The Spectrophotometric Determination of Copper with Bis-3,3'-(5,6-Dimethyl-1,2,4-Triazine)

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The Spectrophotometric Determination of Copper with Bis-3,3'-(5,6-Dimethyl-1,2,4-Triazine)[1]

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Abstract. A new reagent, bis-3,3'-(5,6-dimethyl-1,2,4-tri-azine), BDMT, is proposed for the colorimetric determination of copper. The reagent is water soluble and is easily prepared in the laboratory. An intensively colored orange complex, $Cu(BDMT)_2^{+1}$, is formed upon reaction of copper(I) ion and the reagent in aqueous solution at pH 5.0. The complex exhibits a wavelength of maximum absorption at 444 mμ with a molar absorptivity of 9,700. The perchlorate salt of the complex is readily extracted into nitrobenzene from aqueous solution. A proposed spectrophotometric method for the determination of copper is both accurate and precise.

Shortly after the wide acceptance of 1,10-phenanthroline as a colorimetric reagent for iron, interest in this type of polyamine was reflected by the synthesis of various new compounds containing the ferroin group. Many of these new compounds were merely substituted 1,10-phenanthrolines which were later found to be ideal reagents for the colorimetric determination of copper(I) ion. Among these, the most sensitive reagent for copper(I) is 2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline (6). Other popular reagents for copper(I) ion are cuproine;2,2'-biquinoline (1) and neocuproine; 2,9-dimethyl-1,10-phenanthroline (5).
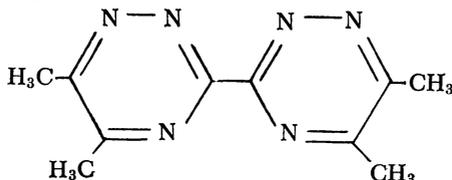
Bis-3,3'-(5,6-dimethyl-1, 2,4-triazine)

Although there is only one reference to bis-3,3'-(5,6-dimethyl-1,2,4-triazine) in the literature (2), the compound has interesting possibilities as an analytical reagent. The multiplicity of nitrogen atoms in positions suitable for metal ion coordination is readily recognizable. It will be shown in this work that this compound fulfills every expectation as a spectrophotometric reagent for copper.

EXPERIMENTAL

Apparatus and Reagents

All absorbance measurements were made with a Cary Model

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14 recording spectrophotometer. Matched silica cells, 1.00 cm., were used for all measurements. A Beckman Zeromatic pH meter equipped with a saturated calomel electrode and a glass electrode was used for all pH measurements.

The chelating agent, BDMT, was prepared by the method described by Dedichen (2). A slurry of 40g. (0.375 mole) of dithiooxamide in 800 ml. of 20% ethyl alcohol was placed in a one liter beaker. Hydrazine hydrate was added dropwise with stirring to the suspension until all the dithiooxamide had reacted. At this point, the suspension had changed in color from orange to tan with no detection of solid orange dithiooxamide. The solid reaction product, oxalhydrazidine, was collected by filtration and washed with cold 20% alcohol. Into a 250 ml. beaker, cooled in an ice bath, was placed 19.2g. (0.224 mole) of 2,3-butanedione. To this cold solution, 13g. (0.112 mole) of oxalhydrazidine was added slowly with vigorous stirring. The solid reaction product was recovered from the breaker and washed with cold water. The reagent was recrystallized twice from water using Norite decolorizing charcoal and dried in a vacuum desiccator for one day. The product had a melting point of 166-167°C. (lit. 166°C). Over all yields of approximately 50%, based on dithiooxamide, were realized by this procedure. Anal. Calcd. for $C_{10}H_{12}N_6$: C, 55.53; H, 5.60; N 38.87. Found: C, 55.66; H, 5.43 N, 38.71.

Copper wire, 6.4g., was dissolved in 50 ml. of concentrated nitric acid and diluted to one liter. Aliquots of this solution were used in the determination of copper electrolytically. The concentration was found to be 0.0997 moles/liter.

Solutions of the reagent, approximately 1×10^{-2} M, were prepared by dissolving accurately weighed samples of the reagent of approximately 0.5g. in water, and diluting to volume in a 250 ml. volumetric flask.

