INFRARED SPECTRAL AND MAGNETIC PROPERTIES OF BASIC COPPER(II) NITRATE PRODUCED BY SLOW TITRATION METHOD

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ABSTRACT The main purposes for this work are to formulate and characterize the infrared (IR) and magnetic moment of the compounds resulted from the slow titration of copper(II) nitrate with sodium hydroxide and in the reverse procedures in an aqueous solution. The titration is carried out with various concentrations and at a constant temperature, ~ 19 ^{o}C, and monitored using *p*H meter with the rate of the titration~ 1 mL per minute. The corresponding data of change in mole ratio of Cu^{2+}/OH^{-} against *p*H reveals that the end point of the titration occurs at *p*H about 8, leading to stoichiometry formula, $3Cu(NO_3)_2{\cdot}5Cu(OH)_2$, but $Cu(NO_3)_2{\cdot}5Cu(OH)_2$ in the reverse procedure (OH^{-}/Cu^{2+}). The pale blue for the former but deep blue compounds were isolated and then characterized IR spectroscopy and magnetic moment. Both compounds containing nitrate ion are evident from the corresponding IR spectra, and their magnetic moment values which were found in the range of 1.7-1.9 BM, are to be normal for copper(II) salt corresponding to one unpaired electron in the electronic configuration.

Keywords: Slow titration, copper(II), nitrate-hydroxide, infrared, magnetic moment.

1. INTRODUCTION

One of the common qualitative tests for the presence of copper(II) is the formation of blue deposits on the addition of bases, for example, NaOH. This simply blue precipitate is often commonly identified as $Cu(OH)_2$, which on further heating produces a black precipitate CuO. However, by careful observation on the reversed order of addition, a slight deep blue color is observed. Therefore, it comes to believe that the two slightly different blue colors of the two products due to a different order of addition should result in the different chemical formula. It is the idea that leads us to perform the study, which is to be the main objective to determine the compounds by slow titration.

It has been well known for years that the blue minerals of basic copper(II) nitrate of *gerhardtite*, Orthorhombic-Disphenoidal (http://webmineral.com/data/Gerhardtite.shtml; Bovio & Locchi, 1982) and *Rouaite*, Monoclinic-Sphenoidal (http://webmineral.com/data/Rouaite.shtml#.X_ubsRZS_v8; Ramesh & Madhu. 2015);

both contain $Cu(NO_3)_2 \cdot 3Cu(OH)_2$, while *likasite* contains $Cu(NO_3)_2 \cdot 5Cu(OH)_2$ (https://www.mindat.org/min-2399.html; Effenberger, 1986). The syntheses for the three members of the copper(II) hydroxyl nitrate family and the corresponding Powder-XRD, have been reported by Yoder, et al. (2010). The first time preparation of *gerhardtite* might be reported by Cumming and Gemmell (1913) and thermal investigation of *gerhardtite* has also been reported (Ilcheva et al., 1979), while Aguirre et al. (2011) reported simple route for the preparation of copper(II) hydroxyl salt, $Cu(NO_3)_2 \cdot 3Cu(OH)_2$, by the reaction of copper(II) nitrate trihydrate with $Mg(OH)_2$.

Thus, it is possible that the mixing solution of copper(II) nitrate with hydroxide might contain basic copper(II) nitrate. Since the characteristics of the copper(II) compound is determined mainly by the role of the $3d^9$ electronic configuration, the magnetic moment which corresponds to the one unpaired electron ranging about 1.7-2.0 BM is an indicative parameter (Cotton & Wilkinson, 1972; Day and Selbin, 1969; and Figgis, 1966). Moreover, the typical infrared of the corresponding nitrate might support its anionic presence. For these reasons, the reaction of copper(II) nitrate and sodium hydroxide in aqueous solution by slow reaction as reported by King and Cooper (1965) for copper(II) sulfate was performed and the results are reported.

