel ion is involved in bond formation with the donating nitrogen atoms of the oximic portion of the two ligand molecules. The ligands prepare a clear square planar configuration around the nickel(II) ion through oximic nitrogens in an overall octahedral geometry including nitrate counter ions. In the literature, there are similar studies with regard to the complexation between Ni(II) and *vic*-dioximes at the same structures [13, 24]. It should be noted, other possible structures involving oxygens and other heteroatoms in the molecule were studied, but the proposed structures resulted in the most stable structural geometry and the lowest energy values. These energy values, for the resulting 1 : 1 and 1 : 2 complexes, were calculated as 54.72 and 113.21 kcal mol^{-1}, respectively.

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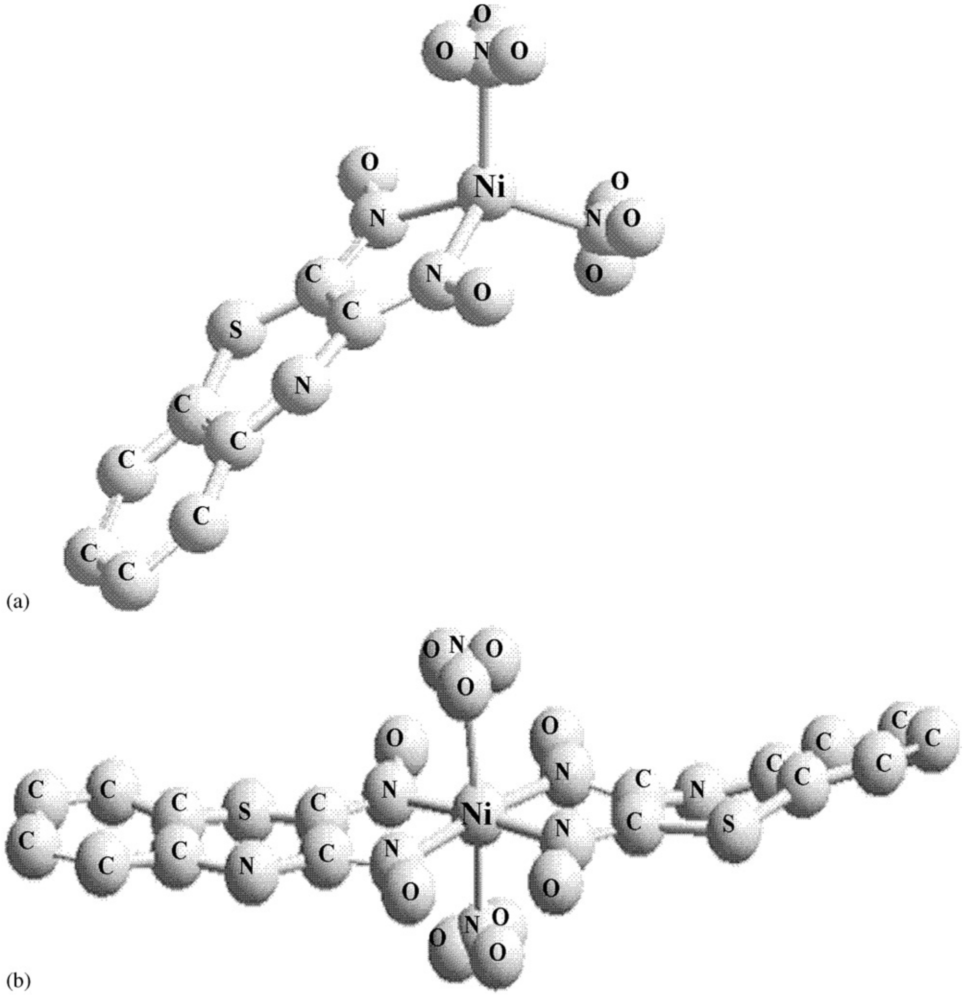

Figure 5. Hyperchem proposed structure of the resulted complexes for the interaction of H_2L molecules with Ni(II) ions; (a) and (b) show the structures of 1 : 1 and 1 : 2 metal-to-ligand complexes, respectively. To show further clearly the nitrate atoms were grouped more closely than those were predicted by Hyperchem.