A buffer solution was prepared one molar in sodium acetate and 0.5 molar in acetic acid. The reducing agent was prepared by dissolving 50g. of hydroxylamine hydrochloride in 500 ml. of deionized water.

Stock solutions of diverse ions were prepared at concentrations such that a fiftyfold dilution would equal the concentrations shown in Table VI.

All other reagents were analytical grade and were used as received.

Investigation of the Reagent.

The solubility of the reagent was determined in a variety of common organic solvents.

Ultraviolet spectra of the reagent in solutions of pH 0.90 to 12.00 were obtained. One ml. portions of 1.059×10^{-2} M BDMT

(0.5616g./250 ml.) were mixed with small portions of either one molar sodium hydroxide or one molar hydrochloric acid to obtain the desired pH.

An absorptimetric study of the reactivity of BDMT toward transition metal ions was performed. Solutions approximately 0.1 N in nickel(II) and cobalt(II) ion were prepared by the dissolution of weighed amounts of hydrated nickel and cobalt perchlorate salts and standardized by electrodeposition. Standard iron solutions were prepared from a stock solution of ferrous ammonium sulfate which was previously standardized with standard sulfato-cerate.

A 2×10^{-2} M solution of ruthenium (III) chloride was prepared by dissolving a weighed amount of ruthenium chloride in 15% hydrochloric acid. The standard copper solution was used for the copper system. Absorption spectra in the visible region of the spectrum were recorded.

The Copper (I)-bis-3,3'-(5,6-dimethyl-1,2,4-triazine) System.

Optimum conditions for the formation of the cuprous complex in aqueous solution were determined on solutions containing copper ion, hydroxylamine hydrochloride, the reagent, and varying amounts of dilute sodium hydroxide and hydrochloric acid. The pH values varied from 1.75 to 12.00 in the presence of a fiftyfold excess of reagent to metal ion.

The methods of continuous variations (4) and mole ratio (7) were used to determine the composition of the copper(I) complex in aqueous solution. The mole ratio study was carried out on a series of solutions containing 5 ml. of $3.986 \times 10^{-4}M$ copper, 2 ml. of 10% hydroxylamine hydrochloride, 5 ml. of acetate buffer and varying amounts of $1.003 \times 10^{-2}M$ reagent solutions. The final concentrations of reagent varied from $4.052 \times 10^{-5}M$ to $200.6 \times 10^{-5}M$. The determination of the combining ratio of BDMT and copper (I) by the method of continuous variations was carried out on a series of solutions prepared from 3.917×10^{-3}M reagent and 3.986×10^{-3}M copper stock solutions. The solutions were combined in amounts to vary the copper to reagent ratio from 0.1 to 0.9. Two ml. of 10% hydroxylamine hyrochloride and 3 ml. of acetate buffer were added to each solution. Data were recorded from the measurement of the absorption spectrum of each solution.

The conformance of the system to Beer's Law was determined over the concentration range of 7.97×10^{-6} to 1.59×10^{-4}M. Solutions containing a 40:1 ratio of reagent to metal ion were prepared at pH 5.0. Each solution contained one ml. of 10% hydroxylamine hydrochloride and 2 ml. of acetate buffer. The absorbance values for these solutions were obtained at 444mμ.

To determine the effect of time on the stability of the copper

complex, a solution containing a constant concentration of copper, 7.972×10^{-5} M, was prepared by adding a 50:1 excess of reagent to metal ion and the required amount of reducing agent and buffer. The absorbance of this solution was obtained over a marked period of time.

In the presence of perchlorate ion, the bis-[bis-3,3'-(5,6-dimethyl-1,2,4-triazine)]-copper(I) complex was extracted from aqueous solution into nitrobenzene. Solutions containing varying concentrations of copper, reducing agent, buffer, and perchlorate ion, were extracted with two-10 ml. volumes of nitrobenzene. The combined extracts were filtered through cotton into a 50 ml. volumetric flask and diluted to volume with additional solvent. Absorbance values were recorded against corresponding solvent reference solutions.

