AN ABSTRACT OF THE THESIS OF

Qihua Hu for the Master of Science Degree

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Title: Titrimetric Studies of Cu(II)-dimethylglyoxime Complexes in Solution

Abstract approved: W.G. Davies

This thesis describes investigations into the nature of the complexes formed between the copper(II) ion and dimethylglyoxime in solution. Titrimetric methods were employed. The pH and/or the absorbance of the solutions being titrated were monitored.

When a copper(II) solution is titrated with sodium dimethylglyoximate (Na_2dmg), a grey-green precipitate is formed and a sharp increase in pH occurs at a point corresponding to a Cu : dmg stoichiometry of 1 : 1.

In the photometric studies, a buffered solution of Na_2dmg was titrated with Cu(II), while monitoring the absorbance at 430 nm. A plot of absorbance against volume of titrant shows two points of discontinuity, one corresponding to a Cu : dmg ratio of 1 : 2 and a second at a Cu : dmg ratio of 2 : 1. This result is direct evidence for the existence not only of the well-known 1:2 complex but also of a previously unreported 2:1 complex. A further investigation of the variation of absorbance with pH suggests that this 2:1 complex contains four copper atoms.

Although the precipitate has a 1:1 stoichiometry, and although other workers have postulated the existence of a complex of this composition in solution, no evidence for this complex in solution was found in these investigations.

The resolution of this contradiction is a compelling motive for further investigations on this system.

Titrimetric Studies of Cu(II)-dimethylglyoxime Complexes in Solution

A Thesis
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by

Qihua Hu

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D. Wayne Beckham

Approved for the Major Division

Faye Vowell

Approved for the Graduate Council

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INTRODUCTION

1.1 SYMBOLISM

In this thesis the species dimethylglyoxime (i.e., 2-3 butanedione dioxime) will be indicated by using the shorthand form H_2dmg. The hydrogen dimethylglyoximate ion will be indicated by $Hdmg^-$ and the dimethylglyoximate ion as by dmg^{2-}. When considering the glyoximate species in general, the form dmg will sometimes be used. Thus, for example, the copper: dimethylglyoxime ratio will be referred to as the Cu : dmg ratio.

1.2 HISTORICAL BACKGROUND

The work described in this thesis is an extension of earlier work on the oxidation of Cu(II)-dimethylglyoxime by the persulfate ion. Under certain circumstances, a bright transient purple-pink color is produced. This color is probably due to the species $Cu(III)(Hdmg)_2$, isoelectronic with the well known species $Ni(II)(Hdmg)_2$, shown in Figure 1.

Previous work on the kinetics of the oxidation was undertaken by Yang Cao[1] with mixed success. However, work on the oxidation reaction was hampered by not knowing exactly what was present in the solution before the oxidant was added. Accordingly, it was decided to suspend the investigation of

oxidation, and to concentrate on the nature of solutions containing Cu(II) ions and dimethylglyoxime at various ratios and at various pH values.

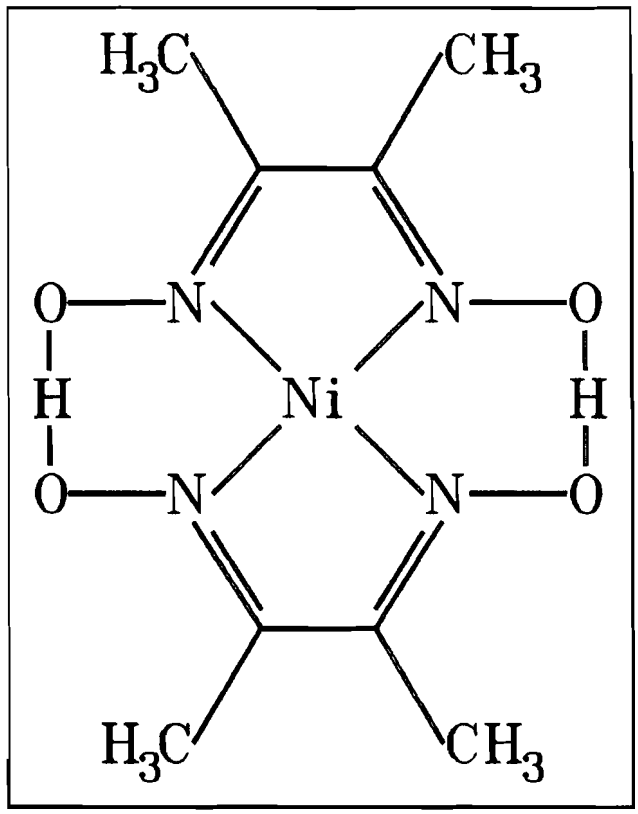

Figure 1: Structure of $Ni(Hdmg)_2$

Only a few reports of studies of aqueous solutions of Cu(II)-dimethylglyoxime complexes can be found in the literature. In 1961 Dyrssen and Hennichs[2], using solvent extraction techniques, established the existence of $Cu(II)(Hdmg)_2$ in solution, and measured the equilibrium constant for:

$$Cu^{2+} + 2\ Hdmg^{-} \rightleftharpoons Cu(Hdmg)_2$$

They found that $\log \beta_2 = 19.24$. In addition they estimated a value of $pK_a = 9.4$ for the $Cu(Hdmg)_2$ complex.

It is possible to obtain crystals with the formula $Cu(Hdmg)_2$ by reacting an alcoholic solution of copper(II) acetate and dimethylglyoxime, and recrystallizing the resulting solid. Several X-ray studies have been performed on these blood-red crystals. Figures 2 and 3 show ball-and-stick and space-filling representations of the latest of these

studies by Vaciago and Zambonelli[3] at liquid nitrogen temperatures. As can be seen from the ball-and-stick diagram, the two dimethylglyoxime ligands attached to each copper atom do not lie in the same plane as they do in the nickel(II) complex. Instead, each copper is five co-ordinated in a square-pyramidal configuration, and forms part of a centrosymmetric complex containing two $Cu(Hdmg)_2$ entities. Each copper is surrounded by four N atoms at the base of the pyramid and an oxygen atom at a

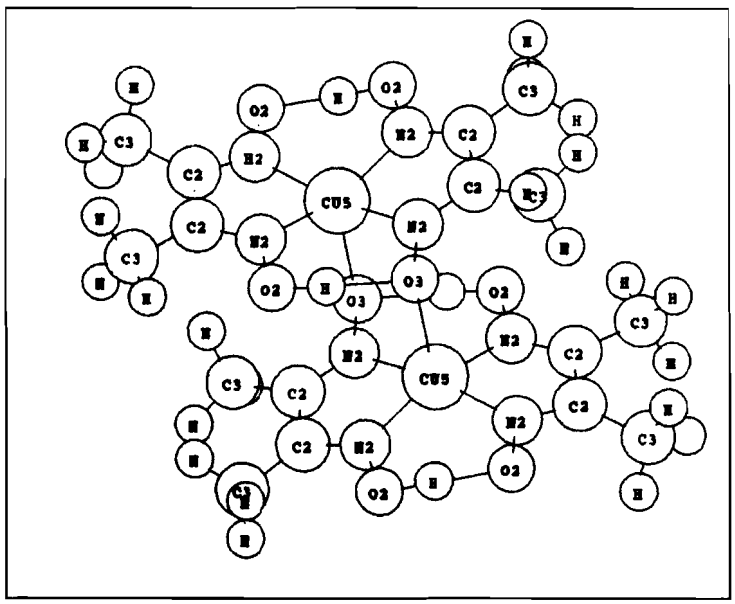

Figure 2: Ball-and-Stick Diagram of the Structure of $Cu(Hdmg)_2$

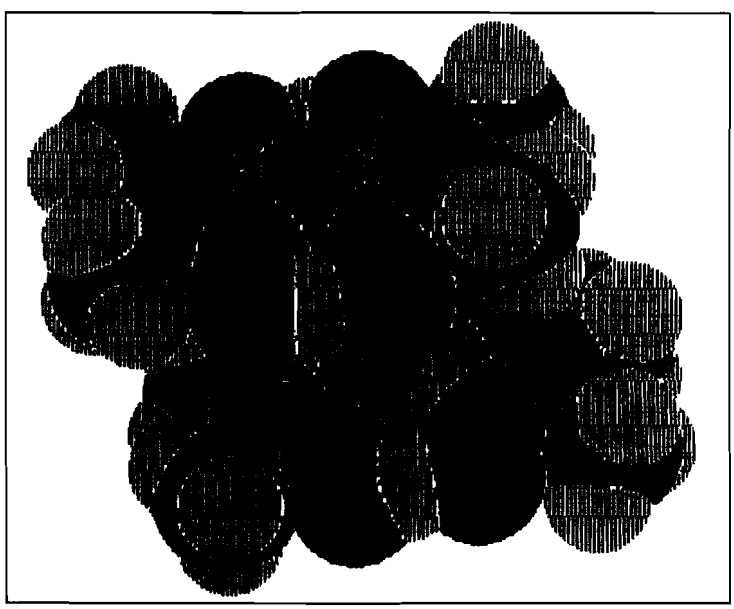

Figure 3: Space-Filling Diagram of the Structure of $Cu(Hdmg)_2$

somewhat longer distance at its apex. This oxygen atom belongs to the other $Cu(Hdmg)_2$ entity. Note also that the hydrogen bonding between two dimethylglyoxime ligands present in the Ni(II) compound is also present in the Cu(II) complex.

In 1977 Morpurgo and Tomlinson[4] published a study of the species present in Cu(II)-dimethylglyoxime solutions. Although they used both UV-visible and ESR spectrometry in their investigations, their central investigation involved the titration of Cu(II)-dimethylglyoxime-$HClO_4$ mixtures with NaOH. The pH changes occurring during these titrations were measured with a glass electrode. Five different concentrations of Cu(II) were used ranging from 1×10^{-3} mol Cu(II) per liter down to 1×10^{-4} mol Cu(II) per liter. In one series they used a Cu-H_2dmg ratio of 1:2, while in a second series the ratio was 1:1. From the first series they were able to obtain the value $\log \beta_2 = 18.65$ for the 1:2 complex $Cu(Hdmg)_2$. They were also able to explain the data obtained for the second series in terms of the tetrameric 1:1 complex $[\{Cu(Hdmg)(OH)\}_4]$, and the following equilibrium:

$$2\ Cu(Hdmg)_2 + 2\ Cu^{2+} + 4\ H_2O \rightleftharpoons [Cu(Hdmg)(OH)]_4 + 4\ H^+$$

They obtained values ranging from 12.63 to 13.89 for log K of this equilibrium.

Overall, Morpurgo and Tomlinson concluded that for solutions with a copper to dimethylglyoxime (H_2dmg) ratio of 1:2, the predominant species present is $Cu(Hdmg)_2$ over a pH range of 2.5 to 11.0. For solutions in which the Cu : H_2dmg

ratio is 1:1, the predominant species is the tetramer [{Cu(Hdmg)(OH)}$_4$] at least in the pH range 5 to 6.5.

Morpurgo and Tomlinson also analyzed the green-brown precipitate which often forms in more concentrated solutions containing equal amounts of Cu(II) and dimethylglyoximate ions. They found the composition to generally correspond to Cu(Hdmg)(OH) with some variability.

Further evidence of the nature of Cu(II)-dimethylglyoxime solutions was uncovered almost accidentally during research at Emporia State University[1] in the spring of 1991. The oxidation of Cu(II)-dimethylglyoxime solutions by persulfate ions was being investigated by Yang Cao under the direction of Dr. W. G. Davies. In the course of this investigation it was discovered that if 0.001 M $CuSO_4$ solution was added to an excess of Na_2dmg solution at a pH of 10.5, then the absorbance at 520 nm was proportional to the concentration of Cu(II). These results are shown in Figure 4. The value of R^2 was found to be 0.999. This excellent linearity is particularly impressive in view of the fact that the experiments from which the data were derived were not designed to check on Beer's Law. The fact that Beer's Law is obeyed is very convincing evidence that only one Cu-dmg complex is involved. Since there is an excess of dimethylglyoxime, this complex is almost certainly $Cu(Hdmg)_2$, or a deprotonated version of it.