3.2.2. KINFIT program. When the ligand, L (=H_2L), reacts with nickel(II), M, it may form a 1 : 1 ML, 1 : 2 ML_2 or both 1 : 1 and 1 : 2 $ML + ML_2$ complexes or any other possible forms. According to the experimental results, we only encountered one type of complexation, $ML + ML_2$ (following model) in DMF solution.

$$M + L \leftrightarrow ML, \quad K_1 = [ML]/[M][L]$$

$$ML + L \leftrightarrow ML_2, \quad K_2 = [ML_2]/[ML][L]$$

The mass balances of this possible model in solution can be solved to obtain equations for the concentration of free metal [M] or free ligand [L] (equations (1)–(3)).

$$C_M = [M] + [ML] + [ML_2] \tag{1}$$

$$C_L = [L] + [ML] + 2[ML_2] \tag{2}$$

$$\beta_2[L]^3 + K_1(1 + K_2(2C_M - C_L))[L]^2 + (1 + K_1(C_M - C_L))[L] - C_L = 0 \tag{3}$$

where C_M, C_L and β_2 ($= K_1 \cdot K_2$) denote the initial metal ion concentration, the initial ligand concentration and the overall stability constant, respectively. The following equation (equation (4)) can interpret the expected absorbance for this case:

$$A_{exp} = \varepsilon_{ML}[ML] + \varepsilon_{ML2}[ML_2] + \varepsilon_L[L] + \varepsilon_M[M] \tag{4}$$

where ε values are the molar absorptivities of the species indicated and A_{exp} denotes the expected absorbance. However, because of the lack of absorbance for metal ions (at the working wavelength) the term showing that is negligible and does not contribute in evaluating signal, therefore the equation could be simplified to equation (5).

$$A_{exp} = \varepsilon_{ML}[ML] + \varepsilon_{ML2}[ML_2] + \varepsilon_L[L] \tag{5}$$

To evaluate the stepwise stability constants from the calculated values of absorbance intensity *versus* $[Ni^{2+}]/[L]$ molar ratio data the nonlinear least-squares curve-fitting program KINFIT [25] was used, in which the expected absorbance intensity of solution is given by Beer–Lambert equation (equation (5)). The program is based on the iterative adjustment of calculated values of absorbance intensity to the observed values by using the Wentworth matrix technique [26] or the Pawell procedure [27]. Adjustable parameters are the stepwise stability constants of the complexes present in solution and the corresponding absorbance intensities depending on the model adopted. The free metal ion, [M], or the free ligand concentrations, [L], were calculated by using the Newton–Raphson procedure. Once the values of either [M] or [L] had been obtained by using the estimated values of the stability constants at the current iteration step of the program, the refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance intensity for all experimental points were minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares, and the standard deviations of the data.

All the resulting signal/molar ratio data were best fit to the corresponding model (with sum-of-squares of the residuals less than 0.005), which further supports the formation of the species in solution and indicating that this model was correct. This improved significantly the overall fit and the model fit very well the experimental points (see figure 6 for details). Thus, the stepwise formation constants of the complex species were evaluated by fitting the absorbance/molar ratio data to this model and the results are summarized in table 1. As expected, comparison of the values of the stability constants, K_1 for 1 : 1 and K_2 for 1 : 2 (metal : ligand) determined for the complexes, shows that the stability constants for ML and ML_2 are of the same order of magnitude.

3.2.3. DATAN program. The complexation data were studied to evaluate the stoichiometry and the stability constants of the complexes in solution by using DATa ANalysis (DATAN) [28], the principle component analysis (PCA), method. The experimental spectra are the only "Input" required by the program. Output of DATAN is pK values, number of principal components, concentration distribution diagrams, and pure spectrum of each assumed species. Defining a three-component model