The effects of diverse ions on the copper(I) system were investigated by the addition of varying amounts of diverse ion to the complex system containing 5.07 p.p.m. of copper(I). Into separate 50 ml. volumetric flasks containing one ml. of the ion to be tested, 10 ml. of $3.986 \times 10^{-4}M$ standard copper solution, one ml. of 10% hydroxylamine hydrochloride, 10 ml. of 1.039×10^{-2} M BDMT, and 4 ml. of acetate buffer were mixed together.

Recommended Procedure

Dissolve the sample containing copper by appropriate means. Adjust the pH of the solution to approximately four. To a 5 ml. aliquot containing from 0.5 to 10 p.p.m. of copper in a 50 ml. volumetric flask, add 2 ml. of hydroxylamine hydrochloride, 5 ml. of acetate buffer and at least a fortyfold excess of BDMT. Measure the absorbance of the solution in one centimeter cells with an appropriate spectrophotometer at a wavelength to 444 mμ. From a previously prepared calibration curve, determine the amount of copper in the unknown sample.

Discussion

The reagent, BDMT, is soluble in acetone, benzene, chloroform, diethyl ether, ethyl alcohol, methyl alcohol, nitrobenzene, pyridine, and water.

Bis-3,3'-(5,5-dimethyl-1,2,4-triazine), as a free base (pH 11), exhibits a wavelength of maximum absorption at 242 mμ, $\varepsilon = 11,500$, with a diminished peak at 345 mμ, $\varepsilon = 562$. As the pH of the aqueous solution of BDMT is decreased, the 345 mμ peak gradually disappears and the 241 mμ peak undergoes a bathochromic shift to 253 mμ.

The ligand under consideration forms colored coordination compounds with the divalent ions of cobalt, nickel, iron and ruthenium, and with monovalent copper. Absorptimetric data on the various metal systems are summarized in Table I.

It is apparent that the copper and iron complexes are worthy of further investigation. The iron system is the subject of a separate investigation. These metal complexes are more intensely colored than those formed with 2,2'-bipyridine, 2.2'-bipyridine, 2,2'-bipyrimidine, or 1,10-phenthroline. Although the ruthenium complex appears to merit investigation, color development is very pH sensitive and required prolonged heating. The cobalt complex appeared colored to the eye, but the absorption spectrum showed only a gradual rise from 400 to 580mμ, with no definite peak.

Table 1.   Absorptimetric Data on Metal Ion Complexes. (pH = 5.0)

Metal Ion	λmax(mμ)	ε
Co(II)	[a]	.....
Cu(I)	444	9,700
Fe(II)	408	12,200
	493	15,000
Ni(II)	410	15
Ru(II)[b]	412	13,200

[a] No absorption maximum observed.
[b] pH = 3.7.

The effect of pH on the copper complex was ascertained. The results of a pH study are presented in Table II. The data show that color formation attains a maximum at a pH of 5.0. It was found that the acetate buffer, at pH 5.0, was adequate for all determinations.

Table 2.   Effect of pH on the Cuprous Complex (Conc. Cu = 3.986 x 10^{-5} M, Conc. BDMT = 2.006 x 10^{-3} M)

pH	$A_{444 m\mu}$
1.75	0.024
3.70	0.361
5.00	0.381
7.00	0.370
9.00	0.350
12.00	0.189

Results of the mole ratio study are presented in Table III. It is apparent that a thirtyfold excess of reagent is required to obtain maximum and reproducible color formation.

Table 3.   Mole Ratio Study of the Copper(I) Bis-3,3'-(5,6-dimethyl-1,2,4-triazine) System (Conc.Cu = 3.986 x 10^{-5}M, pH = 5.0)

Ratio of ligand to Copper (I)	$A_{444 m\mu}$
1	0.045
5	0.240
10	0.330
20	0.365
30	0.377
40	0.379
50	0.381