2. EXPERIMENTAL METHODS

2.1 Materials

The common chemicals, $Cu(NO_3)_2 \cdot 3H_2O$, and NaOH were purchased from Aldrich and used as they are received.

2.2 Preparation of samples

In principle, the samples were prepared according to slow reaction method (King & Cooper, 1965; Tanaka & Koga, 1990), which involved two stages:
(1) Copper(II) nitrate solution (20 mL, *x* M; *x* = 0.2, 0.3, and 0.4) was titrated slowly (~ 1 mL/min.) with a solution of NaOH of the similar concentration with continuously stirring at about 19 ^oC. The titration was monitored by recording *p*H of the solution mixture on the volume of NaOH added (0.5 mL). Upon completion of the titration at pH ≈ 8, the pale blue precipitate that occurs was filtered, washed with water three times then dried on aeration at ≤ 60 ^0C and stored over silica gel in a desiccator.
(2) Conversely, the similar concentration but on the reverse titration procedure was performed. Thus, Na(OH) solution (20 mL, *x* M; *x* = 0.2, 0.3, and 0.4) was titrated slowly (~ 1 mL/min.) with a solution of copper(II) nitrate of the similar concentration with continuously stirring at about 19 ^oC. Upon completion of the titration at pH ≈ 8, the deep blue precipitate that occurs was filtered, washed with water, and then dried on aeration at ≤ 60 ^0C and stored over silica gel in a desiccator.

2.3 Characterization of Samples

Infrared spectrum. The (pale blue) powder compound (with KBr-pellet) was ground and pressed into the cell, then the spectrum is recorded within the range 500 - 4000 cm^{-1} on an Infrared Spectrophotometer.

Magnetic moment. The method of measuring magnetic moments follows the steps adopted from the manual for the

Department of Inorganic Chemistry, The School of Chemistry, UNSW. The balance is mounted on a table with a hole. Through this hole, a magnet-free chain of about 80 cm long is suspended from the bottom of the balance and protected by a glass tube casing. The sample powder which has been packed as tightly as possible in about 5 cm long Gouy tube (exactly to the spout mark) was then weighed with and without the influence of magnetic field. The molar susceptibility, χ_M, was calculated from the mass difference value, the tube calibration parameter, and the diamagnetic correction value of the compound calculated according to Pascal's constant (Figgis & Lewis, 1960). The magnetic moment value, μ_{ef}, was calculated according to the formula, $\mu_{ef} = 2.828 \sqrt{(\chi_M.T)}$ BM, where T = temperature (K) of sample.

3. RESULTS AND DISCUSSION

3.1 The Compund Produced According to Reaction Stoichiometry

The reaction between the copper(II) nitrate solution (0.2, 0.3, and 0.4 M) and the NaOH solution (0.2, 0.3, and 0.4 M) were performed by gradual titration at ~ 19 ^oC produce a pale blue fine precipitate. The typical relationship data between *p*H of the solution mixture and the mol ratio of Cu^{2+} titrated with OH^- at slow rate of titration are collected in **Table S1** (Appendix) and the typical curve is shown in **Figure 1.** While those of the reverse, OH^- titrated with $Cu^{2+,}$ are collected in **Table S2** (Appendix), and the corresponding typical curve are shown in **Figure 2**. Both, show a mid equivalence point of titration curve at *p*H ≈ 8.0 with the mol ratio ≈ 1.25 (OH^-/Cu^{2+}), and ≈ 0.6 (Cu^{2+}/OH^-), respectively. This suggests that the precipitation of reaction is considered to complete at pH ≈ 8.0. Therefore, the empirical formula proposed for the pale blue precipitates might be estimated by stoichiometry method (King and Cooper, 1965) as $3Cu(NO_3)_2{\cdot}5Cu(OH)_2$, and $Cu(NO_3)_2{\cdot}5Cu(OH)_2$, respectively, neglecting the presence of hydrate.