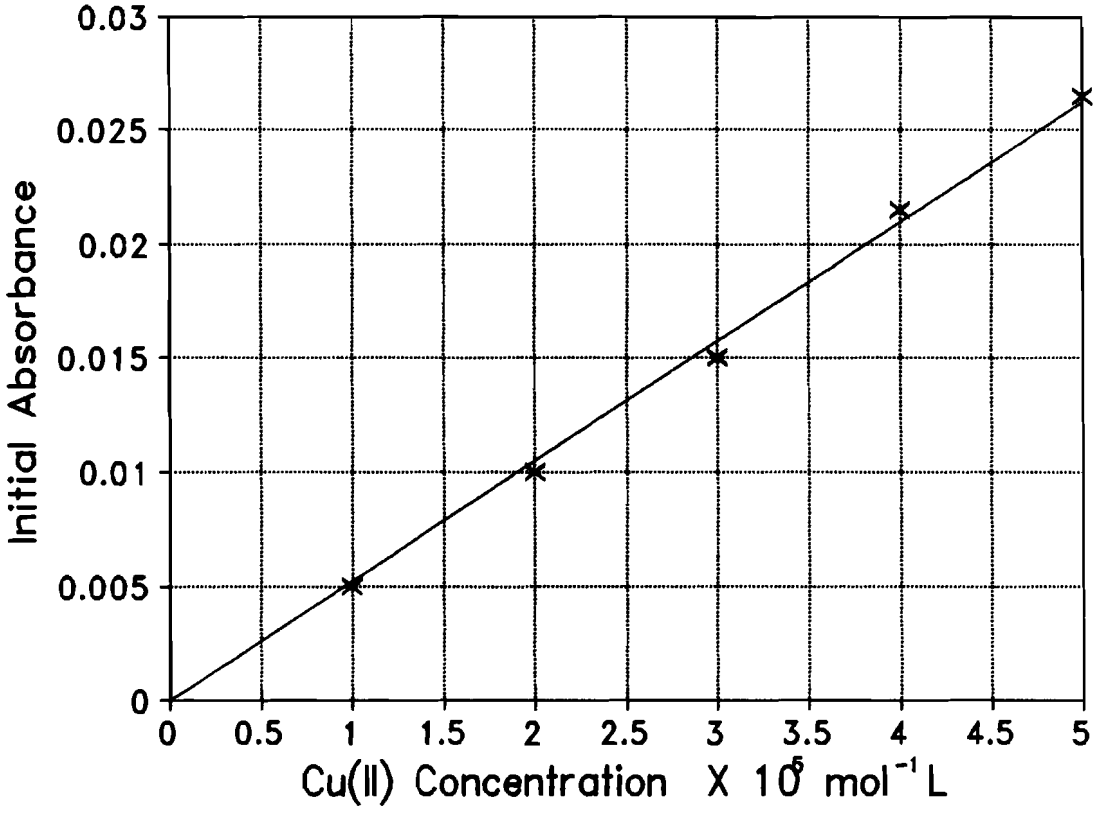

Figure 4: Variation of Initial Absorbance with Cu(II) Concentrations

1.3 PROPOSED INVESTIGATION

The work done by Yang Cao, described in the previous section, suggested a fruitful line of investigation for Cu(II)-dimethylglyoxime solutions, namely a photometric approach. The use of a dipping probe photometer makes it peculiarly easy to add a reagent to a solution and measure the photometric result. By using a different technique from that used by Morpurgo and Tomlinson, it was hoped to confirm or contradict their interpretation of their results. The existence of the 1:2 compound $Cu(Hdmg)_2$ appears reasonable and

has been proposed by several investigators[2], but the existence of a 1:1 tetramer is supported only by Morpurgo and Tomlinson's work.

Before this work could be undertaken, it was useful to find a quick way to analyze both the copper(II) sulfate and the sodium dimethylglyoximate solution used. Neither crystalline $CuSO_4 \cdot 5H_2O$ nor $Na_2dmg \cdot 8H_2O$ has an exact stoichiometric amount of H_2O in it. It was proposed to titrate solutions of Na_2dmg against HCl of known composition, and also against $CuSO_4$ solutions monitoring the pH of the solution. It was known from previous work[5] that the second titration is probably stoichiometric with a Cu:dmg ratio of 1:1. At the same time, it was hoped to find titrimetric evidence for the existence of $Cu(Hdmg)_2$ in these solutions.

Secondly, attention would be focused on determining under what circumstances Cu(II)-dimethylglyoxime solutions obey Beer's Law. By using a dipping probe colorimeter the absorbance throughout the titration could be monitored. Hopefully, these photometric titration studies would give evidence of the existence of copper(II) complexes other than $Cu(Hdmg)_2$ in solution. It was also anticipated that these studies would shed insight on the influence of pH on the formation of these complexes.

EXPERIMENTAL

2.1 APPARATUS

a) Potentiometric titrations

In the potentiometric titration studies described below, all of the measurements were carried out at room temperature in a beaker with a star magnetic stirrer. A Horizon Model 5998-10 pH meter was used to measure the pH of solutions during the titration.

b) Photometric titrations

The photometric titration studies involved the use of a Brinkmann Model PC 700 dipping probe photometer. The apparatus used is shown in Figure 5.

The dipping probe photometer utilizes a fiber-optic cable to conduct the light coming from a tungsten lamp in the

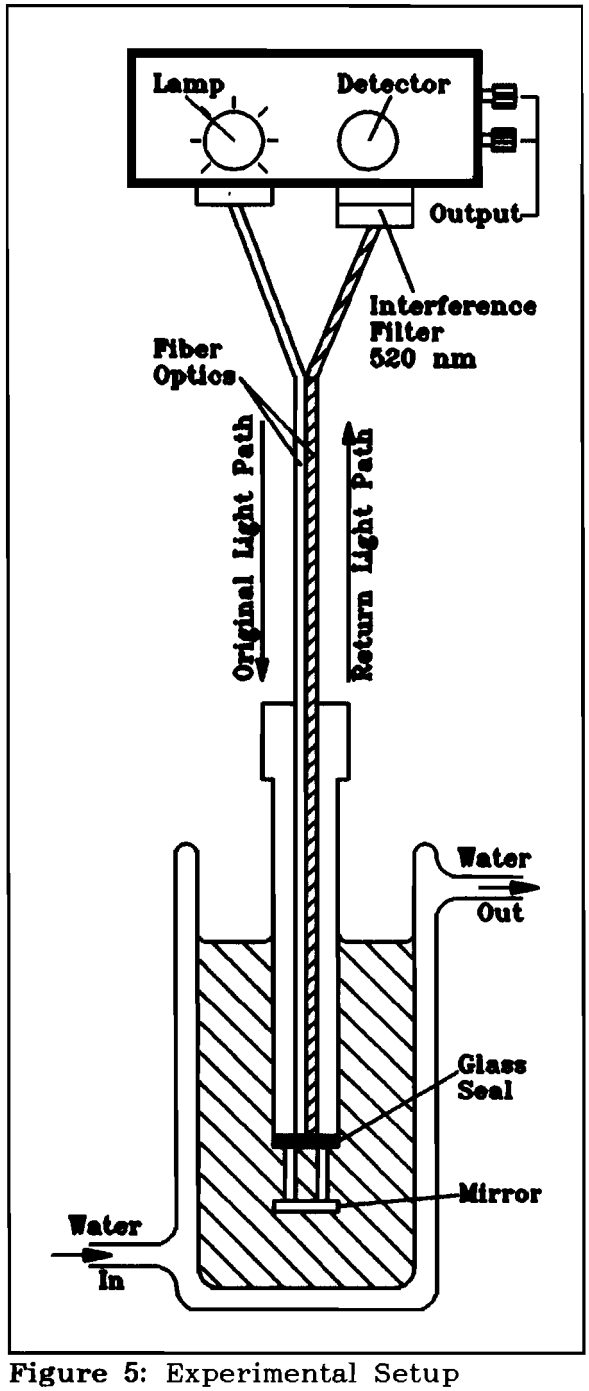

Figure 5: Experimental Setup

main housing into the solution. The light traverses a fixed length of solution, after which it is reflected back through the solution by a mirror firmly attached to the end of the probe. The light then enters a second fiber-optic cable and passes back into the main housing. Finally, the light passes through an interference filter onto a photodetector.

The advantage of this setup is that one can take the photometer to the solution in a large container, rather than having to place the solution inside a small cell inside the photometer. As a consequence one can add a reagent to a solution and watch the photometric consequences very readily. A drawback to this method is that only one wavelength can be investigated at a time. A second drawback is the use of glass for the fiber-optic cable. This restricts measurements to wavelengths above 420 nm. In this work the filter used was a 430 nm filter with a band width of ± 10 nm. This was the lowest wavelength filter available for the instrument.

The photometric titration studies were carried out at 25 ± 0.02°C in a double-walled Pyrex beaker similar to that shown in Figure 5. Mixing was accomplished with a star magnetic stirrer. A Haake constant temperature bath, Model F 423, with a mercury thermoregulator was used to circulate the water through the outer jacket of the beaker.

Instead of using the dial of the photometer for data readout, a digital voltmeter was attached to the output terminal at the back of the instrument. This terminal is

intended for a pen recorder, but it gives a voltage proportional to the light intensity. The 100% light absorption was measured in distilled water or in the initial solution of each run when colorless. Using a digital voltmeter in this way proved to be both more precise and more convenient than reading the dial. The results were converted into transmittance and then converted into absorbance.

2.2 REAGENTS

The reagents used in this study were the following:

1) Copper(II) sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$]: ACS reagent grade; Baker & Adamson Chemical Company.

2) Dimethylglyoxime sodium salt octahydrate [$Na_2dmg \cdot 8H_2O$]: Sigma Chemical Company.

3) Sodium borate octahydrate [$Na_2B_4O_7 \cdot 10H_2O$] (Borax): Fisher Scientific Company.

4) Boric acid [H_3BO_3]: General Drug & Chemical Corp.

5) Potassium phosphate monobasic [KH_2PO_4]: ACS reagent grade; Fisher Scientific Company.

6) MOPS 3-(4-Morpholino)-propanesulfonic acid [$C_7H_{15}NO_4S$]: Eastman Kodak Company.

7) EPPS 4-(2-hydroxyethyl)-1-piperazinepropane-sulfonic Acid [$C_9H_{20}N_2O_4S$]: Eastman Kodak Company.

8) AMPSO3-[(1,1-Dimethyl-2-hydroxy-ethyl)amino]-2-hydroxy-propanesulfonic Acid [$C_7H_{17}NO_5S$]: Sigma Chemical Company.

9) MES 2-[N-Morpholino]ethane-sulfonic acid Hemisodium Salt [$C_6H_{12.5}NO_4SNa_{0.5}$]:Sigma Chemical Company.

10) CAPS 3-[Cyclohexylamino]-1-propanesulfonic acid [$C_9H_{19}NO_3S$]:Sigma Chemical Company.

11) Potassium chromate [K_2CrO_4]: Mallinckrodt Chemical Works.

12) Sodium hydroxide (diluted from ampoule to exactly 1N): ss267-100, Fisher Scientific Company.

13) Hydrochloric acid solution (0.5N): Fisher Scientific Company.

Distilled water was used to prepare all of the solutions.

TITRIMETRIC STUDIES

3.1 POTENTIOMETRIC STUDIES

The initial studies in this work involved the use of sodium dimethylglyoximate as the titrant. Because dimethylglyoxime, H_2dmg, is a very weak acid with a pK_{a1} value of 10.46[6], the dimethylglyoximate ion dmg^{2-} is a very strong base. It was hoped to detect any reaction of this ion with the Cu(II) ion by monitoring the pH.

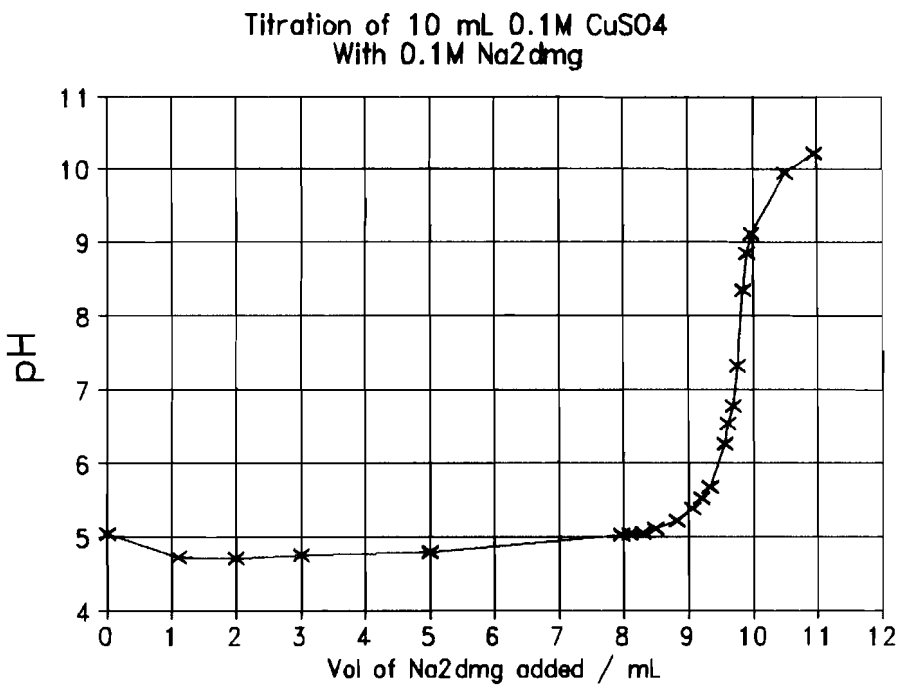

Figure 6: Titration of 10 mL 0.1M $CuSO_4$ with 0.1M Na_2dmg

Figure 6 shows the results obtained when 10 mL of 0.1 M $CuSO_4$ solution was titrated with 0.1 M Na_2dmg solution. Initially the dmg^{2-} ion reacts with the Cu(II) ion and there is little change in pH. Once the volume added exceeds 8 mL, the rate of change of pH with volume begins to increase until it reaches a maximum close to 9.84 mL.

The addition of Na_2dmg to the $CuSO_4$ solution is accompanied by a darkening of the solution and the eventual formation of a green-brown precipitate. This is presumably the same precipitate which Morpurgo and Tomlinson found to have the approximate formula $[\{Cu(Hdmg)(OH)_4\}]$. Certainly, the end point obtained here is within 2% of a 1:1 copper to dimethylglyoxime stoichiometry, and thus is in agreement with Morpurgo and Tomlinson's result. The small discrepancy from exact stoichiometry is most probably caused by the non-stoichiometric amount of H_2O in the $CuSO_4 \cdot 5H_2O$, or the $Na_2dmg \cdot 8H_2O$ crystals used in making the solutions.

