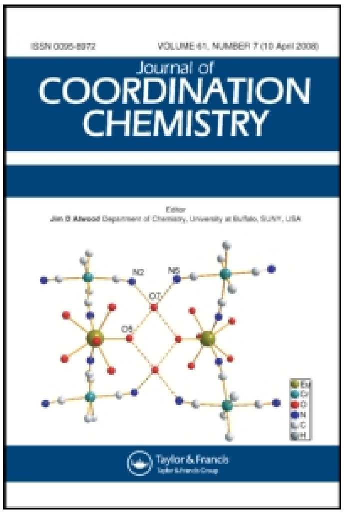

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Theoretical study of the spectral behavior of the complex of a recently synthesized aminoxanthone derivative with copper(II) ion in water and methanol

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Theoretical study of the spectral behavior of the complex of a recently synthesized aminoxanthone derivative with copper(II) ion in water and methanol

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The complexation of a recently synthesized aminoxanthone derivative, 1-({2-[(2-aminoethyl) amino]ethyl}amino)-6-methyl-9*H*-xanthen-9-one with Cu(II) in methanol and water solutions, was investigated by spectrofluorimetric and spectrophotometric methods. The possible molecular geometries, bindings, and spectroscopic properties for the formed complex were theoretically studied in detail by the Hyperchem program. The stoichiometry of the complex was determined from spectrophotometric molar ratio methods at 20°C. The spectral data were further treated by KINFIT program to calculate the formation constant of the 1 : 3 complex and its molar absorptivity. Program DATAN was used to calculate the spectral behavior of the complex in each solution for different mole ratios. A simple equation for the determination of complex stability constant was also evaluated from titration data. Under the optimal conditions, the ligand can be used as a fluorometric indicator for measuring Cu^{2+} ions in aqueous solution.

Keywords: Aminoxanthone; Complexation; Copper(II); Spectrofluorimetry

1. Introduction

Xanthone is a yellow pigment in plants such as *Gentianaceae* and a planar aromatic ketone of C_{2v} symmetry that has been shown to have very closely spaced $n\pi^*$ and $\pi\pi^*$ triplet states [1, 2]. Xanthones are secondary metabolites commonly occurring in a few higher plant families, and in fungi and lichens. Their taxonomic importance in such families and their pharmacological properties have aroused interest [3]. Various bioactivities of xanthones including cytotoxic, antitumor, anti-inflammatory, antifungal, enhancement of choline acetyl-transferase activities and inhibition of lipid peroxidase, have been described [4]. Due to their role in photochemical and photobiological reactions, the triplet states of aromatic ketones continue to receive attention from both experimental and theoretical points of view [5–13].

Computational chemistry is a multidisciplinary area of science helpful to rationalize experimental observations, provide information not amenable to direct observation,

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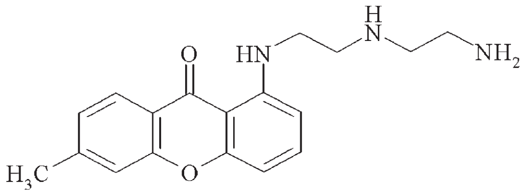

Figure 1. The chemical structure of aminoxanthone L.

and even make predictions concerning the outcome of possible investigations, and is widely accepted by experimental scientists as a valuable complement to interpretations of data. In particular, molecular modelling has been warmly embraced by the chemical community [14].

Complexation of xanthones with heavy metals has rarely been reported in the literature. Thus, the purpose of this work is to investigate the complexation and the stability constants of a recently synthesized aminoxanthone derivative with some transition and heavy metal ions in methanol and water solutions spectrofluorometrically using suitable theoretical computer aided programs. Among different metal ions tested, a highly selective complexation of the ligand L with Cu^{2+} ions was observed. The structure of L is shown in figure 1.

2. Experimental

2.1. *Materials*

L was synthesized and purified as described elsewhere [15]. Analytical grade nitrate salts of metal ions and tetraethylammonium perchlorate (TEAP) (all from Merck), used in the solution studies, were of the highest purity available and used without purification except for vacuum-drying. Reagent grade methanol (Merck) was used as received. Doubly-distilled and deionized water was used throughout. Ionic strength was established at 0.04 M TEAP where necessary.