Indeed, the syntheses of family of basic copper(II) nitrate salts have been reported about hundred years ago, $Cu(NO_3)_2{\cdot}3Cu(OH)_2$ prepared from heating the trihydrate copper(II) nitrate (Cumming & Gemmell, 1913; Shiota et al., 2015). This is known as *gerardtite* or *rouaite* (Frost et al., 2005). While, $Cu(NO_3)_2{\cdot}5Cu(OH)_2$ is known as *likasite* (Frost et al., 2005) which has also been prepared (together with *gerardite* and *rouaite*) by Yoder et al. (2010). It was synthesized by slow addition (1 mL/min) of 50 mL of 0.1 M NaOH to a mixture of 30 mL of 0.1 M copper(II) acetate and 10 mL of 0.1 M sodium nitrate with stirring for about 20 h. From the study, it has been reported that *gerhardtite* is the most stable at room temperature, while the detailed thermal stability of this compound has also been reported (Ilcheva, Maneva & Bozadziev, 1979). However, we surprisingly obtain the formula *likasite* in our work *via* titrating NaOH with $Cu(NO_3)_2$ procedure in an aqueous solution. On the reverse procedure, however, to the best of our knowledge, titrating $Cu(NO_3)_2$ with NaOH results in the "new" basic copper(II) nitrate compound, $3Cu(NO_3)_2{\cdot}5Cu(OH)_2$, which has not been reported at all by anyone.

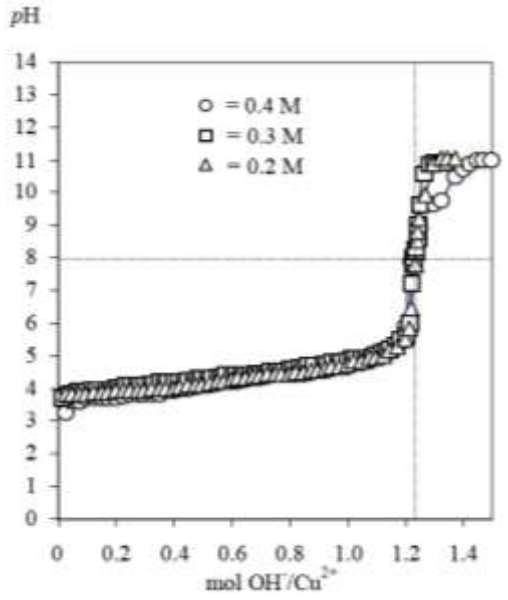

Figure 1. Changes in *p*H on the titration of 20 mL $Cu(NO_3)_2$ solution with NaOH (0.2, 0.3 and 0.4 M) on a rate of ~ 1 mL/minute at ~ 19 ºC.

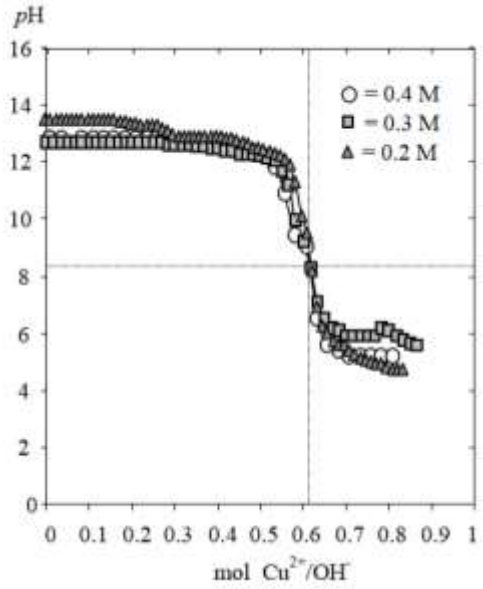

Figure 2. Changes in *p*H on the titration of 20 mL NaOH solution with $Cu(NO_3)_2$ (0.2, 0.3 and 0.4 M) on a rate of ~ 1 mL/minute at ~ 19 ºC