The titration of standardized 0.1000 M HCl with 0.1 M Na_2dmg was also investigated with the intent to standardize the Na_2dmg solutions. A typical result is shown in Figure 7. An excellent end point was obtained. Three repetitions of this titration gave end points of 9.91 ±0.01 mL.

The addition of Na_2dmg to HCl produces a white precipitate of dimethylglyoxime H_2dmg which has very limited solubility in water. Though the occurrence of this precipitate undoubtedly contributed to the sharpness of the

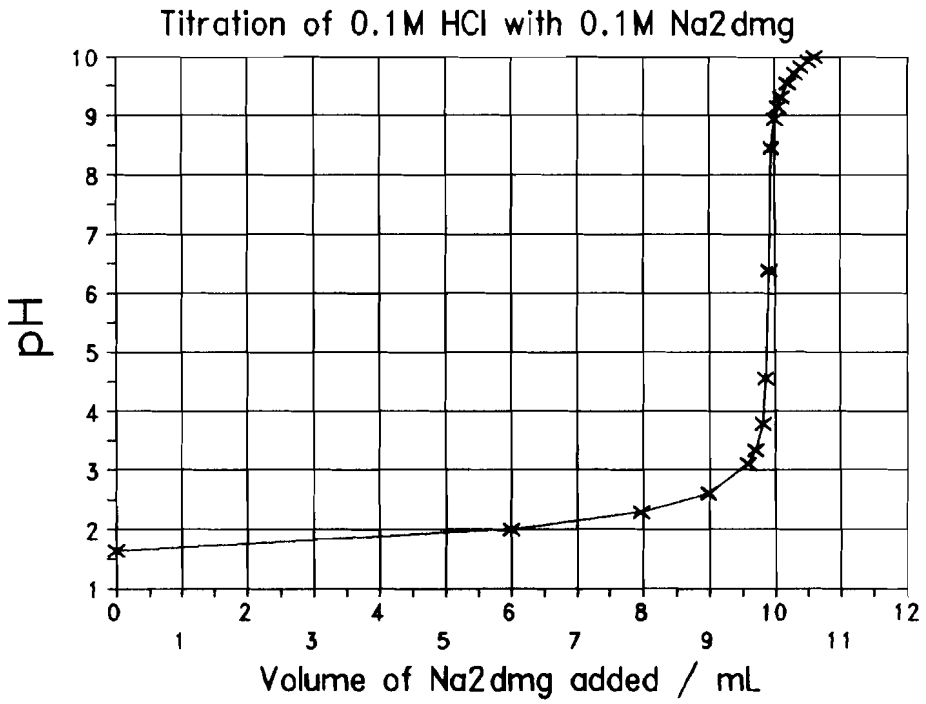

Figure 7: Titration of 10 mL 0.1000 M HCl with 0.1 M Na_2dmg

end point, it proved to be a nuisance in other respects. It was hoped to obtain evidence for the formation of $Cu(Hdmg)_2$ by titrating an equimolar mixture of $CuSO_4$ and HCl with Na_2dmg. The result was a sharp end point corresponding to the formation of what appeared to be mixed precipitate of the 1:1 copper - dimethylglyoxime compound and dimethylglyoxime itself. Because of this further investigations in this direction were abandoned.

3.2 PHOTOMETRIC STUDIES

All the photometric work described in this section

involved the use of a 430 ± 10 nm filter. This was the shortest wavelength possible with the glass fiber optics of the Brinkmann Model PC 700 dipping probe spectrophotometer. Since all of the solutions involved absorb more strongly in the ultraviolet than in the visible region, use of this filter made it possible to employ more dilute solutions than would otherwise have been possible.

a) Beer's Law Studies

The first photometric investigation was a test of how well a solution of $Cu(Hdmg)_2$ obeys Beer's Law with the apparatus to be employed in later investigations. A 0.005 M $Cu(Hdmg)_2$ solution was prepared by adding 3.043 g $Na_2dmg.8H_2O$ (10 mmol) to a 1 liter volumetric flask containing 50 mL of 0.100 M $CuSO_4$ solution and 20 mL of 0.500 M HCl, and then diluting to the mark. A 0.05 M phosphate buffer with a pH of 7.0 was also prepared. An aliquot of 200 mL of this buffer was pipetted into a jacketed beaker similar to that shown in Figure 5, and the probe from the photometer was inserted into it. The reading from the photometer in the buffer solution was taken as 100% transmittance. Then known volumes of 0.005 M $Cu(Hdmg)_2$ were added from a buret, and the transmittance of the resulting solution was measured. Two trials were performed. In the first trial a straight line with an R^2 value of 0.9997 and a slope of 639.8 was obtained. In the second trial the R^2 was 0.998 and the slope was 653.0. The

result of the first of these trials is plotted in Figure 8. As can be seen, $Cu(Hdmg)_2$ solutions obey Beer's Law very well under these experimental conditions.

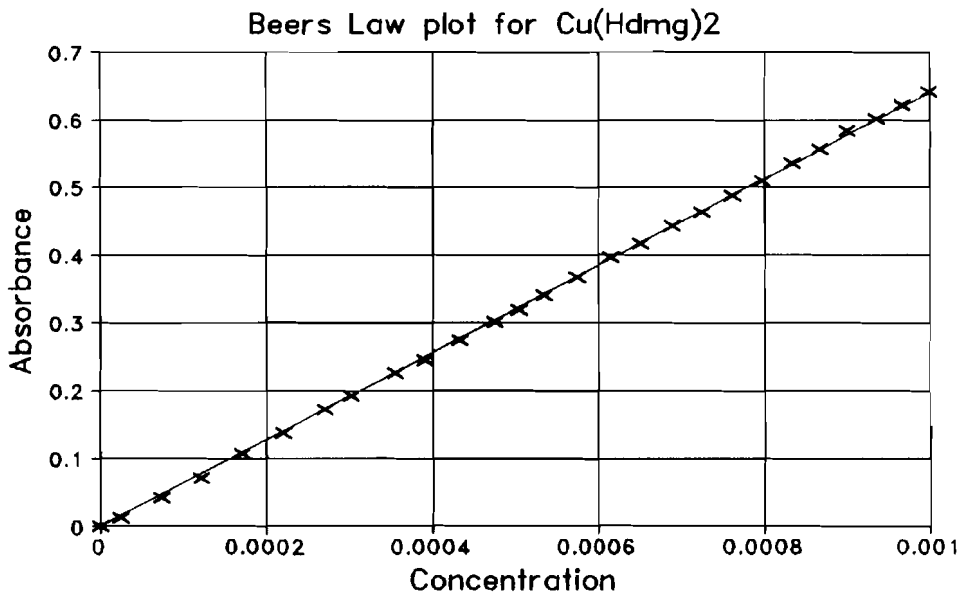

Figure 8: Beer's Law Plot for $Cu(Hdmg)_2$

Next, similar experiments were done with K_2CrO_4 solutions which are known to obey Beer's Law. A solution which was 0.001 M in K_2CrO_4 and 0.050 M in NaOH was added from a buret into a jacketed beaker containing 200 mL 0.050 M NaOH solution. The absorbance was measured using the dipping probe as in the previous experiment. The results are shown in Figure 9. Instead of the straight-line behavior mandated by Beer's Law, a line with a slight, but obvious, downward curvature was obtained. (The initial slope of this curve is shown in the figure as a straight line.)

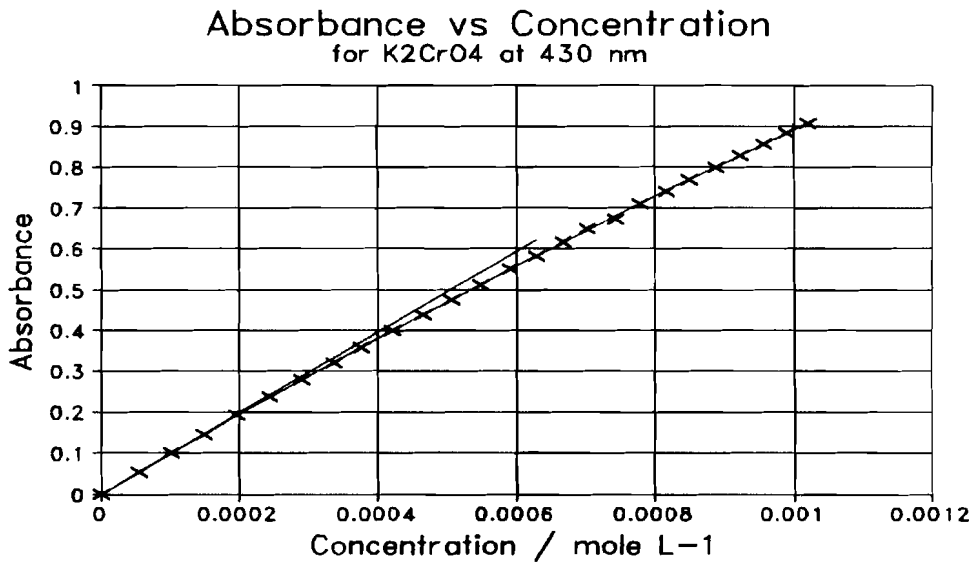

Figure 9: Beer's Law Plot for K_2CrO_4

b) Titration Studies

i) A Typical Titration

Most of the experiments described in this section involved the titration of 200 ± 0.1 mL of a buffered solution of Na_2dmg with a solution of $CuSO_4$ added from a buret. The buffered solution was placed in the jacketed beaker shown in Figure 5. In most cases 0.02 ± 0.0001 mmol of Na_2dmg was titrated. The buffers used were from those listed in section 2.2. Initially, the concentration of the buffer was 0.05 M, but in later runs this was reduced to 0.005 M. Since in most cases only 6 mL of $CuSO_4$ solution was added from the buret, the dilution of the solution was never more than 3 or 4 percent.

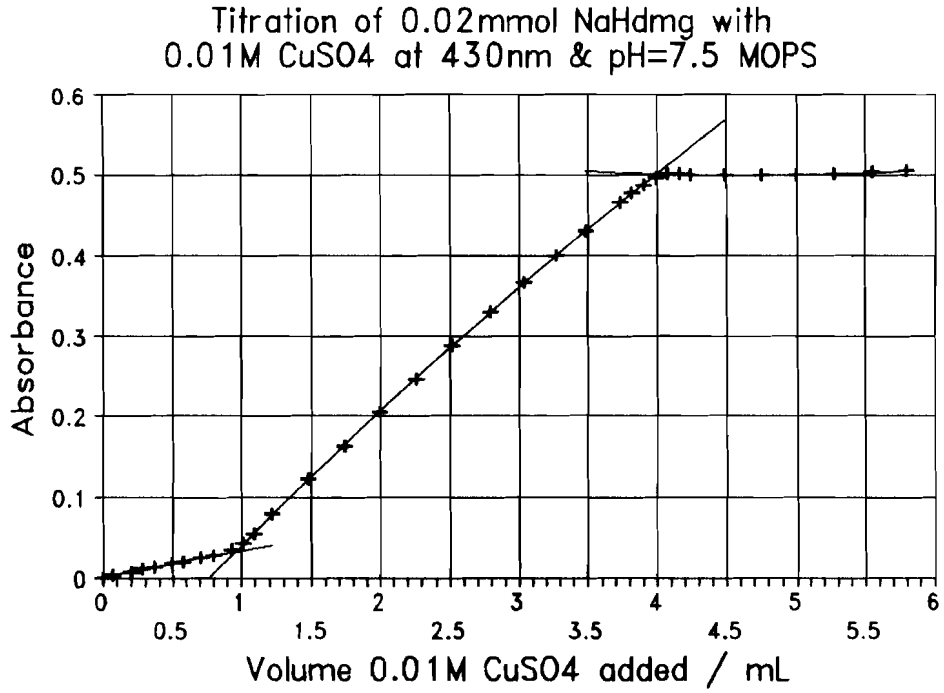

Figure 10: A Typical Titration of NaHdmg with 0.01 M $CuSO_4$

The results from a typical run are shown in Figure 10. In this run 0.02 mmol of Na_2dmg was dissolved in 0.05 M MOPS buffer with a pH of 7.5, and was titrated with 0.01M $CuSO_4$. The plot of absorbance versus volume $CuSO_4$ added consists of three obvious segments. In the first segment the absorbance is proportional to the volume of $CuSO_4$ added. This continues until 0.01 mmol of $CuSO_4$ has been added (a ratio of 1 Cu to 2 dmg). In the second section the rate of change of absorbance with volume of titrant becomes suddenly larger. This section is approximately, but not exactly, linear. When 0.04 mmol of $CuSO_4$ is reached (a ratio of 2 Cu to 1 dmg), a second abrupt

change in slope occurs and a third segment is reached in which the absorbance remains constant or decreases slowly. It should be noted that none of these plots showed any sharp discontinuity at 2 mL added which corresponds to a ratio of 1 Cu to 1 dmg.

In all titrations the initial solution in the beaker was colorless. However, as $CuSO_4$ solution was added, the solution became light brown. After 0.01 mmol of $CuSO_4$ had been added, the change in slope of the absorbance was accompanied by a slow change of color from light brown to yellow. By the time 0.04 mmol had been added, the solution was completely yellow and remained so with further additions of $CuSO_4$.