2.2. *Apparatus*

All fluorescence spectra were recorded on a Perkin–Elmer luminescence spectrometer LS-30, equipped with a xenon lamp, a 7 µL fused silica flow cell and a peristaltic pump. Excitation and emission bandwidths were both set at 10 nm. In all measurements, the temperature was kept at $20.0 \pm 0.1°C$ using a Huber polystat K6-3 (operating with a cooling machine; Germany) thermostat assembly including a water bath circulating system, and a glass double layer vessel connected to the bath. This vessel was put on a magnetic stirrer (~300 rpm). Spectrophotometric measurements were carried out on a CECIL 9000 (UK) spectrophotometer equipped with an electrical thermostat device. All theoretical calculations were performed on a Pentium IV 1994 (256 MB, 80 GB) computer.

2.3. *Spectral data collection*

To study the formation of Cu(II)–L in solution 10 mL of the ligand solution (1.34×10^{-5} M) in the given solvent was placed in the titration vessel and thermostated at the desired temperature. The excitation and fluorescence emission spectra of L were obtained in methanol and aqueous solutions in the absence and presence of increasing amounts of copper(II) ion. After each addition of a known amount of the copper(II) solution, the fluorescence measurements were carried out. In addition, in a typical experiment, 3.5 mL of the ligand solution (9.54×10^{-5} M) in the given solvent was placed in a 1 cm optical path quartz cell. Then known amounts of copper(II) solution were added in a stepwise manner 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. The ionic strength of the solution was stabilized with 0.04 M of TEAP.

3. Results and discussion

3.1. *Solution studies*

In a preliminary experiment, complexation of L in methanol and water in the presence of transition and heavy metal ions Pb^{2+}, Cd^{2+}, Fe^{2+}, Ag^{+}, Hg^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Tl^{+} and Cu^{2+} was studied spectrofluorometrically. In contrast to Cu^{2+}, no detectable changes of the fluorescence intensities of L solutions were observed during the titration with these ions. The titration of L solution with Cu^{2+} ion showed clear decreases of the fluorescence intensity of the solution. Figure 2 (a and b) shows the excitation and emission spectra for the complexation of L (1.34×10^{-5} M) in the presence of (0.0 to 1.03, 2.05, 3.08, 4.10, 5.13, 6.15, 7.18, 8.21, 9.23, 10.3, 11.3) $\times 10^{-6}$ M concentrations of Cu^{2+} ion in methanol and water solutions. The excitation and emission spectra showed two maxima centered at 410 and 500 nm in methanol solution and 405 and 520 nm in water, respectively. There was no change in the position of these spectra in the presence of Cu^{2+} ion, except for a decreased intensity as a function of increasing concentration of Cu^{2+}. Figure 2 also shows no significant difference between the position of the maxima of excitation spectra in both solvents (about 5 nm, only) while the wavelengths corresponding to the maxima of the emission spectra are not the same (about 20 nm longer for the case in which water was used as solvent). This may be due to lower lipophilic capability of water and hence, less stability of the aromatic system responsible for emission of light.

The fluorescence intensity of L in methanol and water solutions was monitored as a function of Cu^{2+} to ligand molar ratio at 20°C. The resulting fluorescence/molar ratio plots are shown in figure 3. Addition of Cu^{2+} to the ligand solution causes a rather sharp and linear decrease in the fluorescence intensity of solution until a molar ratio of 1/3 is reached. Further addition of the Cu^{2+} ions has no measurable effect on the fluorescence intensity. The resulting plots reveal the formation of a stable 1 : 3 (metal : ligand) complex in solution. High influence of Cu^{2+} ions on the fluorescence intensity of the ligand says that the xanthone moiety is involved directly in complex formation. Oxygen of the carbonyl group of the xanthone and the first NH are involved in complex formation between L and copper(II).