3.2 Infrared Spectrum

Theoretically, there are four normal modes for free nitrate ions (group D_{3h}) such as KNO_3, namely stretching symmetry, ν_1 (A_1'), *out of plane*, ν_2 (A_2''), stretching asymmetry, ν_3 (E'), and *in-plane* bands, ν_4 (E'), which appears the widest and strongest while the other three are very weak. Of the four kinds of normal modes, only the first is inactive in the IR spectrum (Cross, 1960; Nakamoto, 1997). The four normal modes are identified at the range of 700-1500 cm^{-1}, being at ~ 1000 cm^{-1}, 831 cm^{-1}, 1310 cm^{-1}, and 720 cm^{-1}, respectively.

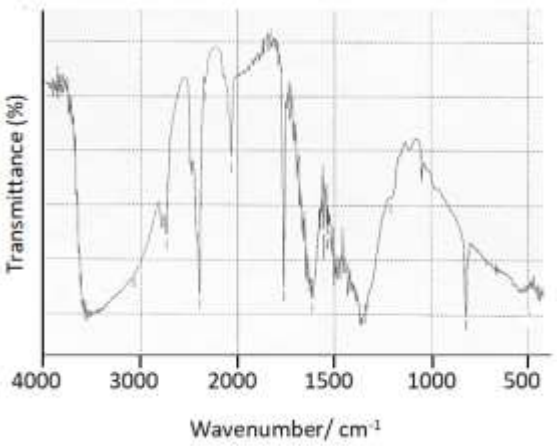

Figure 3. IR spectrum of $Cu(NO_3)_2 \cdot 3H_2O$

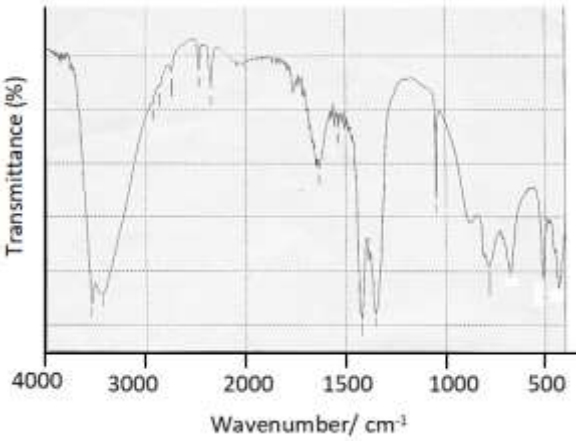

Figure 4. IR spectrum of $3Cu(NO_3)_2 \cdot 5Cu(OH)_2$

The IR of $Cu(NO_3)_2 \cdot 3H_2O$, as a reference, shown in **Figure 3** is expected to reveal the anionic characteristics of the nitrate. The wide absorption at ~ 1350 cm^{-1} is assigned as a normal mode of asymmetric stretching, ν_3 (*E*'), the sharp absorption at ~810 cm^{-1} as a normal mode of *out of plane*band, ν_2 (A_2''), while *in-plane* band, ν_4 (*E*') is not detected, and the stretching symmetry, ν_1 (A_1') shows its trace at ~ 1050 cm^{-1}.

But for coordinated nitrate ions (group C_{2v}), stretching symmetry, ν_1 (A_1') becomes active and generally occurs at ~ 970-1034 cm^{-1}, the *out of plane* band, ν_2 (A_2''), is shifted slightly lower, 780-810 cm^{-1}, stretching asymmetry, ν_3 (*E*'), is cleaved into two bands at position ~ 1250-1531 cm^{-1}, likewise, the *in-plane* band, ν_4 (*E*'), undergoes cleavage [Cross, 1960; Nakamoto, 1997]. Thus the nitrate ion in copper(II) nitrate seems very likely to show minor coordination.