A further behavior of the solutions during these titrations is worth noting. In the middle section of the titration the rate at which the absorbance attained a steady value after each addition of $CuSO_4$ was noticeably slower than in the other two sections. This behavior was particularly evident in the early part of this segment. It occasionally required as long as 20 minutes before a steady absorbance reading was obtained. On the average, a titration took about two hours to complete.

ii) Variation with pH

Runs similar to that described above were performed using a variety of buffers at a variety of pH values. With only a few exceptions, which will be discussed later, the plots

obtained all had three clearly defined segments intersecting at points close to a 1:2 and a 2:1 Cu:dmg ratio. The first segment of these plots were all very similar, but the second and third segments depended not only on the pH, but also to a certain extent on the buffer used.

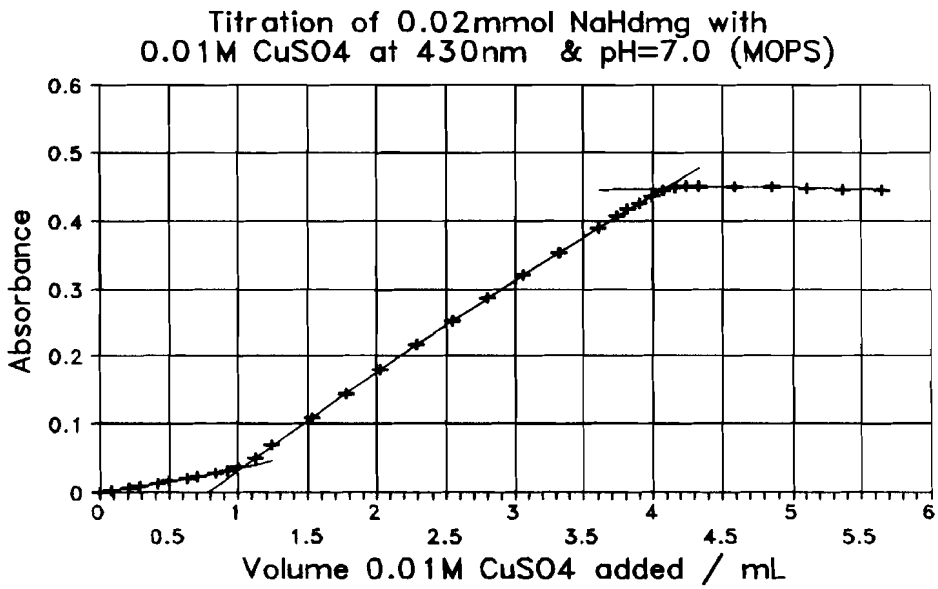

Figure 11: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$ in pH=7.0 MOPS Buffer(0.05 M)

Figures 11, 12, and 13 show the results of three runs using the same buffer but different pH values. The buffer used was 0.05 M MOPS, and the pH values employed were 7.0, 7.5 and 8.0. As can be seen from these plots, the first segment is virtually identical in all three runs, having almost the same slope and the same termination volume of 1 mL (0.01 mmol Cu). The second segment, by contrast, is pH dependent, the slope increasing with pH. Nevertheless, in all

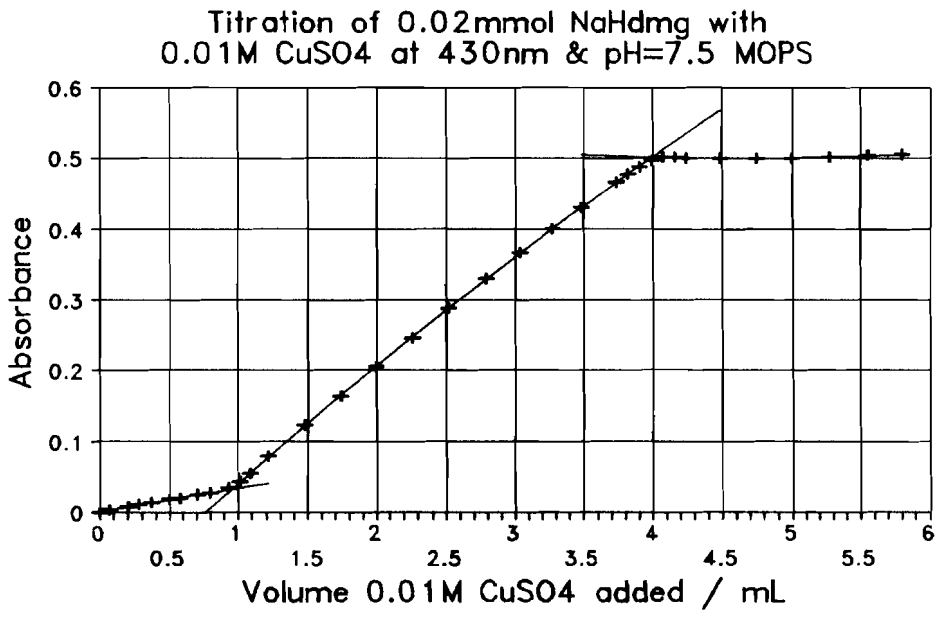

Figure 12: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$ in pH=7.5 MOPS Buffer(0.05 M)

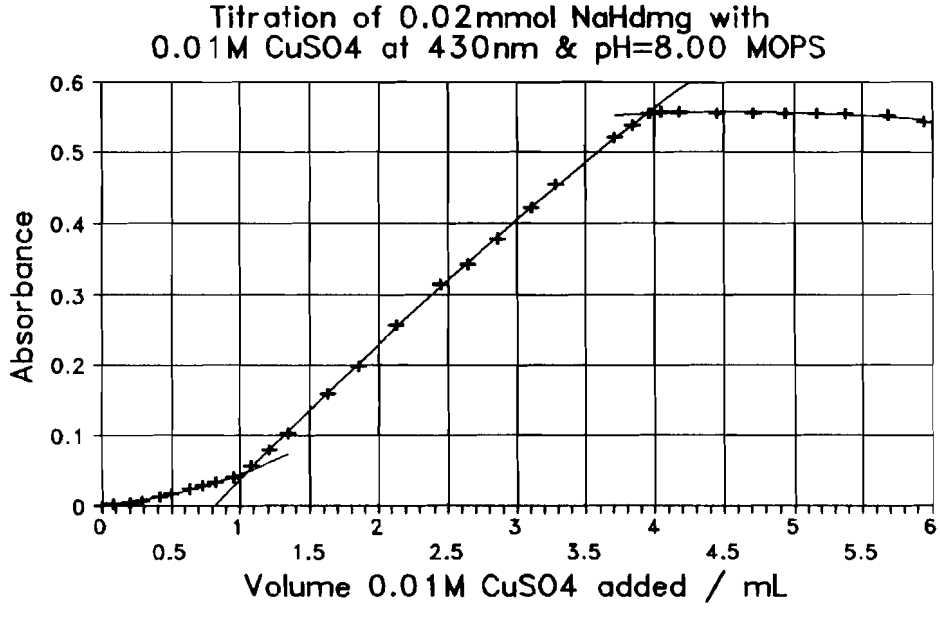

Figure 13: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$ in pH=8.0 in MOPS Buffer(0.05 M)

three cases the middle segment terminates fairly abruptly at a volume close to 4 mL. At this point the absorbance remains constant, or changes only slowly with the addition of titrant.

Figures 14, 15, 16, and 17 show the results obtained with a second buffer, namely 0.05 M borate solution. In this series titrations were performed at four different pH values. Again, the first segment is virtually identical in all four runs. As in the MOPS buffer case, the slope of the middle segment shows a pH dependence. The slope increases as we move from a pH of 8.5 to 9.2. Thereafter it changes very little as the pH is increased to 9.6 and then to 10.1. The final segment is more or less parallel to the axis at pH value of 8.5, but has an obvious negative slope at the three highest pH values. Also worth noting is that the point of intersection between the second and third segments is usually a little larger than the stoichiometrically exact 4.0 mL.

iii) Effect of Buffers and Buffer Concentrations

In addition to the experiments just described which explored the effect of changing the pH while keeping the buffer constant, other experiments were performed in which the pH was kept constant but the buffer was changed. Figure 18 shows the results obtained at a pH of 8.0 with three different buffers, namely EPPS (pK = 8.0), MOPS (pK = 7.2) and Borate (pK = 9.3).

The three buffers give essentially the same results

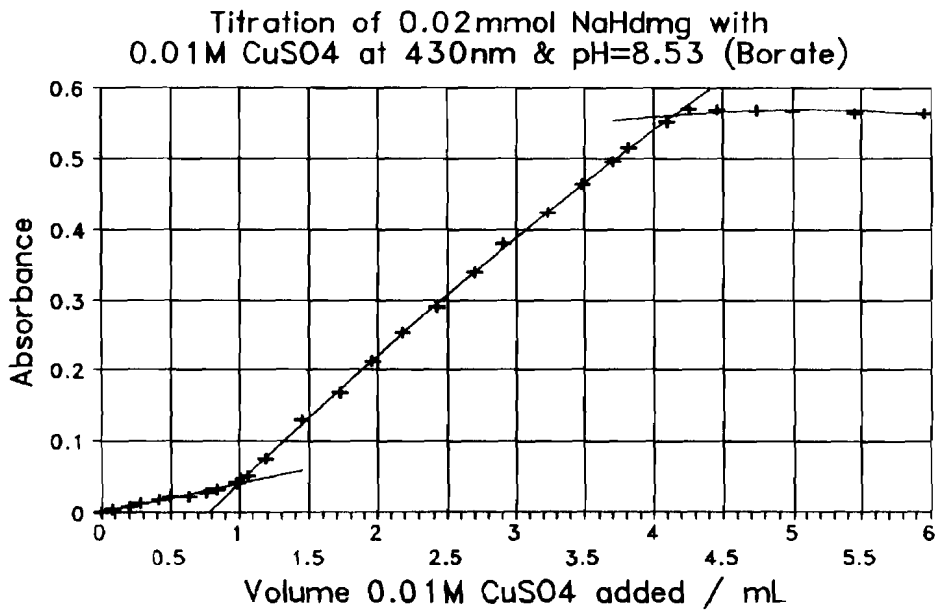

Figure 14: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$ in pH=8.5 Borate Buffer(0.05 M)

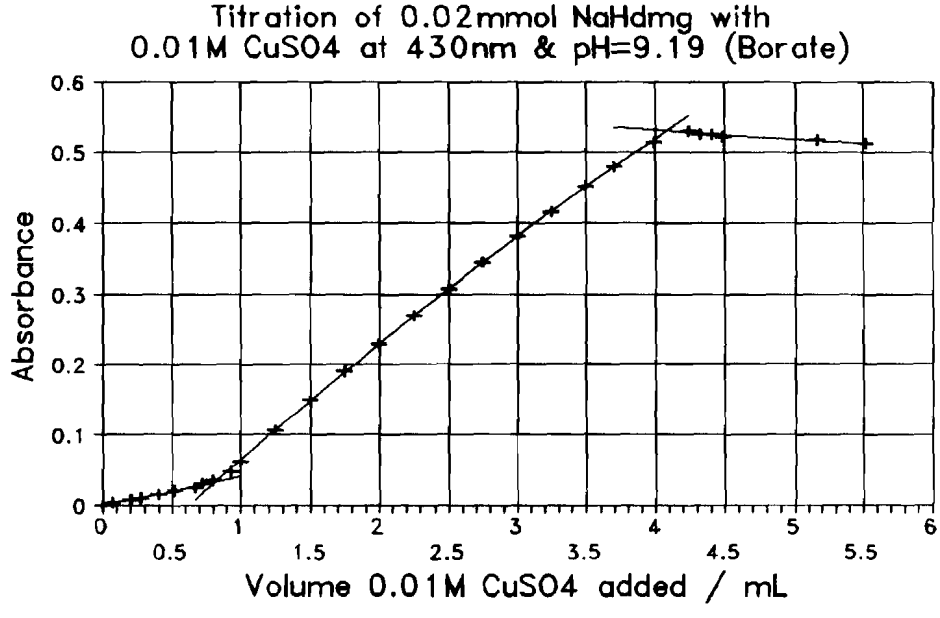

Figure 15: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$ in pH=9.2 Borate Buffer(0.05 M)

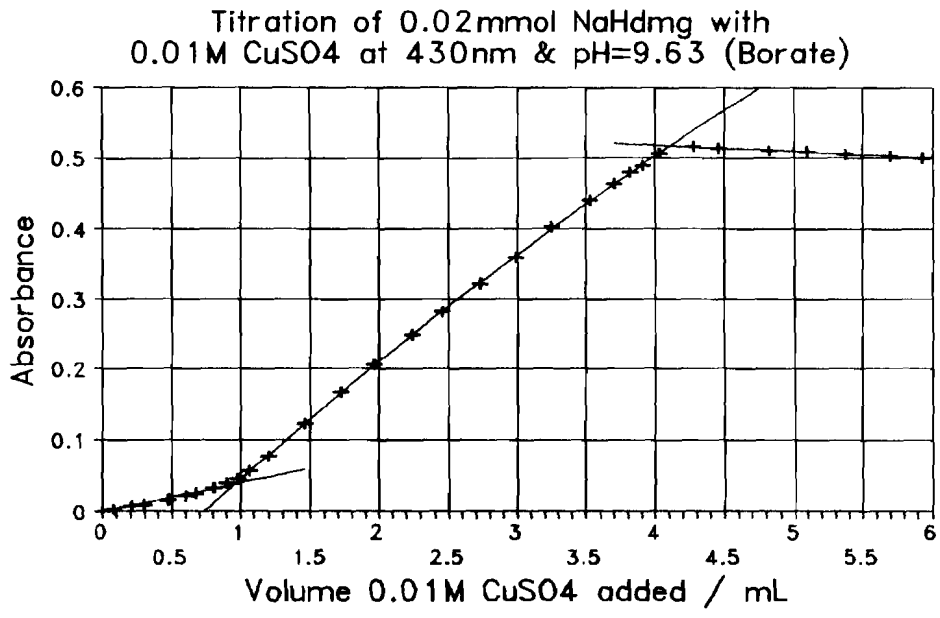

Figure 16: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSo_4$ in pH=9.6 Borate Buffer(0.05 M)