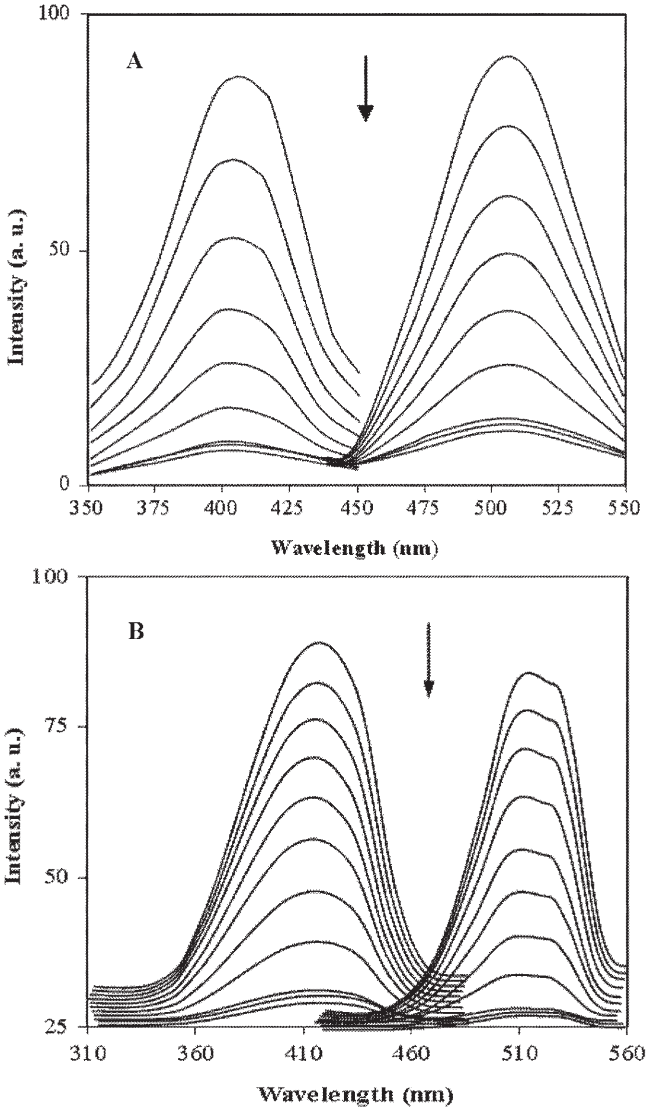

Figure 2. Excitation and emission spectra for complexation of L (1.34×10^{-5} M) in the presence of increasing amounts of Cu^{2+} in MeOH (a) and in water (b).

In order to obtain further information about the complexation of L with Cu^{2+}, the electronic absorption spectra of L were obtained in the presence of various concentrations of Cu^{2+} in both water and methanol. The results are shown in figure 4. Figure 4(a) shows the change in spectral characteristics of L, (9.54×10^{-5} M) in the presence of increasing amounts, (0.00, 4.40, 8.79, 13.20, 17.60, 20.00, 26.40, 30.80, 35.20, 39.60, 40.01, 48.40, 52.80, 60.10, 74.80, 104.01, 148.01, 221.00) $\times 10^{-6}$ M, of Cu^{2+} in methanol. Figure 4(b) shows the spectral titration of L (9.54×10^{-5} M) with (0.00, 2.86, 5.71, 8.57, 11.40, 14.30, 17.10, 20.00, 22.90, 25.70, 28.60, 31.40, 34.30, 37.10, 41.40, 51.40, 68.60, 94.30, 114.00, 143.00) $\times 10^{-6}$ M concentrations of Cu^{2+} in water.

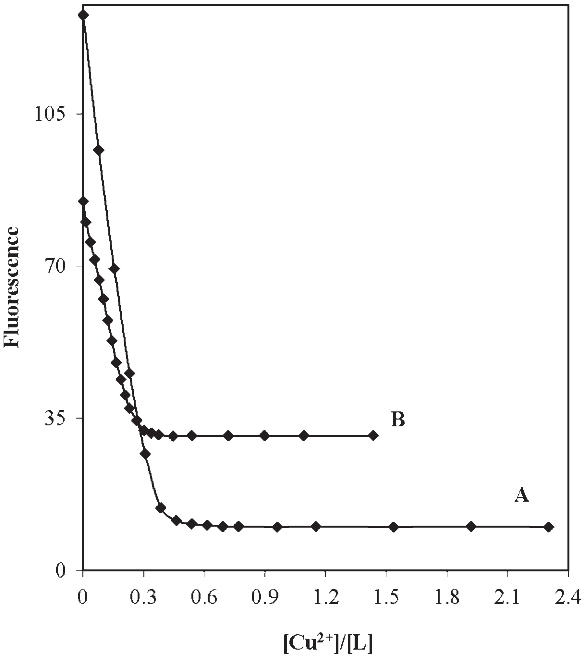

Figure 3. Fluorescence/molar ratio plots for complexation of L (9.54×10^{-5} M) with Cu^{2+}; A, in MeOH and B, in water ($\lambda_{ex} = 400$ and $\lambda_{em} = 520$ nm).