Both compounds, $3Cu(NO_3)_2 \cdot 5Cu(OH)_2$ and $Cu(NO_3)_2 \cdot 5Cu(OH)_2$, show the same IR spectrum as shown in **Figure 4**. Relative to the spectrum of **Figure 3**, **Figure 4** reveals the presence of very strong split bands ν_3 (*E*') at ~ 1350 cm^{-1} and 1420 cm^{-1}, a very sharp band, ν_1 (A_1') at ~ 1050 cm^{-1}, strong band, ν_2 (A_2'') which shifted slightly lower at ~ 800 cm^{-1}, and the split band ν_4 (*E*') at 500 - 700 cm^{-1}. Thus, it is very clear that there is a nitrate ion in the precipitate from the dropwise reaction between a solution of copper(II) nitrate and sodium hydroxide, and this nitrate ion is probably to be bound in coordination with the metal ion, Cu^{2+}.

3.3 Magnetic Property

For the basic copper(II) nitrate salt from the reaction of copper(II) nitrate with the addition of dropwise sodium hydroxide, $3Cu(NO_3)_2 \cdot 5Cu(OH)_2$ - Samples 1-3, all samples are paramagnetic with a magnetic moment of about 1.95 - 1.97 BM (**Table 1**). While for the salt produced from the reverse procedure reaction, $Cu(NO_3)_2 \cdot 5Cu(OH)_2$ - Sample 4-6, they are paramagnetic with the slightly lower magnetic moment of ~ 1.73-1.76 BM. These are normal paramagnetic for spin-only value for Cu^{2+} species, but with a

small orbital contribution for $3Cu(NO_3)_2{\cdot}5Cu(OH)_2$, and this is mostly found in Cu(II) species which have an observed range moments of 1.7 - 2.2. BM (Day & Selbin, 1969). Theoretically, the value of the spin only magnetic moment, μ_s, for the d^9 system is, 1.73 BM and with the full orbital contribution, $\mu_{(S+L)}$ is 3.0 BM (Mabbs & Machin, 1973). Thus, values of the magnetic moment found in this work confirm strongly the presence of copper(II) in the two compounds.

Table 1. Magnetic moment of basic copper(II) nitrate

Sample	Formula	T/K	$\chi_M/10^{-6}$ per Cu^{2+}	μ_{ef} /BM
1 (0.2M)	$3Cu(NO_3)_2{\cdot}5Cu(OH)_2$	294	1628	1.97
2 (0.3M)	$3Cu(NO_3)_2{\cdot}5Cu(OH)_2$	295	1595	1.95
3 (0.4M)	$3Cu(NO_3)_2{\cdot}5Cu(OH)_2$	296	1591	1.95
4 (0.2M)	$Cu(NO_3)_2{\cdot}5Cu(OH)_2$	294	1257	1.73
5 (0.3M)	$Cu(NO_3)_2{\cdot}5Cu(OH)_2$	296	1270	1.74
6 (0.4M)	$Cu(NO_3)_2{\cdot}5Cu(OH)_2$	296	1304	1.76

4. CONCLUSION

The slow titration between the copper(II) nitrate and NaOH in solution produces the pale-blue solid basic copper(II) nitrate. The addition of NaOH solution to $Cu(NO_3)_2$ solution dropwise at a rate of about 1 mL per minute at ~ 19 ºC produces pale blue compound. The precipitation of reaction is considered to complete at *p*H ≈ 8, and it is estimated as $3Cu(NO_3)_2{\cdot}5Cu(OH)_2$. In the reverse procedure of titration, the precipitation of blue solid compound which is also complete at *p*H ≈ 8 is estimated as $Cu(NO_3)_2{\cdot}5Cu(OH)_2$. The magnetic moment of the two compounds are normal paramagnet corresponding to one unpaired electron with a small orbital contribution observed in Cu(II). The infrared spectrum indeed reveals the presence of a nitrate group which is very likely to be coordinated to the copper(II) ion in each of the salts.