The formula of the copper (I) complex was determined by the method of continuous variations. The data obtained are shown graphically in Figure 1. The results show the existence in solution of one complex with a composition of one mole of copper (I) and two moles of BDMT.
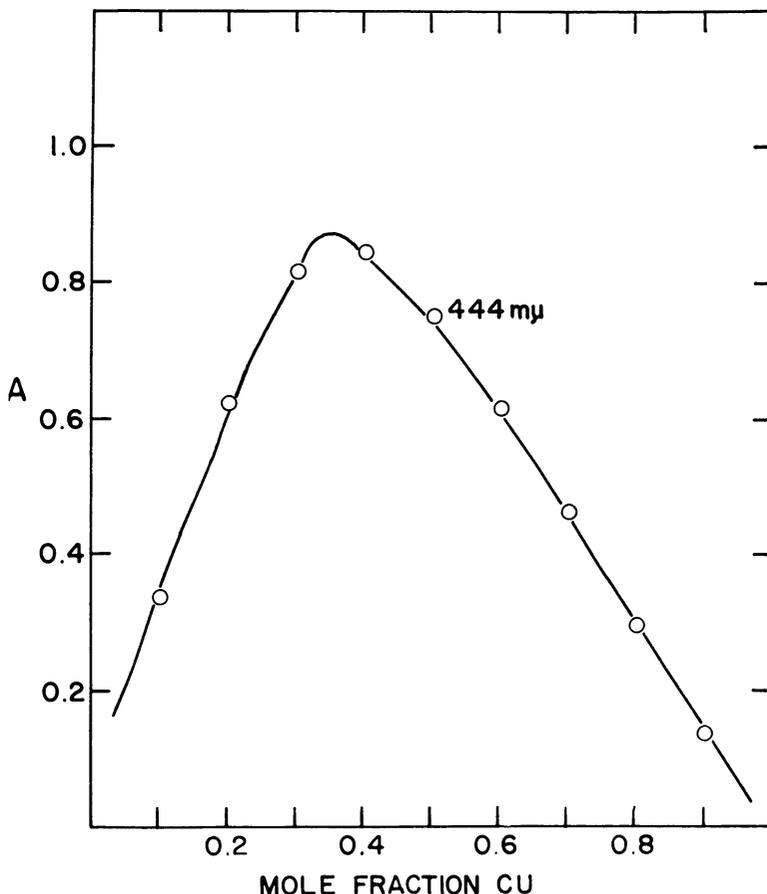

Figure 1.   Continuous Variations Study of Copper (I)

The copper (I)-bis-3,3'- (5, 6-dimethyl-1,2,4-triazine) complex was found to obey Beer's Law over a concentration range of 7.792×10^{-6} to $159.4 \times 10^{-6}M$ copper (I) ion. Data for the study are presented in Table IV. The visible spectra of the copper (I) complex are shown in Figure 2. The best value for the molar absorptivity is 9,700 at 444 mμ.

The stability constant for the reaction.

$$2BDMt + Cu^+ = Cu(BDMT)^+{}_2$$
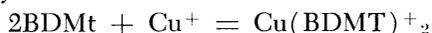
can be described as:

$$K = k_1k_2 = \frac{[Cu\ (BDMT)^+{}_2]}{[Cu^+]\ [BDMT]^2}$$

Table 4.   Data for Beer's Law Study. Copper (I) Bis-3,3'-(5,6-dimethyl-1, 2, 4-triazine)System(Conc. BDMT = 3.371 x $10^{-3}M$, pH= 5.0)

Concentration of Copper present (M x 10^6)	$A_{444\ m\mu}$
7.792	0.075
39.85	0.361
79.72	0.784
119.6	1.156
159.4	1.571