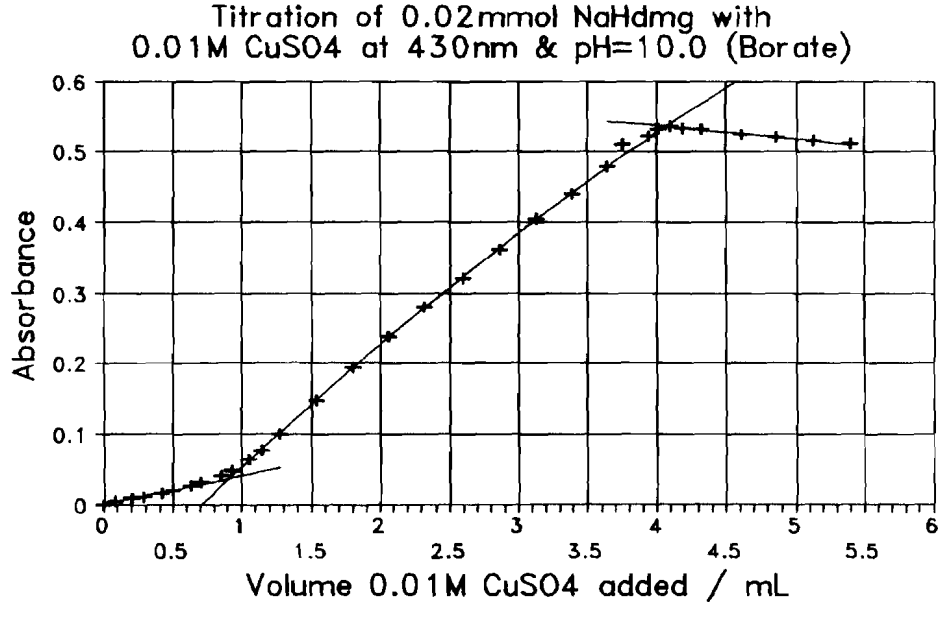

Figure 17: Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$ in pH=10.0 Borate Buffer(0.05 M)

except for the last eight points in the EPPS titration. The end-point appears prematurely at about 3.7 mL, and the last section of the plot corresponds to a much lower absorbance than that obtained for the other two buffers. This anomalous behavior was attributed to the formation of a precipitate which was observed visually a few minutes after the completion of the titration.

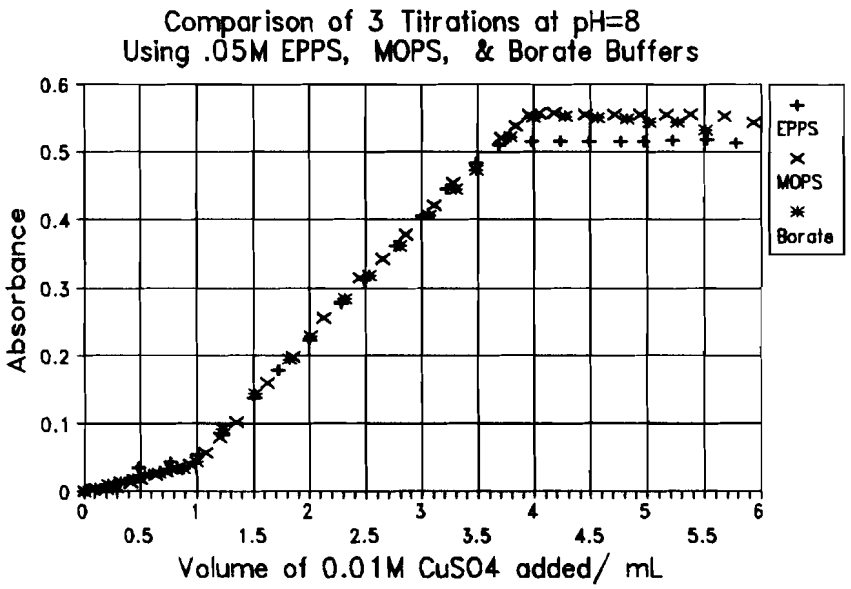

Figure 18: Comparison of Three Runs all at pH=8.0 but with Different Buffers(EPPS, MOPS, and Borate)

The excellent agreement among the three buffers shown in Figure 18 should be viewed with a certain degree of caution. Repeated titrations, using the same pH and the same buffer, occasionally showed some discrepancies. An example is shown in Figure 19. Although the initial parts of the plots agree quite well, there is an obvious difference at and after the

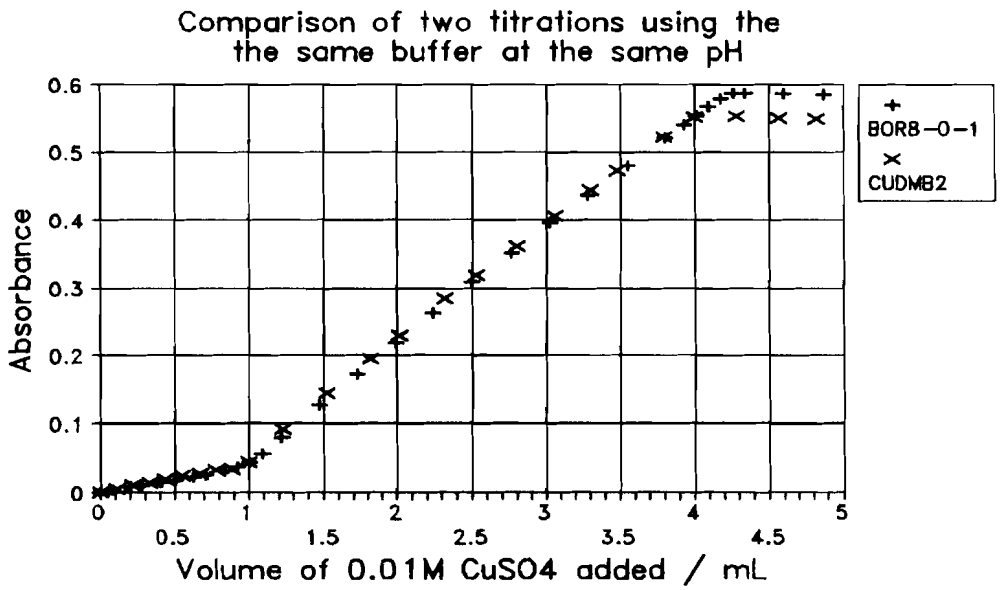

Figure 19: Repetitions of the Same Titration in pH 8.0 Borate Buffer(0.05 M)

second end point. The run labelled BOR8-0-1 showed a distinctly higher absorbance at the conclusion of the run than did the run labelled CUDMB2. In addition, the discontinuity in slope occurred at about 4.3 mL rather than at the exact stoichiometric value of 4.0 mL.

Attention was now focussed on whether the titration results depend on the concentration of the buffer employed. Originally, a concentration of 0.05 M was chosen for all buffers. This was now reduced to 0.005 M. Runs were made at a pH of 8.0 using 0.005 M solutions of EPPS, MOPS and borate as buffer. The borate runs showed anomalous behavior and were abandoned.

The plots in Figure 20 contain the results obtained

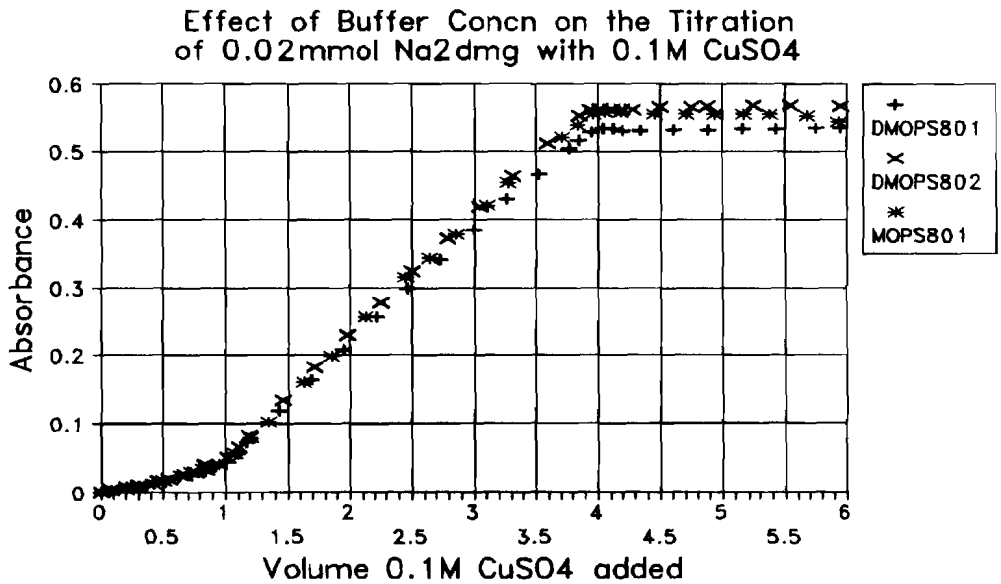

Figure 20: Effect of Buffer Concentration on Titration Plot Using 0.005 M and 0.05 M MOPS at pH 8.0

using a MOPS buffer. The two runs DMOPS801 and DMOPS802 refer to a dilute 0.005 M MOPS buffer, while the run MOPS801 used a 0.05 M MOPS buffer. As can be seen, the two runs with the dilute buffer do not agree very closely. The run with the concentrated buffer gives results which are intermediate between the other two runs. If there is a dependence on buffer concentration, it is smaller than the scatter which can occur between repeat runs of the same titration.

The results obtained for a pH of 8.0 using an EPPS buffer are shown in Figure 21. This time the two runs using 0.005 M buffer, namely DEPPS801 and DEPPS802, are in close agreement with each other. Moreover, they agree well with the results obtained using the more concentrated 0.05 M buffer.

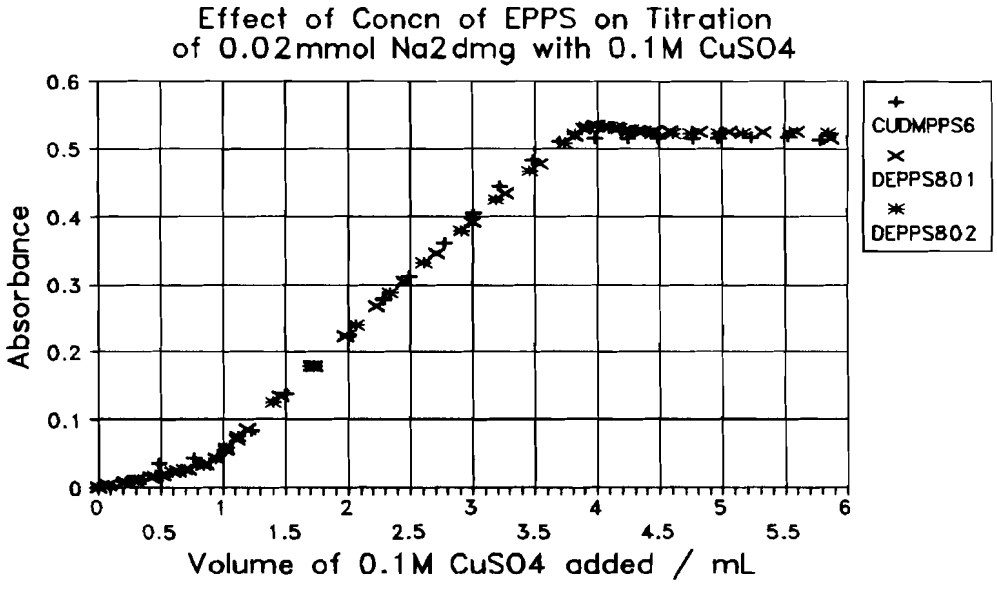

Figure 21: Effect of Buffer Concentration on Titration Plot Using 0.05 M and 0.005 M EPPS at pH 8.0

c) Reverse Titration Studies

In addition to titrating NaHdmg with $CuSO_4$, a few titrations were also performed in the reverse direction. This proved to be much more difficult than the forward titration. If $CuSO_4$ is added to a buffer mixture, a precipitate forms for the two buffers tried, namely MOPS and borate. Accordingly, a known aliquot of Na_2dmg was first added to the volumetric flask before the addition of $CuSO_4$ followed by buffer.

A second, more serious, difficulty was the time taken for the absorbance to stabilize at a constant value. Only two titrations were performed. The first was exploratory in nature, but the second took over 8 hours to perform!