Addition of Cu^{2+} clearly decreases the absorbance of L ($\lambda_{max} = 420$ nm) and growth of a new peak at 505 nm is indicative of interaction between the ligand and the Cu^{2+}. Titration with increasing amounts of Cu^{2+} into the ligand solution produced spectra with a well-defined isosbestic point at 450 nm, in methanol, and 460 nm in water, and a shift of the absorption band of the ligand to longer wavelengths from 420 to 505 nm suggest complex formation between L and Cu^{2+}. In addition, in the two different solvents, it was found that with the exception of Cu^{2+} metal ions have no effect on the spectral characteristics of L.

The absorbance of L in methanol and water solution was monitored as a function of Cu^{2+} to ligand molar ratio, at 20°C. For both experiments, the data collection wavelength was set at $\lambda_{max} = 505$ nm, which is the λ_{max} of the formed complex. The resulting absorbance/molar ratio plots are shown in figure 5. Addition of Cu^{2+} to L solution causes a rather sharp and linear increase in the absorbance until a molar ratio of 1/3 is reached. After this metal-to-ligand molar ratio, further addition of the Cu^{2+} concentrations resulted in no change in the absorbance of the system. Such a sharp and clear inflection point at 1 to 3 (metal to ligand) molar ratio and only one isosbestic point are indicative of the formation of a stable 1 : 3 (metal : ligand) complex in solution. Experimentally, we have seen that, during the titration, the color of the solution goes from initially yellow, purple into red. Because of the presence of a xanthone part in the ligand and its strong interaction with light (shifting in wavelength and change in colour), any change in light properties of the ligand must be due to complexation of this part of the molecule. Thus, the suitable excitation and emission wavelengths, in the fluorometric measurements, are those that interact with light in the xanthone.

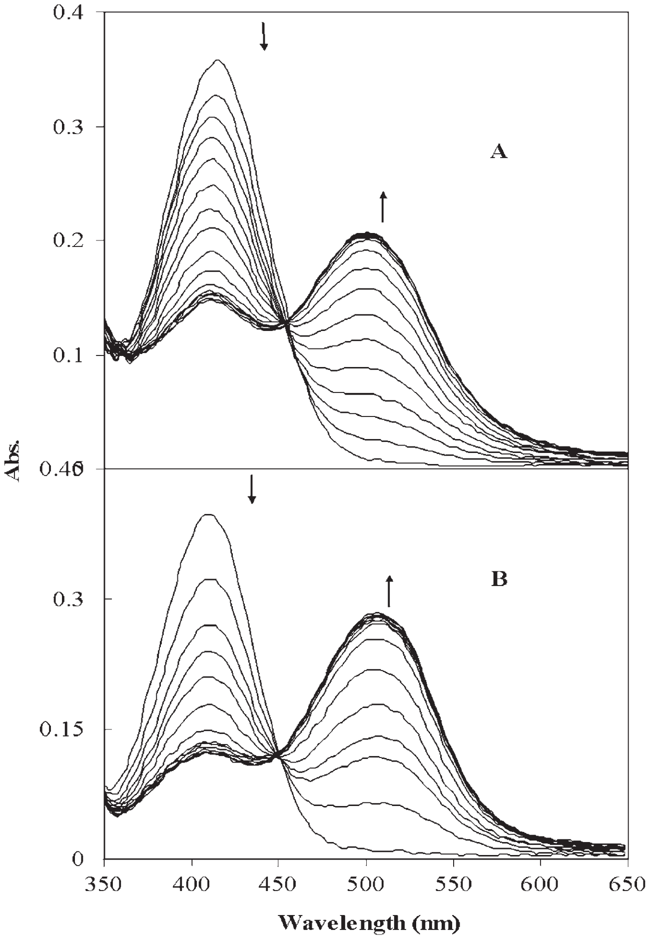

Figure 4. Electronic spectra for complexation of L (9.54×10^{-5} M) with increasing amounts of Cu^{2+}; A, in MeOH and B, in water.