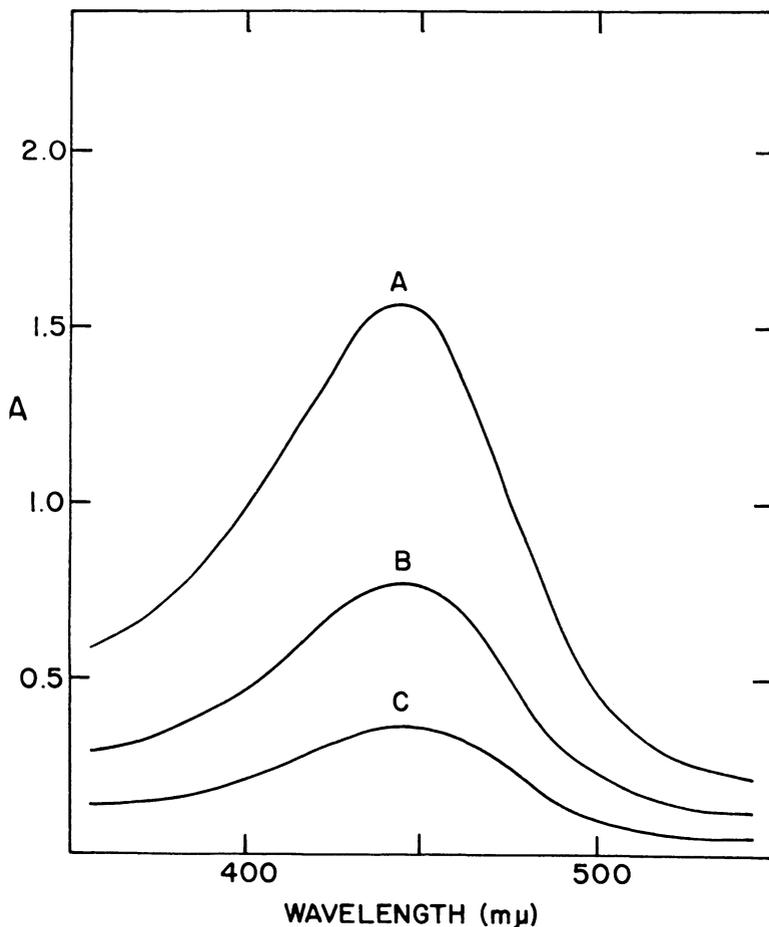Figure 2.   Absorption Spectra of the Copper (I) Bis-3,3'-(5,6-dimethyl-1,2,4-triazine) Complex A, 159.4 x 10-6 M; B, 79.72 x 10-6 M; C, 39.85 x 10-6 M.

Assuming that the value obtained above for the molar absorptivity is accurate, that there is only one colored species absorbing at tne measured wavelengths, that the absorbing species is a 2:1 complex, and that there are no competing reactions between the ligand and hydrogen ion, then the calculation of the stability constant is relatively simple. (These assumptions are valid in view of the observations described in the preceding discussion).

Table V contains all data used in the calculation of the stability constant from the continuous variations data. The log K value obtained for the bis-[bis-3,3'-(5,6-dimethyl-1,2,4-triazine)]-copper (I) complex was 8.4 ± 0.3.

Table 5.   Data for the Stability Constant Calculation of the Bis-3,3'-(5,6-dimethyl-1,2,4-triazine)-Copper (I) Complex

Mole Frac. Cu	A/ε_{444} x 10^5	$[Cu+]_t$ x 10^4	$[BDMT]_t$ x 10^4	Log K
0.1	3.474	0.399	3.525	7.9
0.2	6.402	0.797	3.134	8.1
0.3	8.391	1.196	2.742	8.3
0.4	8.742	1.594	2.350	8.5
0.5	7.742	1.994	1.959	8.6
0.6	6.371	2.392	1.567	8.6
0.7	4.794	2.790	1.175	8.7
0.8	3.093	3.189	0.783	8.6
0.9	1.423	3.587	0.392	8.6

In the presence of a large excess of reagent (40:1), the color intensity of the complex was found to be essentially constant over a period of three hours. Maximum color is developed with a lower ratio of reagent, but this color intensity decreases in a much shorter period of time.

The perchlorate salt of the copper(I)-BDMT complex is extractable from aqueous solution into nitrobenzene. The molar absorptivity of the copper (I) complex in nitrobenzene is 11,100 at the wavelength of maximum absorption of 468 mμ.

Bis-3,3'-(5,6-dimethyl-1,2,4-triazine) reacts as a non selective reagent toward transition metal ions. Iron, nickel, cobalt, chromium, and ruthenium interfere with the determination of copper (I) due to colored compounds which are formed. Anions which form copper (I) complexes interfere with color development, as shown in Table VI. The method of calculating relative error is essentially the same as that proposed by Fortune and Mellon (3). Results of the analysis on synthetic samples, using the previously described procedure, are presented in Table VII.