In this titration the solution to be titrated was

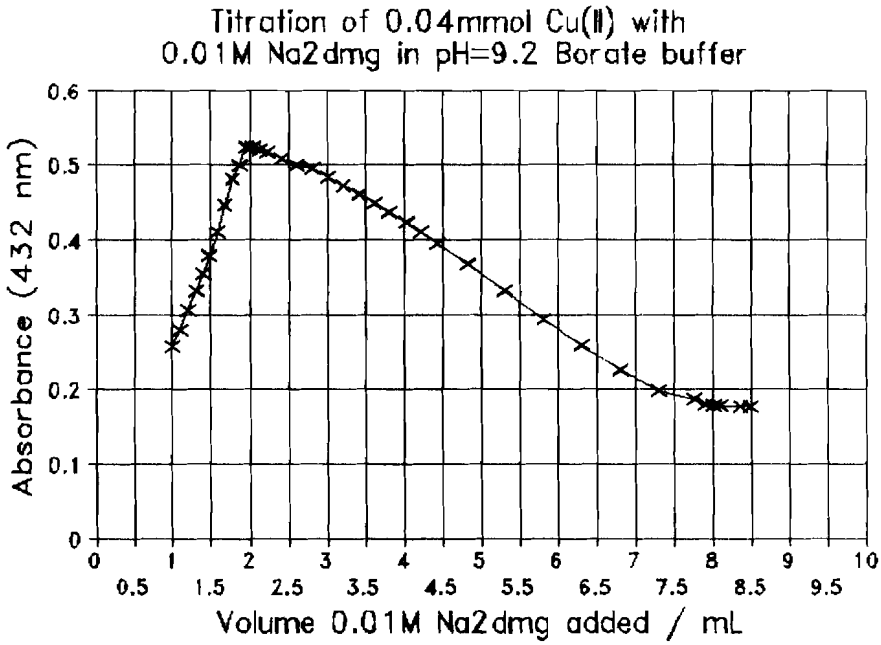

Figure 22: Titration of 0.04 mmol Cu(II) with 0.01 M Na_2dmg in Borate Buffer at pH 9.2 (The volume added includes the original aliquot of 0.01 mmol Na_2dmg equivalent to 1 mL of 0.01 M Na_2dmg.)

prepared by adding 2.383 g of $Na_2B_4O_7 \cdot 10H_2O$ (0.05 mol) to a 500 mL volumetric flask containing 10 mL of 0.01 M $CuSO_4$ solution, 2.5 mL of 0.01 M Na_2dmg solution and diluted to the mark. A 200 mL aliquot of the solution was pipetted into the titration beaker. This aliquot contained 0.01 mmol Na_2dmg (equivalent to 1 mL of 0.01 M Na_2dmg). This was titrated with the 0.01 M Na_2dmg. The results are given in Figure 22. Again, a three-segment plot is obtained. Initially the absorbance increased with the addition of Na_2dmg solution, but at a volume of 2 mL (0.01 mmol dmg originally in the solution + 0.01 mmol added from the buret) the absorbance suddenly began to decrease.

This decrease continued until about 8 mL of Na_2dmg had been added. At this point the absorbance remained constant with the further addition of Na_2dmg solution.

The first discontinuity is fairly sharp at a Cu : dmg ratio of 2:1. The second discontinuity is not so well defined, but can reasonably be assigned to a Cu : dmg ratio of 1:2. It should be noted that, there is no discontinuity at 4 mL corresponding to a Cu : dmg ratio of 1:1.

d) Difficulties with Buffers

It has already been noted that the use of a 0.05 M EPPS buffer resulted in the production of a precipitate toward the end of a photometric titration. A similar difficulty with precipitation was found when 0.05 M CAPS (pK = 10.4) was used.

A second difficulty was encountered when MES (pK = 6.1) was used. In this case the pH was in the vicinity of 6. At this pH the reaction accompanying the second segment in the photometric titrations was exceedingly slow. Often more than 30 minutes were required for the absorbance reading to stabilize at a constant value. Accordingly, experiments using this buffer were abandoned.

A third difficulty encountered with some buffers was the reaction between the Cu(II) ion and the buffer. Evidence for this behavior was found both for AMPSO and phosphate buffers.

In Figure 23 a comparison of the results obtained using a 0.05 M AMPSO buffer at a pH of 8.9 with those obtained using

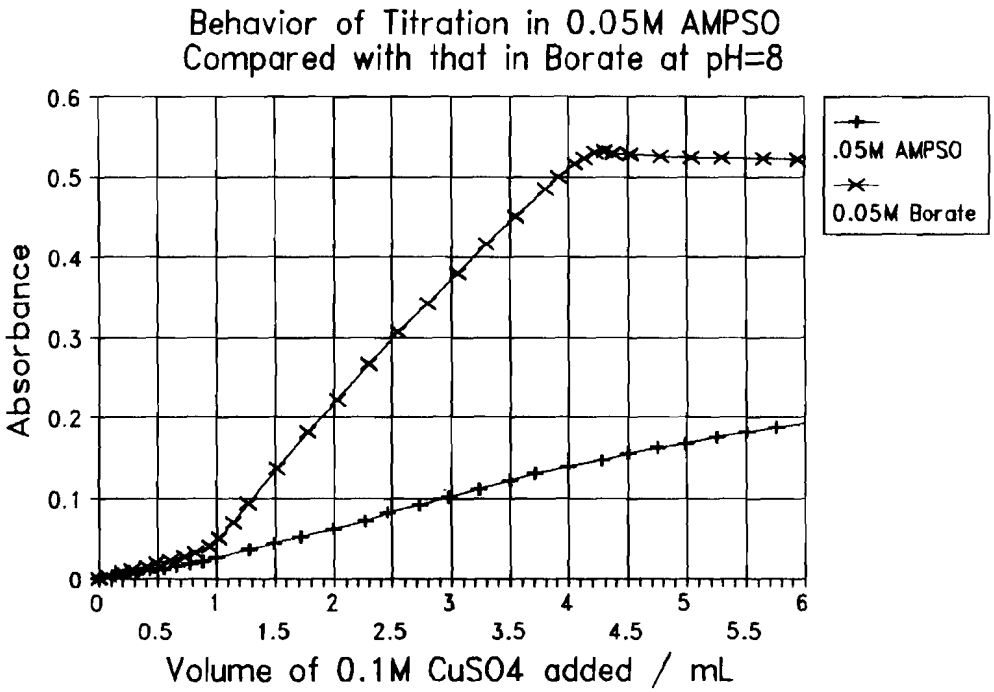

Figure 23: The Behavior of AMPSO Buffer Compared to the Behavior of Borate Buffer

a 0.05 M Borate buffer and a pH of 9.0 is shown. The typical three-segment behavior in other buffers is completely absent in the AMPSO case. Presumably AMPSO forms a much more stable complex with Cu(II) than does dimethylglyoxime. The behavior of phosphate buffer is similar to that of AMPSO, although there is some semblance of a second segment in this case.

e) Variation of Absorbance with pH

The titrations described in the previous section were centered on the stoichiometry of the species involved. The work described in this section involved an investigation of

the relationship between absorbance and pH with the intent to measure the stability constant of at least one of the complexes believed to exist in this solution, namely the 2:1 complex. Solutions of $CuSO_4$ and Na_2dmg were added in a 2:1 ratio to a flask containing the acid form of a buffer and made up to the mark. A solution of NaOH was then gradually added from a buret to an aliquot of this solution. The value of the pH and the absorbance were measured after each addition of base. The variation of absorbance with pH could thus be studied.

The experimental setup was similar to that employed previously; 200 mL of the solution to be measured were placed in a jacketed beaker equipped with a magnetic stirrer. Both a dipping photometer probe and a glass electrode were immersed in this solution. The buret for the addition of NaOH was placed above the beaker. A preliminary measurement using water in the jacketed beaker was used to find the value of the reading corresponding to 100% transmittance. Because of time constraints, only five runs were performed. Three of these were preliminary in nature and will not be described here. In the two runs which will be described, the concentration of the buffer was 0.005 M while the concentration of the NaOH was 0.1 M. In one run the buffer used was MOPS (pK = 7.2), while in the other EPPS (pK = 8.0) was used.

The results of these two runs are plotted together in Figure 24. In this figure the value of the absorbance has

been adjusted to allow for the diluting effect of the added volume of the titrant solution. Although the two curves are similar, they are not identical. Each shows an initial sharp

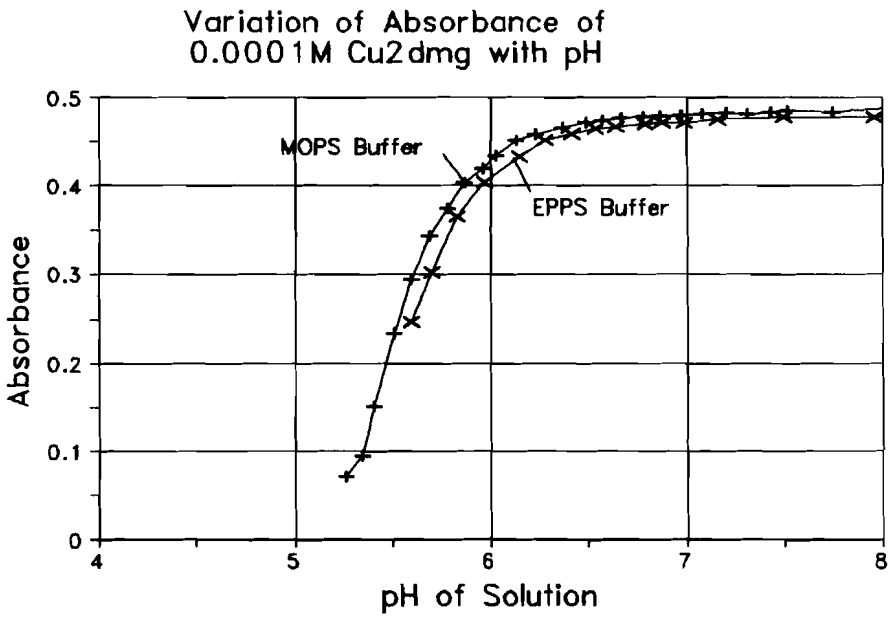

Figure 24: Variation of Absorbance of 0.0001 M Cu_2dmg with Changes in pH

increase in absorbance with pH in the region $5 < pH < 6$. As the pH is increased beyond 6, the rate of change of absorbance decreases more and more gradually until it remains essentially constant above a pH value of 7.

DISCUSSION

4.1 CONCLUSIONS

The most important finding of the investigations described in this thesis is the discovery of the three-segment plots obtained when dimethylglyoxime is titrated with Cu(II) at constant pH using a photometric probe. An idealized model of these results is shown in Figure 25.

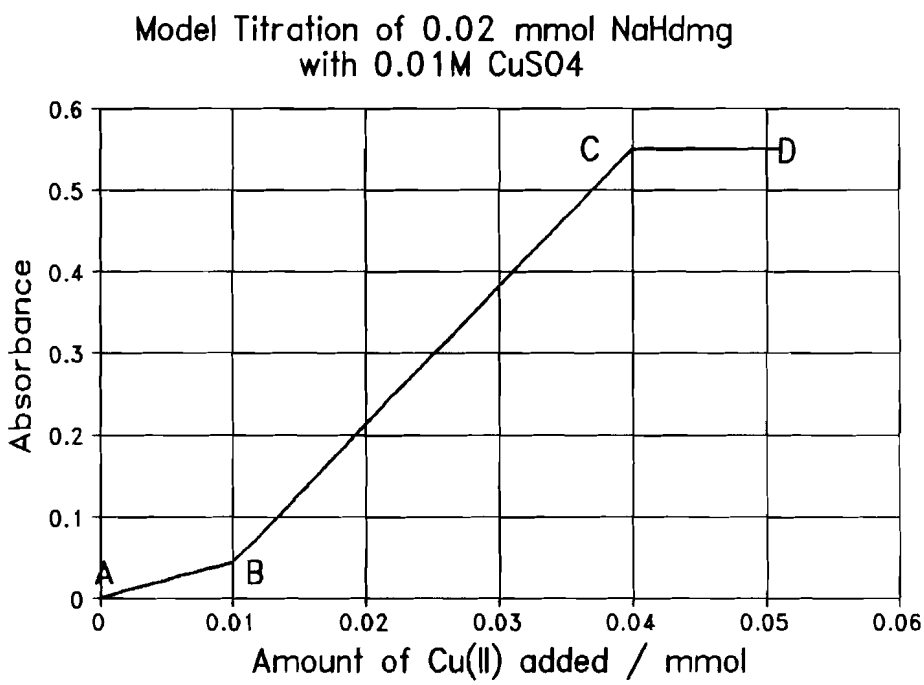

Figure 25: Model Titration of 0.02 mmol NaHdmg with 0.01 M $CuSO_4$

It is easy to explain the idealized straight line plot of Figure 25 in terms of two successive chemical reactions, both of which proceed to completion. The section AB of Figure 25 corresponds to the formation of the 1:2 complex according to the equation:

$$Cu^{2+} + 2\ H_2dmg \rightarrow Cu(Hdmg)_2 + 2\ H^+. \qquad [1]$$

At the pH values used, the only important uncomplexed dmg species is H_2dmg. Reaction [1] occurs until all the available H_2dmg is consumed at point B. Once this has occurred, the Cu^{2+} ions being added from the buret begin to consume the 1:2 complex while forming the 2:1 complex according to the equation:

$$3\ Cu^{2+} + Cu(Hdmg)_2 + 4\ H_2O \rightarrow 2\ Cu_2(dmg)(OH)_2 + 6\ H^+. \qquad [2]$$

Reaction [2] continues until all the $Cu(Hdmg)_2$ has been consumed. This occurs at point C in Figure 25. Beyond this point no further reaction occurs and consequently the absorbance remains constant as more Cu^{2+} is added to the solution.