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APPENDIX

Table S1. Data of change in pH of solution on the titration of x M $Cu(NO_3)_2$ with x M NaOH solution (x = 0.2 ; 0.3 ; 0.4) at rate of 1mL/min at ~19 ^oC

20 mL 0.4 M $Cu(NO_3)_2$ + x mL 0.4 M NaOH			20 mL 0.3 M $Cu(NO_3)_2$ + x mL 0.3 M NaOH			30 mL 0.2 M $Cu(NO_3)_2$ + x mL 0.2 M NaOH					
		mol			mol			mol			mol
*p*H	x	OH^-/Cu^{2+}	*p*H	x	OH^-/Cu^{2+}	*p*H	x	OH^-/Cu^{2+}	*p*H	x	OH^-/Cu^{2+}
3.25	0.5	0.025	3.8	0.5	0.025	3.7	0.5	0.017	4.9	30.5	1.017
3.6	1	0.05	3.8	1	0.05	3.8	1	0.033	4.9	31	1.03
3.6	1.5	0.075	3.8	1.5	0.075	3.85	1.5	0.05	4.95	31.5	1.05
3.7	2	0.1	3.8	2	0.1	3.9	2	0.067	4.95	32	1.067
3.7	2.5	0.125	3.85	2.5	0.125	3.9	2.5	0.083	5	32.5	1.083
3.7	3	0.15	3.85	3	0.15	3.9	3	0.1	5.05	33	1.1
3.7	3.5	0.175	3.85	3.5	0.175	3.95	3.5	0.117	5.1	33.5	1.117
3.7	4	0.2	3.9	4	0.2	4	4	0.133	5.15	34	1.133
3.75	4.5	0.225	3.9	4.5	0.225	4	4.5	0.15	5.2	34.5	1.15
3.8	5	0.25	3.9	5	0.25	4	5	0.167	5.3	35	1.167
3.8	5.5	0.275	3.9	5.5	0.275	4	5.5	0.183	5.5	35.5	1.183
3.8	6	0.3	3.9	6	0.3	4.05	6	0.2	5.6	36	1.2
3.8	6.5	0.325	3.95	6.5	0.325	4.05	6.5	0.217	6	36.5	1.217
3.8	7	0.35	4	7	0.35	4.1	7	0.233	7.2	36.8	1.2267
3.9	7.5	0.375	4	7.5	0.375	4.1	7.5	0.25	7.8	36.9	1.23
3.9	8	0.4	4	8	0.4	4.1	8	0.267	7.9	36.95	1.232
3.95	8.5	0.425	4.05	8.5	0.425	4.1	8.5	0.283	8	37	1.233
4	9	0.45	4.1	9	0.45	4.1	9	0.3	8.2	37.1	1.237
4.05	9.5	0.475	4.1	9.5	0.475	4.15	9.5	0.317	8.3	37.15	1.238
4.1	10	0.5	4.1	10	0.5	4.15	10	0.333	8.6	37.3	1.243
4.1	10.5	0.525	4.15	10.5	0.525	4.2	10.5	0.35	9	37.4	1.247
4.15	11	0.55	4.2	11	0.55	4.2	11	0.367	9.65	37.5	1.25
4.2	11.5	0.575	4.2	11.5	0.575	4.2	11.5	0.383	10.6	38	1.267
4.2	12	0.6	4.25	12	0.6	4.2	12	0.4	10.9	38.5	1.283
4.2	12.5	0.625	4.3	12.5	0.625	4.2	12.5	0.417	10.9	39	1.3
4.25	13	0.65	4.3	13	0.65	4.2	13	0.433	10.9	39.5	1.317
4.3	13.5	0.675	4.35	13.5	0.675	4.25	13.5	0.45	10.9	40	1.333
4.3	14	0.7	4.35	14	0.7	4.25	14	0.467			
4.35	14.5	0.725	4.4	14.5	0.725	4.3	14.5	0.483			
4.4	15	0.75	4.4	15	0.75	4.3	15	0.5			
4.4	15.5	0.775	4.45	15.5	0.775	4.3	15.5	0.517			
4.4	16	0.8	4.45	16	0.8	4.3	16	0.533			
4.45	16.5	0.825	4.5	16.5	0.825	4.35	16.5	0.55			
4.45	17	0.85	4.5	17	0.85	4.35	17	0.567			
4.5	17.5	0.875	4.55	17.5	0.875	4.4	17.5	0.583			
4.55	18	0.9	4.55	18	0.9	4.45	18	0.6			
4.55	18.5	0.925	4.6	18.5	0.925	4.45	18.5	0.617			
4.6	19	0.95	4.65	19	0.95	4.45	19	0.633			
4.65	19.5	0.975	4.65	19.5	0.975	4.45	19.5	0.65			
4.65	20	1	4.7	20	1	4.45	20	0.667			
4.75	20.5	1.025	4.8	20.5	1.025	4.5	20.5	0.683			
4.75	21	1.05	4.8	21	1.05	4.5	21	0.7			
4.8	21.5	1.075	4.9	21.5	1.075	4.5	21.5	0.717			
4.9	22	1.1	4.95	22	1.1	4.55	22	0.733			
5	22.5	1.125	5	22.5	1.125	4.55	22.5	0.75			