CONCLUSIONS

From the data and observations described in this investigation, the following conclusions can be formulated.

Table 6. Effect of Various Ions on Color Formation. Copper (I) Bis-3,3'-(5,6-dimethyl-1,2,4-triazine) system. Concentration of Copper = 5.07 p.p.m.

Ion	Concentration p.p.m.	Source	Relative Error %
Fe^{+2}	98	$FeSO_4$	very large
Ni^{+2}	100	$NiCl_2$	−2.4
Co^{+2}	104	$Co(NO_3)_2$	+2.2
Mn^{+2}	102	$MnSO_4$	+0.4
Cr^{+3}	108	$CrCl_3$	+5.7
Zn^{+2}	101	$ZnCl_2$	−0.8
Al^{+3}	87	$AlCl_3$	+1.0
Mg^{+2}	101	$MgCl_2$	−0.8
Ca^{+2}	99	$CaCl_2$	+0.4
VO_2^+	62	Na_3VO_4	+0.4
PO_4^{-3}	102	K_2HPO_4	−1.6
$C_6H_5O_7^{-3}$	99	$Na_3C_6H_5O_7$	−5.1
F^-	98	KF	−1.2
$S_2O_3^{-2}$	101	$Na_2S_2O_3$	very large
SCN^-	96	KSCN	ppt.
SO_4^{-2}	100	K_2SO_4	−1.8

Table 7. Evaluation of the Reagent. Copper System.

Sample	Copper Present p.p.m.	Copper Found p.p.m.
S_1	0.51	0.49
S_2	2.53	2.36
S_3	5.06	5.13
S_4	7.60	7.57

The ligand, bis-3,3'-(5,6-dimethyl-1,2,4-triazine), is readily soluble in water and most common organic solvents.

The ligand forms colored reaction products with the divalent ions of iron, cobalt, nickel, and ruthenium, and with monovalent copper.

The bis-[bis-3,3'-(5,6-dimethyl-1,2,4-triazine)] − copper (I) complex exhibits a wavelength of maximum absorption at 444 $m\mu$ with a molar absorptivity of 9,700 in aqueous solution of pH 5.0. Beer's law for this system is obeyed over the concentration range of 8.0 to 160 x 10^{-6} M.

The log K for the copper (I) complex was observed to be 8.4.

The copper(I)-bis-3,3'-(5,6-dimethyl-1,2,4-triazine) complex can be extracted as the perchlorate salt from aqueous solutions into nitrobenzene. The complex in nitrobenzene exhibits a wavelength of maximum absorption at 468 $m\mu$ and a molar absorptivity of 11,100.

A spectrophotometric method for copper based upon the color formed between the reagent under consideration and the copper (1) ion is both accurate and precise.

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The Solubility and Thermal Decomposition Characteristics of Some Tetraphenylarsonium Compounds

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Abstract. The tetraphenylarsonium perchlorate, perrhenate, permanganate, tetraphenylborate, dichromate, trichoro-cobaltate (II) and tetrachlorozincate (II) salts were isolated and characterized. The solubilities of the pure salts in water at 25° were determined using spectrophotometric methods. Thermal data were obtained for the pure salts using the technique of thermal gravimetric analysis. Results of the above studies show that tetraphenylarsonium chloride is valuable as a precipitant for perchlorate and perrhenate ions. The reagent also shows promise as a precipitant for the dichromate and tetraphenylboron ions.

Tetraphenylarsonium chloride has been widely accepted as an analytical reagent. The compound acts as a precipitant for several univalent anions and for a few divalent anions. It forms the basis for the gravimetric determination of a number of common ions (3,4).

Although a variety of water insoluble tetraphenylarsonium salts have been investigated (4), solubility and thermal stability data have not been reported. It is the purpose of the present investigation to present such data for seven tetraphenylarsonium salts. Absorptimetric data for the tetraphenylarsonium cation were also evaluated.

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