3.2. *Theoretical studies*

3.2.1. Hyperchem program. To examine the stability and propose an optimized structure for the 1 : 3 complex with copper(II), the molecular structures of the uncomplexed ligand and its complex with the copper(II) ion were built with the Hyperchem program (Release 7 for Windows), a molecular visualization and simulation program package [16]. The structure of free ligand was optimized using the 6.31-G* basic 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 complex with copper(II). Finally, the structure of the resulting 1 : 3 complex was optimized using the Lan12mb basis set at the RHF level of theory. The optimized structure of the complex, shown in figure 6, resulted in a molecule with stable five-membered ring chelate, in which the cation is involved in bond formation with the donating oxygen of the xanthone as well as the nitrogen atom of the aniline. Other possible structures involving oxygens and

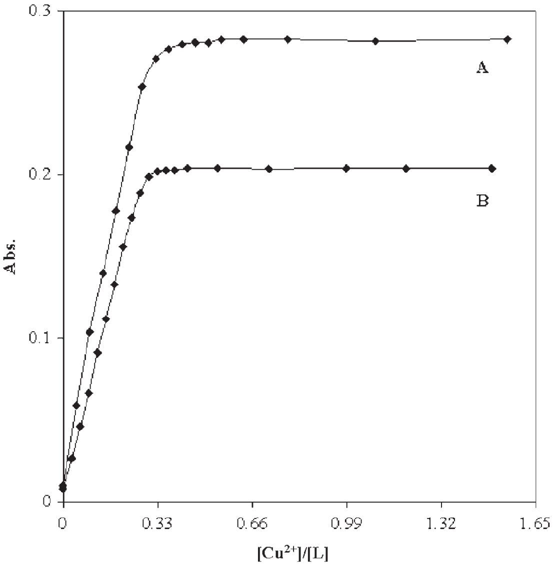

Figure 5. Absorbance/molar ratio data plots for complexation of L (9.54×10^{-5} M) with Cu^{2+}; A, in MeOH ($\lambda_{max} = 502$ nm) and B, in water (3.82×10^{-5} M, $\lambda_{max} = 505$ nm).

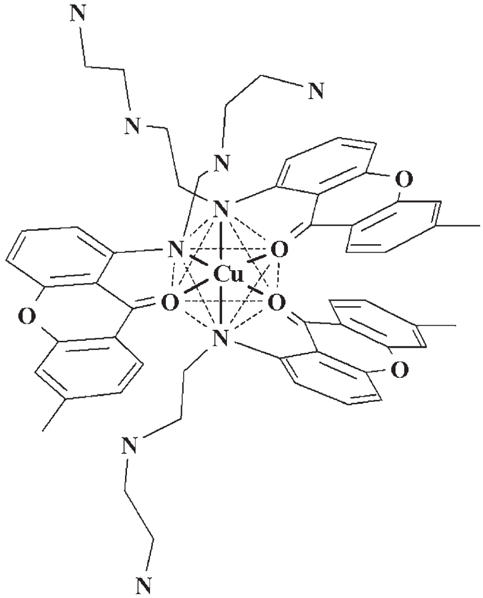

Figure 6. Hyperchem proposed structure of the ML_3 complex for complexation of Cu^{2+} with L.

other nitrogens in the molecule were studied, but among the various isomers the proposed structure resulted in the most stable geometry and the lowest energy value. This calculated energy value, for the resulting 1 : 3 complex, was 37.34 kcal mol^{-1} lower than the calculated energy value for L.