Because the point B corresponds to the completion of Reaction [1], it also corresponds to the exact stoichiometric ratio

$$\frac{n_{H_2dmg}}{n_{Cu}} = \frac{2}{1} \qquad (1)$$

where n_{H2dmg} is the amount of H_2dmg at the start of the titration while n_{Cu} is the amount of Cu^{2+} added at this point. Thus point B corresponds to 0.01 mmol of Cu^{2+} added or 1 mL of

0.01 M $CuSO_4$ added.

Similarly, the point C corresponds to the completion of Reaction [2]. Adding Reactions [1] and [2] gives the overall reaction:

$$4\ Cu^{2+} + 2\ H_2dmg + 2\ H_2O \rightarrow 2\ Cu_2dmg(OH)_2 + 8\ H^+. \qquad [3]$$

At this point the amount of Cu^{2+} added, and the original amount of H_2dmg, again corresponds to an exact stoichiometric ratio:

$$\frac{n_{H_2dmg}}{n_{Cu}} = \frac{4}{2} = \frac{2}{1} \qquad (2)$$

Since the original amount of H_2dmg is still 0.02 mmol, the amount of Cu^{2+} added at point C corresponds to 0.04 mmol or 4 mL of 0.01 M $CuSO_4$.

The first section of the titration line AB corresponds to a solution in which only one absorbing species $Cu(Hdmg)_2$ is present. Accordingly, the absorbance A is given by the equation:

$$A = \epsilon_{12}\ c_{12}\ l \qquad (3)$$

where ϵ_{12} is the molar absorptivity of the 1:2 complex, c_{12} is its concentration and l is the thickness of solution traversed by the light passing through the photometer probe. Furthermore the amount of this complex, n_{12}, is equal to n_{Cu}, the amount of Cu^{2+} added by virtue of Reaction [1]. Accordingly we can write:

$$c_{12}\ V_{total} = n_{12} = n_{Cu} = c_{Cu}\ V_{add} \qquad (4)$$

where c_{Cu} is the concentration of the $CuSO_4$ in the buret (0.01 M), V_{add} is the volume of this solution added from the buret,

and V_{total} is the volume of the solution in the jacketed beaker. Strictly speaking, V_{total} = 200 mL + V_{add} , but the small dilution effect will be ignored and V_{total} taken as a constant 200 mL.

Rearranging Equation (4) yields

$$c_{12} = c_{Cu} \frac{V_{add}}{V_{total}} . \qquad (5)$$

Inserting this equation into Equation (3) yields

$$A = \epsilon_{12} \left(\frac{c_{Cu}}{V_{total}} l \right) V_{add} \qquad (6)$$

which corresponds to the straight-line section AB provided that V_{total} is a constant.

Differentiating Equation (6) with respect to V_{add} gives the slope of line AB

$$Slope = \frac{dA}{dV_{add}} = \epsilon_{12} \left(\frac{c_{Cu}}{V_{total}} \right) l . \qquad (7)$$

This equation shows us that the slope of this line is proportional to the molar absorptivity ϵ_{12}.

The second segment of Figure 25, the line BC, can likewise be explained in terms of the linear replacement of one absorbing species (the 1:2 complex) by a second absorbing species (the 2:1 complex). From Reaction [2], it can be seen that for every mole of Cu^{2+} added beyond point B, 1/3 mole of

$Cu(Hdmg)_2$ is consumed, while 2/3 mole of $Cu_2dmg(OH)_2$ is formed. Accordingly, the slope of segment BC is given by

$$Slope = \frac{dA}{dV_{add}} = \left(\frac{2}{3} \epsilon_{21} - \frac{1}{3} \epsilon_{12} \right) \left(\frac{c_{Cu}}{V_{total}} l \right) \qquad (8)$$

where ϵ_{21} is the molar absorptivity of the 2:1 complex. Since $2\ \epsilon_{21}$ is much larger than ϵ_{12}, the slope of line BC is much larger than that of line AB.

Beyond point C, no further reaction occurs. Since the Cu(II) ion does not absorb at this wavelength, the absorbance remains constant except for a small dilution effect. Accordingly, the line CD is effectively parallel to the x axis.

The results of the photometric titrations performed experimentally and described in Section 3.2 do not correspond exactly with the idealized behavior just described and these discrepancies need to be explained.

Although the first segment appears to be reasonably linear in all the titrations performed, the same is not true of the second segment. It always exhibits downward curvature. Experimentally, it was found that a solution of $Cu(Hdmg)_2$ obeys Beer's Law (See Figure 8). It is not surprising, therefore, that the first segment, which only involves this species, also exhibits Beer's Law behavior. Presumably this comes about because the wavelength employed (430 nm) corresponds roughly to a maximum in the absorption spectrum of $Cu(Hdmg)_2$.

A plausible explanation of the curvature of the second segment is the non-monochromaticity of the light coming through the interference filter used. This filter is rated at 430 ± 10 nm. Furthermore, the color of the solution throughout the second segment is yellow, suggesting that the molar absorption coefficient is much higher at 420 nm, the lower end of the filter's range, than it is at 440 nm, the upper end. This would give a plot of absorbance against concentration (or volume of reactant added) in which the slope decreases with concentration, thus, exhibiting a downward curvature. It is noteworthy that this is the behavior found for K_2CrO_4 solutions shown in Figure 9. Alkaline K_2CrO_4 solutions are known to obey Beer's Law so that their apparent deviations from this Law must be an artifact of the apparatus. Solutions of K_2CrO_4 have a lemon-yellow color quite similar to that of the 2:1 complex and the molar absorptivity at 420 nm is known to be much larger than that at 440 nm.

A second deviation from the ideal straight-line behavior exhibited in some of the plots of the data, such as Figure 23, is the behavior of the discontinuities at points B and C of the idealized plot of Figure 25. These discontinuities are not abrupt but somewhat rounded. The reason for this lies in the magnitude of the equilibrium constants involved. Figure 26 displays the results of some calculations which demonstrate the effect of varying these equilibrium constants. These calculations were kindly performed by Dr. W. G. Davies[7].

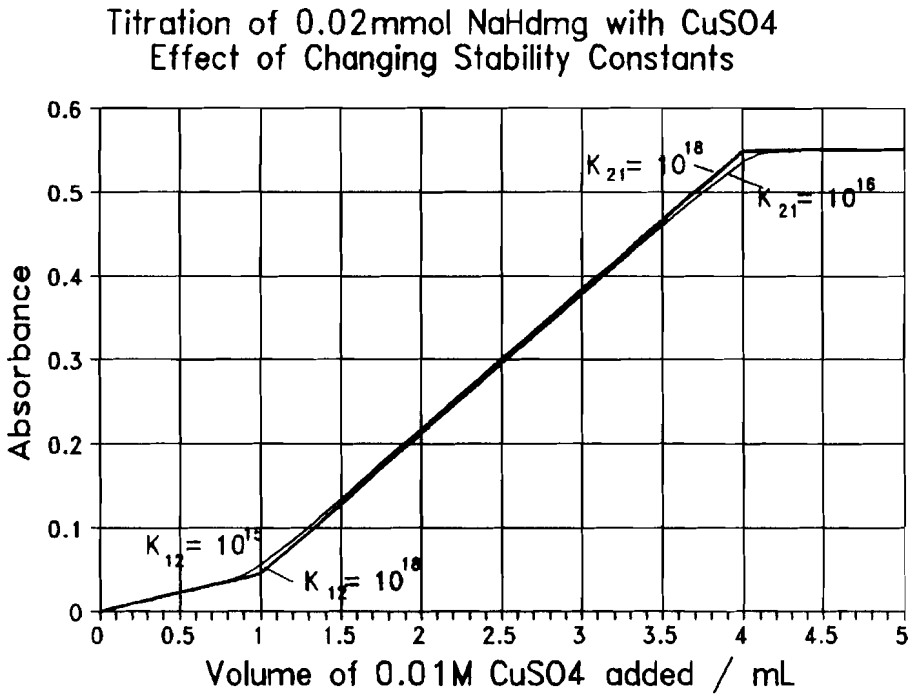

Figure 26: Titration of 0.02 mmol NaHdmg with $CuSO_4$: Effect of Assuming Different Values for the Equilibrium Constants

These calculations were made using the following parameters:

$$e_{12} = 880 \qquad e_{21} = 5500$$

$$K_{12} = \frac{[Cu(Hdmg)_2]}{[Cu]\,[H_2dmg]^2} = 10^{18} \text{ or } 10^{15}$$

$$K_{21} = \frac{[Cu_2dmg]}{[Cu]^2\,[dmg]} = 10^{18} \text{ or } 10^{16}$$

The constants K_{12} and K_{21} are not strictly equilibrium

constants, but depend on the pH. In a buffer solution at constant pH, however, they should both have constant values.

If K_{12} and K_{21} are both set equal to 10^{18}, a result indistinguishable from the straight line plot of Figure 25 is obtained. However if K_{12} is decreased to 10^{15}, or K_{21} to 10^{16}, the appropriate position in the plot becomes rounded rather than sharp, as is shown in Figure 26. Additionally, the slope of the middle segment is altered, causing the "end-point" corresponding to point B, to become lower than the correct stoichiometric value, and an "end-point" corresponding to point C, to become higher than the correct stoichiometric value. Both of these behaviors can be observed in Figures 13, 14, 15, and 16.

In most of the previous discussions the 2:1 complex has been written $Cu_2dmg(OH)_2$. There is strong evidence for the inclusion of two OH ligands in some of Morpurgo and Tomlinson's results[4]. In Figure 27 results obtained from a scan of a plot in Morpurgo and Tomlinson's paper using a digitizing tablet are shown. Their original plot was obtained from measurements of pH during the titration of a solution which was 0.001 M in $HClO_4$, 0.001 M in $Cu(ClO_4)_2$, and 0.001 M in H_2dmg. The titrant was NaOH, of concentration unspecified in the paper. In Figure 27 the excess amount of NaOH is used for the X-axis. The first mole of NaOH added (from -1 to 0) is considered to neutralize the $HClO_4$. The next mole (from 0 to +1) is considered to cause the formation of the 1:2

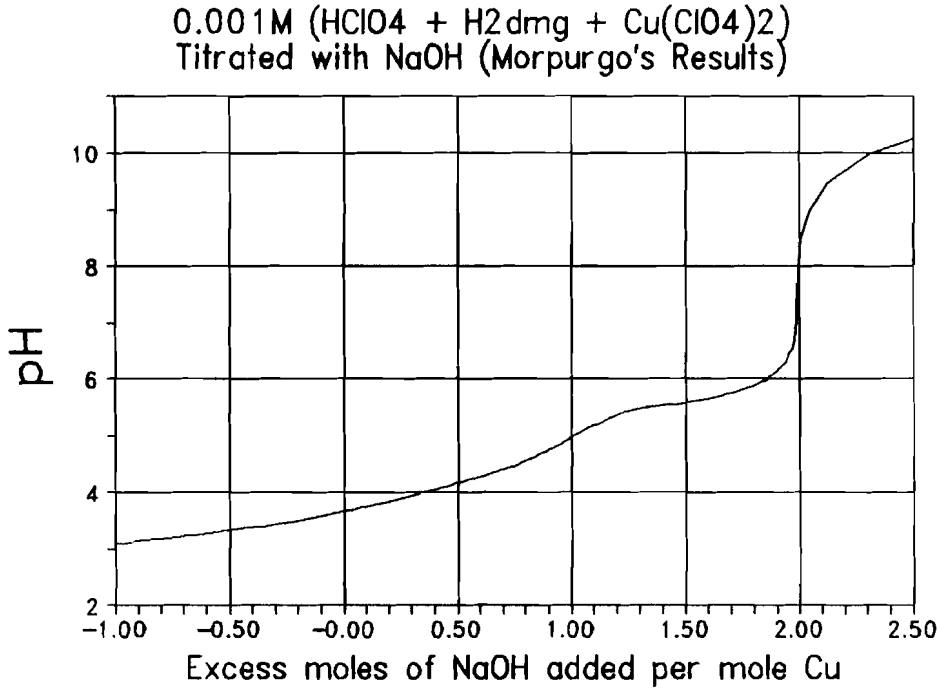

Figure 27: Morpurgo and Tomlinson's Titration of 0.001 M $HClO_4$ + 0.001 M $Cu(ClO_4)_2$ + 0.001 M H_2dmg

complex:

$$\tfrac{1}{2}\ Cu^{2+} + H_2dmg + OH^- \rightarrow \tfrac{1}{2}\ Cu(Hdmg)_2 + H_2O, \qquad [4]$$

and the third mole (from +1 to +2) is considered to cause the formation of the 1:1 complex:

$$\tfrac{1}{2}\ Cu^{2+} + \tfrac{1}{2}\ Cu(Hdmg)_2 + OH^- \rightarrow Cu(Hdmg)(OH) + H_2O. \qquad [5]$$

The overall reaction (from 0 to +2) is therefore:

$$Cu^{2+} + H_2dmg + 2\ OH^- \rightarrow Cu(Hdmg)(OH) + H_2O. \qquad [6]$$

Thus, the addition of an excess of 2 mole NaOH for every initial mole of Cu^{2+} will take Reaction [6] to completion by removing two moles of protons.