5.1	23	1.15	5.15	23	1.15	4.55	23	0.767
5.35	23.5	1.175	5.25	23.5	1.175	4.55	23.5	0.783
5.9	24	1.2	5.5	24	1.2	4.6	24	0.8
7.9	24.5	1.225	5.8	24.3	1.215	4.6	24.5	0.817
8.9	25	1.25	6.45	24.5	1.225	4.65	25	0.833
9.65	25.5	1.275	7.8	24.8	1.24	4.65	25.5	0.85
9.65	26	1.3	8.5	24.9	1.245	4.7	26	0.867
9.75	26.5	1.325	8.8	24.95	1.2475	4.7	26.5	0.883
10.45	27.5	1.375	9.2	25	1.25	4.75	27.5	0.917
10.7	28	1.4	9.9	25.5	1.275	4.75	28	0.933
10.85	28.5	1.425	10.85	26	1.3	4.8	28.5	0.95
10.95	29	1.45	11.05	26.5	1.325	4.8	29	0.967
10.95	29.5	1.475	11.05	27	1.35	4.8	29.5	0.983
11	30	1.5	11.05	27.5	1.375	4.85	30	1

Table S2. Data of change in pH of solution on the titration of *x* M NaOH with*x* M $Cu(NO_3)_2$ solution (*x* = 0.2; 0.3; 0.4) at rate of 1mL/min at ~19 ^oC