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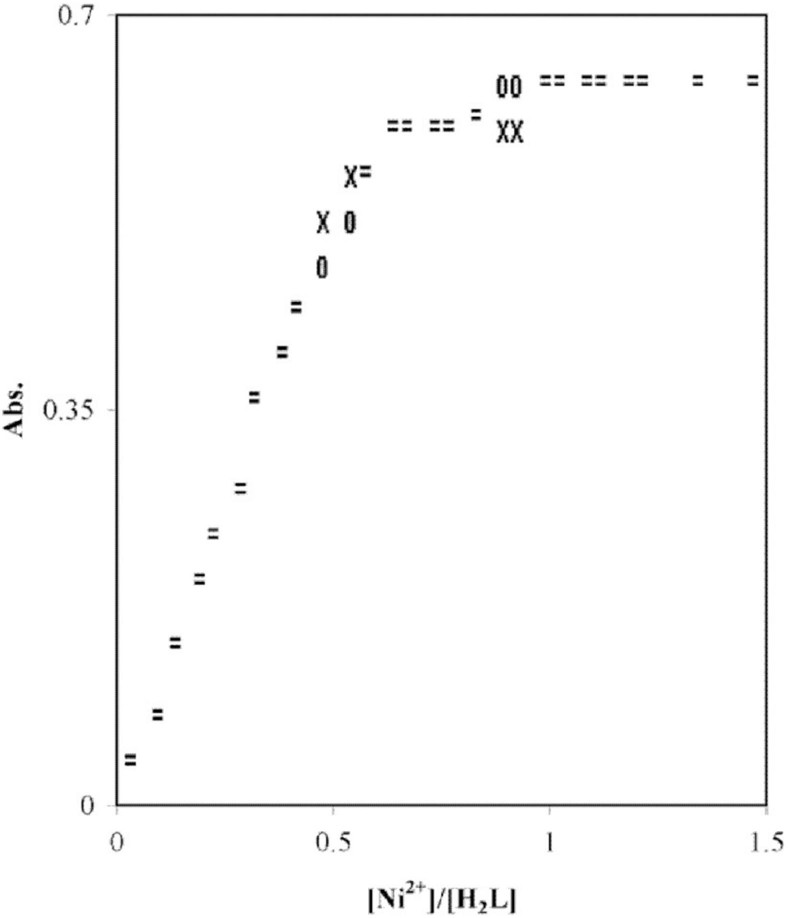

Figure 6. Computer curve-fitting program (KINFIT) output for the corresponding curve plot in figure 3. The absorption intensity/molar ratio data obtained from the titration of H_2L with Ni^{2+} in DMF solution: (×) calculated points; (○) experimental points; (=) experimental and calculated points are the same within the resolution of the plot.

Table 1. Formation constants from DATAN and the non-linear least-squares computer curve-fitting program KINFIT for the spectrophotometric data.

	Formation constants	
Complex	DATAN[a]	KINFIT
ML	5.81×10^{12}	2.28×10^{6} (±0.005)[b]
ML_2		2.45×10^{6} (±0.004)

[a] The calculated value for the overall formation constant, β_2.

[b] Values in the parentheses show the relative errors (%error).

(including L, ML, and ML_2), for the data described in the experimental section, resulted in good agreement between the experimental and theoretical points (figure 7). In addition, as shown in the inset of figure 7, the predicted pure spectral pattern for both the ligand and the complexes are the same as those experimentally obtained (figure 2).

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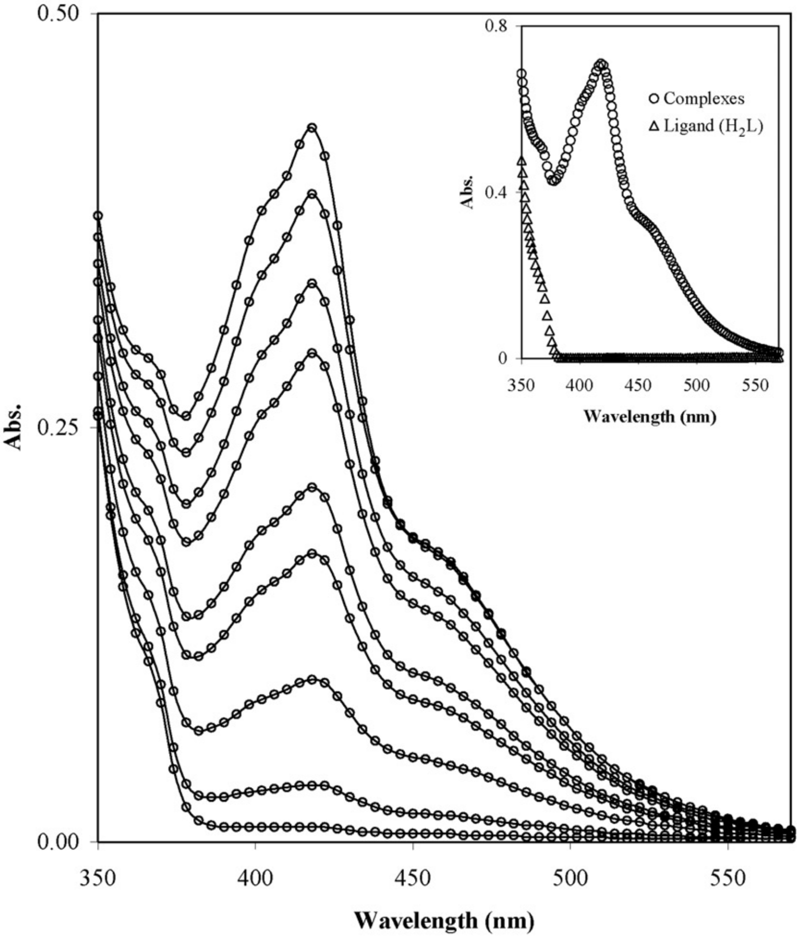