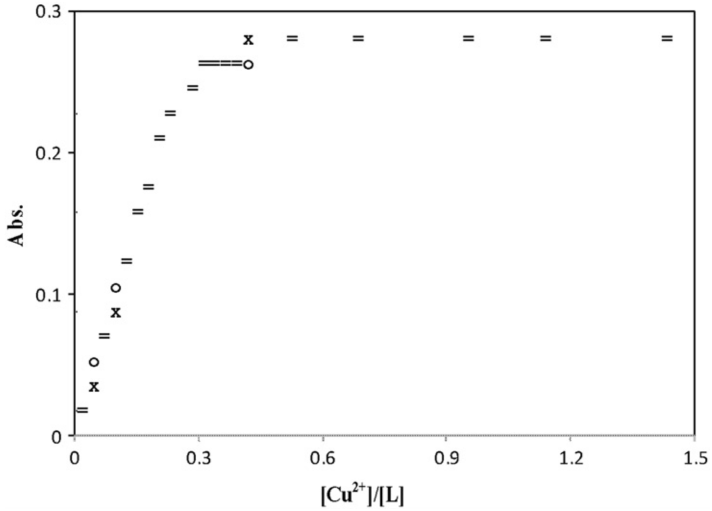

Figure 7. Computer curve-fitting program (KINFIT) output for the corresponding curve plot in figure 3. The absorption intensity/molar ratio data obtained from the titration of L with Cu^{2+} in MeOH solution (as an example): (x) calculated points; (○) experimental points; (=) experimental and calculated points are the same within the resolution of the plot.

3.2.2. KINFIT program. Computer fits of the fluorescence or absorbance-molar ratio data for complexation in two different solvents, using a non-linear least-squares fitting program KINFIT [17] (see Figure 7 as a sample), further support the formation of 1 : 3 metal : ligand complex in solution. For example, when the ligand, L, reacts with copper(II) (M) it may form 1 : 1 ML, 1 : 2 ML_2 or 1 : 3 ML_3 complexes or other possible forms. According to the experimental results, we only encounter one type of complexation, ML_3 (following model) in the solution.

$$M + 3L \leftrightarrow ML_3, \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

The mass balances of this model in solution [18] can be solved to obtain equations for the concentration of free metal [M] or free ligand [L] (equations 1–3).

$$C_M = [M] + [ML_3] \tag{1}$$

$$C_L = [L] + 3[ML_3] \tag{2}$$

$$\beta_3[L]^4 + \beta_3(3C_M - C_L)[L]^3 + [L] - C_L = 0 \tag{3}$$

where C_M, C_L and $\beta_3(=K_1 \cdot K_2 \cdot K_3)$ denote the initial metal ion concentration, the initial ligand concentration and the overall stability constant, respectively. The following equation (equation (4)) provides the expected absorbance for this case:

$$A_{exp} = \varepsilon_{ML_3}[ML_3] + \varepsilon_L[L] + \varepsilon_M[M] \tag{4}$$

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

Table 1. Evaluated formation constant from computer curve-fitting program KINFIT.

	log β_3	
Solvent	Fluorimetry	Photometry
Methanol	15.38 ± 0.23	15.26 ± 0.13
Water	15.11 ± 0.12	15.02 ± 0.10

(at the working wavelength) that term is negligible and the equation could be simplified to equation (5).

$$A_{\text{exp}} = \varepsilon_{\text{ML}_3}[\text{ML}_3] + \varepsilon_{\text{L}}[\text{L}] \tag{5}$$

To evaluate the stepwise stability constants from the calculated values of absorbance intensity *versus* $[\text{Cu}^{2+}]/[\text{L}]$ molar ratio data the nonlinear least-squares curve-fitting program KINFIT was used, in which the expected absorbance intensity of solution is given by the 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 [19] or the Pawell procedure [20]. 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] (in this work) had been obtained by using the estimated value of the stability constant 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 deviation of the data.

All the resulting signal/molar ratio data were best fit to the corresponding model (with sum-of-squares of the residual values less than 0.0002), further supporting the formation of above-mentioned complexed species in solution and indicating that this model was correct. This improved significantly the overall fit, and the model fit very well with the experimental points (see figure 7 for details). Thus, the overall formation constant of the complexes was 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 constant, β_3 for 1 : 3 (metal : ligand) determined for the complexes, showed that the stability constants for ML_3 are of the same order of magnitude for different solvents. Table 1 also shows that the complexation strength in both methanol and water are approximately the same. Nevertheless, the resulting L–Cu^{2+} complex in H_2O is somewhat weaker than that in MeOH solution, due to the increased solvating ability and dielectric constant of water relative to methanol [14, 21, 22].