The investigations performed pursuant to this thesis

provide evidence which suggests that the species which Morpurgo and Tomlinson have classified as a 1:1 complex is in fact a 2:1 complex. Thus, it is necessary to offer an alternative explanation of the end-point obtained by Morpurgo and Tomlinson in terms of a 2:1 complex. This can be done by assuming that this complex has the formula $Cu_2dmg(OH)_2$. Thus an alternative to Reaction [6] is the following:

$$3\ Cu^{2+} + 3\ H_2dmg + 6\ OH^- \rightarrow Cu(Hdmg)_2 + Cu_2dmg(OH)_2 + 4\ H_2O \quad [7]$$

The stoichiometric ratio of Cu^{2+} to H_2dmg is 1:1 and again two protons need to be removed by OH^- ions per mole of Cu^{2+}. It should be realized that Reaction [7] describes the overall reaction. As base is added, the 1:2 complex will first be formed as an intermediate. This intermediate will then react with further Cu^{2+} to form the 2:1 complex. A two-step process like this is clearly indicated by the two points of inflection shown in Figure 27.

Although the 2:1 complex has been formulated as $Cu_2dmg(OH)_2$ based on the findings of this study, there is still the possibility that this complex could be a dimer or a trimer, with the same stoichiometry. The results obtained in the experiments investigating the variation of absorbance with pH shown in Figure 24 strongly support the supposition that the 2:1 complex actually contains four copper atoms rather than two. Evidence for this is shown in Figure 28. The points in this figure are those obtained using a MOPS buffer, and are one of the runs shown in Figure 24. The line in this

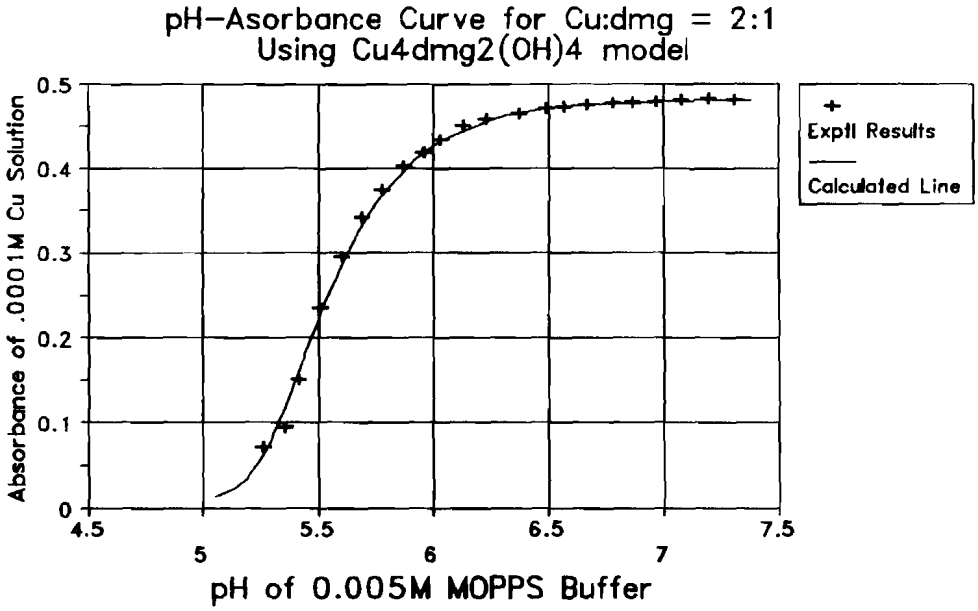

Figure 28: pH-Absorbance Curve for Cu:dmg = 2:1 Using $Cu_4(dmg)_2(OH)_4$ Model

figure has been calculated using a spreadsheet assuming the equilibrium to be as follows:

$$Cu(Hdmg)_2 + 3\ Cu^{2+} + 4\ H_2O \rightleftharpoons Cu_4dmg_2(OH)_4 + 6\ H^+, \quad [8]$$

and using a value of 1.5×10^{-21} for the equilibrium constant. Also used were the values $A_{12} = 0.009$, and $A_{42} = 0.481$ where A_{12} is the value the absorbance would have if the only Cu(II) species present were the 1:2 complex, while A_{42} is the absorbance if only the 2:1 complex were present. A good fit with the experimental results is obtained.

By contrast Figure 29 shows the best curve obtained assuming that the 2:1 species contains only two copper atoms and that the equilibrium is represented by the following:

$$Cu(Hdmg)_2 + 3\ Cu^{2+} + 4\ H_2O \rightleftharpoons 2\ Cu_2dmg(OH)_2 + 6\ H^+. \quad [9]$$

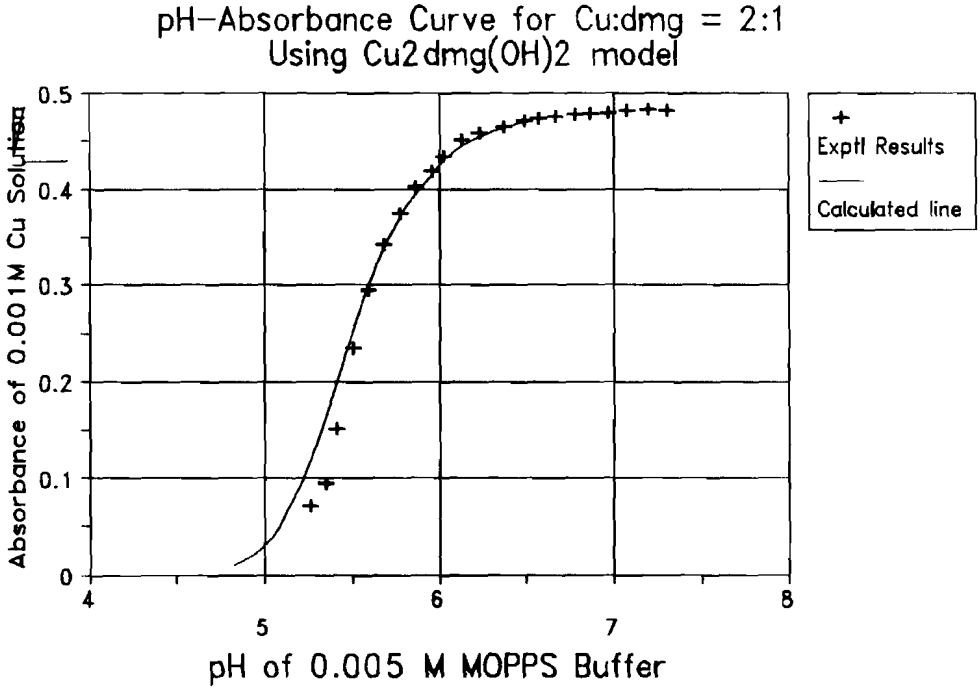

Figure 29: pH - Absorbance Curve for Cu : dmg = 2:1 using $Cu_2dmg(OH)_2$ Model

Here the curve could only be fitted to the experimental points when the pH is greater than about 5.6 and using the value of 3×10^{-25} as equilibrium constant for the reaction. The four points of lowest absorbance are not well accounted for by this model.

As can be seen from Figure 24, the results obtained using a 0.005 M EPPS buffer were similar, but not identical, to those obtained using a 0.005 M MOPS buffer. This discrepancy could possibly be due to differences in ionic strength, or perhaps small specific effect of the buffer.

Of much more concern is the lack of agreement between

these pH-absorbance results and those obtained in the photometric titrations. Both sets of experiments involved the same eventual total Cu(II) concentration, namely 2.00×10^{-4} M, and both involved what was presumably the same eventual concentration of the same 2:1 complex. Nevertheless, both the MOPS and EPPS buffers give a final absorbance of only 0.48, while in the photometric titrations shown in Figures 11 through 21 (and also in the reverse titration of Figure 22) the absorbance is above 0.5 with only one exception (Figure 11). A difference of this magnitude is much larger than the precision of the instrument (0.002 Absorbance Units).

There is a second aspect to the discrepancy between the findings of the two experimental methods. The pH-dependence experiments suggest that above a pH of 7 the absorbance of solutions with a Cu : dmg ratio of 2 : 1 or greater should be virtually independent of pH, though perhaps slightly dependent on the buffer. The photometric titration results, by contrast, do not give a clear picture. The absorbance of the final, horizontal, portion of the titration appears to change with pH, but not in any systematic fashion..

How can this discrepancy be explained? It is suggested here that basically all of the three-segment plots obtained between pH 7 and pH 9 as shown in Figures 11 to 19 should actually be the same. The experimental differences obtained between them should be regarded as artifacts. Two suggestions are offered to explain the variations from one titration to

another. The first is the possibility that this variation is associated with the slowness of the reaction accompanying the second segment of the titration. It could be that if the titration is performed too fast, this reaction is inhibited and unable to come to its true equilibrium value.

A second explanation for these variations is a change in the light intensity with time. A dipping probe photometer is essentially a single-beam instrument. If the light intensity increases or decreases during the course of the titration, the absorbance reading will vary from the true value. The cause of such a variation could be the power supply, or it could be due to the fact that the tungsten lamp was in need of replacement. Unfortunately, the possibility of this source of error was only realized during the very last titration performed when the instrument was deliberately left on overnight, and it was found that the 100% transmission reading had changed.

It should be noted that the occurrence of this variability from one run to another in no way detracts from the stoichiometric results obtained from these titrations. The final absorbance, and the slope of the lines may be affected, but the position of the sudden changes in slope are not. The occurrence of the two discontinuities at 1 mL and 4 mL under a variety if circumstances is direct and compelling evidence of the existence not only of the already-established 1:2 complex, but also of the previously unknown 2:1 complex as

well.

4.2 SUGGESTIONS FOR FURTHER WORK

The work described in this thesis seems to result in a contradiction. Although the existence of a 1:1 precipitate has been confirmed here, considerable doubt has been cast on the existence of a complex with this stoichiometry in solution. Instead of confirming the 1:1 complex, this work has uncovered strong evidence for the existence of a 2:1 complex in solution. The clarification of this apparent dichotomy suggests at least three lines of further investigation.

The first line of investigation should be an attempt to obtain a crystalline sample of the amorphous grey-green precipitate which settles out so readily from many of these solutions. The structure of this 1:1 compound could then be established by X-ray diffraction. Several approaches to obtaining crystals are possible. Since homogeneous precipitation has been used successfully to produce crystals of nickel dimethylglyoxime, the same technique could prove successful here as well. Alternatively, attempts could be made to find a solvent for the precipitate from which crystals could then be obtained.

An attempt should also be made to crystallize out the yellow 2:1 complex. This may not be easy. Experience gained in this investigation suggests that when concentrated

solutions of Cu(II) and Na_2dmg are mixed, a grey-green precipitate, presumably with a 1:1 stoichiometry, is almost always obtained. Nevertheless, an attempt should be made. If crystal of this composition could be obtained and subjected to X-ray diffraction analysis, the existence of the 2:1 complex would be much more firmly established.

A second line of investigation which is worth pursuing is to monitor the pH during the titration of Cu(II) : dmg mixtures with NaOH. As has already been mentioned, work of this nature has already been performed by Morpurgo and Tomlinson. Some of their results are given in Figure 27. The work suggested here would expand Morpurgo and Tomlinson's work in two ways. In the first place, the absorbance as well as the pH would be monitored. In the second place, titrations would be performed on solutions in which the Cu(II) : dmg ratio is 2:1. If we assume , in conformity with the work described in this thesis, that a 2:1 complex exists, then the overall reaction will be:

$$2\ Cu^{2+} + H_2dmg + 4\ OH^- \rightarrow Cu_2dmg(OH)_2 + 2\ H_2O$$

and two OH^- ions will consumed per Cu^{2+} ion. On the other hand, employing the Morpurgo and Tomlinson model yields the equation

$$2\ Cu^{2+} + H_2dmg + 2\ OH^- \rightarrow Cu^{2+} + Cu(Hdmg)OH + H_2O$$

in which only one OH^- is consumed per Cu^{2+} ion. Almost certainly, this reaction will be followed by the precipitation of $Cu(OH)_2$ on the addition of further NaOH:

$$Cu^{2+} + 2\ OH^- \rightarrow Cu(OH)_2.$$

Titration of a 2:1 mixture with NaOH in this way would enable a clear distinction to be made between the two models. At the same time, the data from these titrations would enable evaluations of the appropriate equilibrium constants to be made.

The third line of investigation suggested here is the extension of photometric investigations to wavelengths other than 430 nm. It would be much more convincing if the 2:1 complex model could be shown to apply at other wavelengths. Further investigations should certainly involve the use of a UV-visible spectrophotometer. In particular, the ultraviolet region should be explored. This region is unavailable to the dipping probe colorimeter used above, but it is eminently worth exploring because Cu(II)-dimethylglyoxime complexes absorb more strongly in the ultraviolet than in the visible. A major difficulty in the pursuit of these investigations is the lack of a temperature-controlled cell-holder in the otherwise excellent GCA-McPherson spectrophotometer owned by the Chemistry Department at Emporia State University.

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Qihua Hu

Signature of Author

July 28, 1992

Date

Titrimetric Studies of Cu(II)-dimethylglyoxime Complexes in Solution

Title of Thesis

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