20 mL of 0.4 M NaOH + *x* mL 0.4 M Cu^{2+}			30 mL of 0.3 M NaOH +*x* mL 0.3 M Cu^{2+}						40 mL of NaOH. 0.2 M + *x* mL 0.2 M Cu^{2+}					
		mol			mol			mol			mol			mol
*p*H	*x*	Cu^{2+}/OH^-	*p*H	*x*	Cu^{2+}/OH^-	*p*H	*x*	Cu^{2+}/OH^-	*p*H	*x*	Cu^{2+}/OH^-	*p*H	*x*	Cu^{2+}/OH^-
12.8	0	0	12.7	0	0	11.7	17	0.566	13.45	0	0	12.9	17	0.425
12.8	0.5	0.025	12.7	0.5	0.016	11.2	17.5	0.583	13.45	0.5	0.012	12.8	17.5	0.437
12.8	1	0.05	12.7	1	0.033	9.95	18	0.6	13.45	1	0.025	12.8	18	0.45
12.8	0.5	0.025	12.7	1.5	0.05	9.2	18.5	0.616	13.45	1.5	0.037	12.75	18.5	0.462
12.8	2	0.1	12.7	2	0.066	8.3	19	0.633	13.45	2	0.05	12.7	19	0.475
12.8	2.5	0.125	12.7	2.5	0.083	7.1	19.5	0.65	13.45	2.5	0.062	12.6	19.5	0.487
12.8	3	0.15	12.7	3	0.1	6.5	20	0.666	13.45	3	0.075	12.5	20	0.5
12.8	3.5	0.175	12.7	3.5	0.116	6.2	20.5	0.683	13.45	3.5	0.087	12.45	20.5	0.512
12.8	4	0.2	12.7	4	0.133	6.1	21	0.7	13.45	4	0.1	12.4	21	0.525
12.8	4.5	0.225	12.7	4.5	0.15	5.9	21.5	0.716	13.45	4.5	0.112	12.35	21.5	0.537
12.8	5	0.25	12.7	5	0.166	5.9	22	0.733	13.45	5	0.125	12.3	22	0.55
12.8	5.5	0.275	12.7	5.5	0.183	5.9	22.5	0.75	13.45	5.5	0.1375	12.2	22.5	0.562
12.8	6	0.3	12.7	6	0.2	5.9	23	0.766	13.45	6	0.15	12.1	23	0.575
12.7	6.5	0.325	12.7	6.5	0.216	5.9	23.5	0.783	13.45	6.5	0.1625	11.9	23.5	0.587
12.7	7	0.35	12.7	7	0.233	6.2	24	0.8	13.45	7	0.175	11.3	24	0.6
12.65	7.5	0.375	12.65	7.5	0.25	6.1	24.5	0.816	13.4	7.5	0.187	10.1	24.5	0.612
12.6	8	0.4	12.65	8	0.266	5.9	25	0.833	13.4	8	0.2	9.5	25	0.625
12.55	8.5	0.425	12.65	8.5	0.283	5.8	25.5	0.85	13.35	8.5	0.212	8.15	25.5	0.637
12.4	9	0.45	12.6	9	0.3	5.65	26	0.867	13.35	9	0.225	6.9	26	0.65
12.4	9.5	0.475	12.6	9.5	0.316	5.6	26.5	0.883	13.3	9.5	0.237	6.25	26.5	0.662
12.3	10	0.5	12.6	10	0.333				13.3	10	0.25	5.95	27	0.675
12.2	10.5	0.525	12.6	10.5	0.35				13.3	10.5	0.262	5.7	27.5	0.687
11.85	11	0.55	12.55	11	0.366				13.25	11	0.275	5.6	28	0.7
10.9	11.5	0.575	12.55	11.5	0.383				13.15	11.5	0.287	5.55	28.5	0.712
9.4	12	0.6	12.5	12	0.4				13.05	12	0.3	5.4	29	0.725
9.05	12.5	0.625	12.45	12.5	0.416				12.95	12.5	0.312	5.25	29.5	0.737
6.5	13	0.65	12.4	13	0.433				12.9	13	0.325	5.1	30	0.75
5.6	13.5	0.675	12.4	13.5	0.45				12.9	13.5	0.337	5.05	30.5	0.762
5.4	14	0.7	12.3	14	0.466				12.9	14	0.35	4.95	31	0.775

5.2	14.5	0.725	12.3	14.5	0.483	12.9	14.5	0.362	4.9	31.5	0.787
5.2	15	0.75	12.3	15	0.5	12.9	15	0.375	4.9	32	0.8
5.2	15.5	0.775	12.2	15.5	0.516	12.9	15.5	0.387	4.8	32.5	0.812
5.2	16	0.8	12.15	16	0.533	12.9	16	0.4	4.7	33	0.825
5.2	16.5	0.825	12.1	16.5	0.55	12.9	16.5	0.412	4.7	33.5	0.837
									4.7	34	0.85