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) [23], the principle component analysis (PCA), method. The experimental spectra are the only "Input" required by the program. Output of DATAN

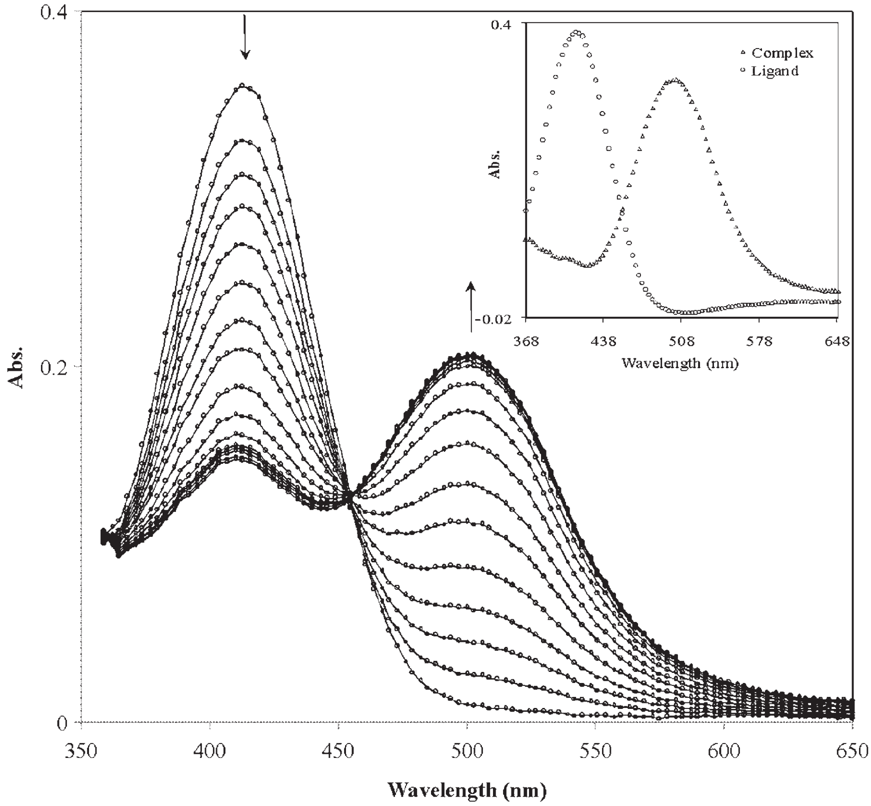

Figure 8. DATAN-fitting of the predicted spectra (solid curves) to the experimental spectrophotometric titration spectra of L with increasing amounts of Cu(II) (circles) for the proposed L and ML_3 two-component model. The inset shows pure spectra from DATAN plot of spectrophotometric data for the two-component model from absorbance measurements of L solution in the absence (○) and in the presence of Cu(II) ions (△).

program is pK values, number of principal components, concentration distribution diagrams, and pure spectrum of each species. Defining a two-component model (including L and ML_3) for the data described in the experimental section, resulted in good agreement between the experimental and theoretical points (figure 8). In addition, as shown in the inset of figure 8, the predicted pure spectral pattern for both the ligand and the complex are the same as those experimentally obtained (figure 4). Other models using more or less component numbers resulted in highly perturbed and very noisy results, which were not reasonable. From the complexation constant evaluation tool-box of the software, the overall formation constant value (β_3), in each solvent, for the formed complex was calculated (table 1) showing that stability constant values obtained by DATAN were comparable with those obtained by KINFIT; the differences are within the experimental errors. These results confirm the β_3 values from other methods.