Figure 7. DATAN-fitting of the predicted spectra (solid curves) to the experimental spectrophotometric titration spectra of H_2L with increasing amounts of Ni(II) ion (circles) for the proposed L, ML, and ML_2 three-components model. The inset shows pure spectra from DATAN plot of spectrophotometric data for the three-component model from absorbance measurements of H_2L solution in the absence (Δ) and in the presence of Ni(II) ions (○).

Other models using more or less component numbers resulted in highly perturbed and very noisy results, which were not reasonable. Furthermore, from the complexation constant evaluation tool-box of the software, the overall formation constant value (β_2) for the formed complexes were calculated and saved in table 1. This table shows that the stability constant values obtained by DATAN were comparable with the ones obtained by KINFIT, the differences within the experimental errors. Figure 8 shows expected variations of the existing components in solution, where the initial concentration of the ligand is approximately the same as the concentration of H_2L (6.8×10^{-6} M) that was experimentally used. Moreover, as the titration went on the concentration of the complexed species increased until the $[Ni^{2+}]/[H_2L]$ molar ratio of 1/2 was reached, beyond which the whole H_2L concentration was converted to products in the end.

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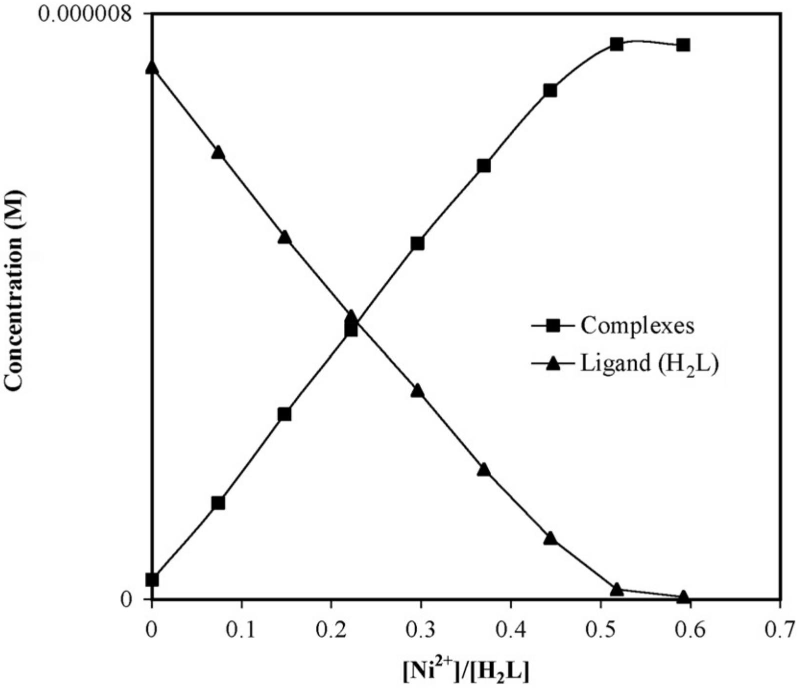

Figure 8. DATAN mole ratio plot for the corresponding model shown in figure 7.

4. Conclusion

The results reported in this work clearly demonstrate the ability of a *vic*-dioxime ligand to coordinate Ni(II). Since the ligand bears a suitable light sensitive moiety, this new *vic*-dioxime may undergo intermolecular changes at the electronic level and could be used as chemosensor for Ni^{2+} by exploiting the light absorption of the sensitive moiety upon interaction with metal centers.

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