3.2.4. Formation constant evaluation from titration data. As a fluorometric indicator in direct titration using 10 mL of 3.05×10^{-5} m of L, the titration with increasing

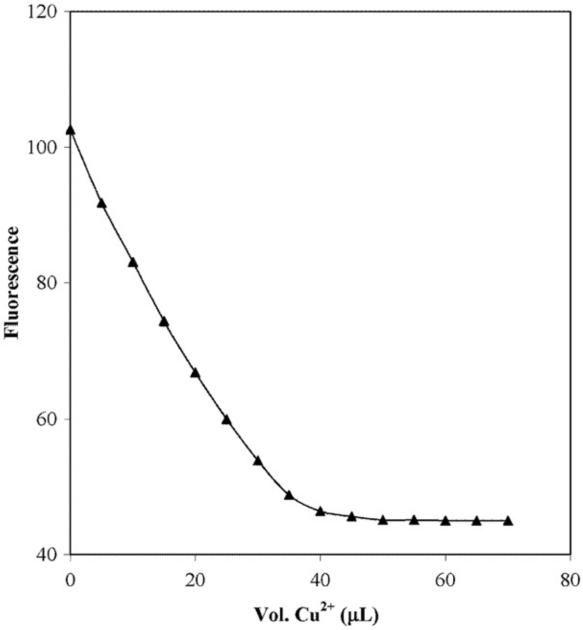

Figure 9. Fluorimetric titration of 10 mL of L (3.05×10^{-5} M) with Cu^{2+} (2.54×10^{-3} M) in water at pH (8).

amounts of Cu^{2+} (2.54×10^{-3} M) until reaching the end point was studied. The result is shown in figure 9.

$$Cu^{2+} + 3L \leftrightarrow CuL_3^{2+} \tag{6}$$

the mass-balance equations for reaction (6) are:

$$C_L = [L] + 3[CuL_3]^{2+} \text{ and } C_{Cu} = [Cu^{2+}] + [CuL_3]^{2+} \tag{7}$$

$$F_t = \left(\frac{[L]}{C_L}\right) \cdot F_0 + \left(\frac{[CuL_3]^{2+}}{C_L}\right) \cdot FC \tag{8}$$

if α is defined as $[L]/C_L$:

$$F_t = \alpha \cdot F_0 + (1-\alpha) \cdot \frac{FC}{3} \tag{9}$$

$$\alpha = \left(\frac{3F_t - F_C}{3F_0 - F_C}\right) \quad \text{and} \quad \beta_3 = \frac{1-\alpha}{((\alpha-1)C_L + 3C_{Cu})\alpha^3 C_L^3} \tag{10}$$

if $3C_{Cu} = C_L$ then $\alpha = \alpha_{1/3}$:

$$\frac{(\alpha_{1/3})^4}{(1-\alpha_{1/3})} = \frac{1}{\beta_3} \times \frac{1}{C_L^3} \tag{11}$$

rearrangement of the above equation gives:

$$p\beta_3 = \log\frac{(\alpha_{1/3})^4}{(1-\alpha_{1/3})} + 3\log C_L \tag{12}$$

Table 2. Evaluated formation constant from DATAN calculations.

	$\log \beta_3$	
Solvent	Fluorimetry	Photometry
Methanol	14.88	14.56
Water	14.76	14.53

where β_3, [L], C_L, C_{Cu}, F_t, F_C, F_0 and $\alpha_{1/3}$ denote the overall stability constant, the free concentration of L, initial concentration of the ligand, initial concentration of Cu^{2+}, observed fluorescence intensity, fluorescence intensity of the ligand when it completely converted to complex, fluorescence intensity of the ligand initially in the absence of the metal ions and the calculated value of α at the one-third point in the titration. By using equation (12), we can evaluate the $\log \beta_3$ (15.38 ± 0.11), which is very near to those obtained from the abovementioned programs.

4. Conclusions

As shown in tables 1 and 2, the $\log \beta_3$ values obtained by different methods are the same within their experimental errors. The results reported in this work clearly demonstrate the ability of a ligand containing a xanthone sub-unit to coordinate Cu(II). Since the ligand bears a suitable light-sensitive moiety, this new xanthone undergoes intermolecular changes at the electronic level and can be used as a chemosensor for Cu^{2+} by exploiting the excitation and emission effects on the light absorption upon interaction with metal centers. Because of the high selectivity of L toward copper(II) in solution, and lack of any interference, aminoxanthone L could be used as a highly sensitive and selective fluorescent and absorptive indicator toward Cu^{2+} in the water and MeOH solutions.

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