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CHELATION OF THE TRANSITION METAL IONS WITH A SERIES OF POLYHYDROXYAMINE COMPOUNDS

by

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ABSTRACT

Chelation was reviewed with emphasis on the work done by contemporary workers.

The following polyhydroxyamine compounds were synthesized, purified and analyzed:

1,2-bis[tris(hydroxymethyl)methylamino]ethane dihydrochloride

1,3-bis[tris(hydroxymethyl)methylamino]propane dihydrochloride

1,3-bis[tris(hydroxymethyl)methylamino]-2-propanone dihydrochloride

1,2,3-tris[tris(hydroxymethyl)methylamino]propane trihydrochloride

The latter two compounds have not been reported in the literature.

Chelates were prepared by reacting the above compounds, and 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol dihydrochloride ("disec") and the "disec" free base, with the ions of the first transition metals. Stability constants were obtained, where appreciable coordination occurred before precipitation of the metallic ion took place. A list of the metal ions studied with one or more chelating agents follows: Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+3}, Mn^{+2}, Zn^{+2} and the rare earth ions.

A stable, solid chelate compound formed by the "disec" free base and cupric ion was produced, recovered, purified, and studied briefly.

The work reported herein was done to further the knowledge of the basic chemistry of the transition metal ion chelates with polyhydroxyamine compounds. Accordingly, structures have been proposed for these compounds.

It is postulated that the bivalent transition metal ions are bonded through the secondary amino nitrogens of the polyhydroxyamines. However, ferric ion is believed to be bonded to the oxygen of the secondary alcohol group in "disec" in addition to the amino nitrogen groups.

INTRODUCTION

Chelation occurs when a metal ion combines with a compound containing two or more electron donor groups so that one or more ring structures are formed. The compounds containing the electron donor groups are called chelating agents or ligands and are usually organic. The metal ion is rarely bonded directly to a carbon atom but is usually attached to strong Lewis bases such as the nitrogen, oxygen or sulfur atoms. Chelate compounds have been reported which contain almost all metals of the periodic table. Copper and other members of the first transition series of metals form some of the most stable chelate compounds reported.

Chelation is one of the important tools in the hands of the modern chemist. It is used extensively by the analytical chemist for both qualitative and quantitative determinations. A good example is the use of the nickel-dimethyl glyoxime chelate for the determination of nickel. Versene (trade name for ethylenediamine tetraacetic acid) and many other chelating agents are widely used in industry. Traces of copper, which catalyze gum formation, in gasoline, are deactivated by chelation. Iron, cobalt and other metals requisite for good plant growth are supplied in the slowly available form of a chelate solution. This method is applied to orchard fertilization wherein iron is required. The medical profession is now utilizing chelate chemistry in many ways. Mercury poisoning is treated by internal dosage of ethylenediamine tetraacetic acid. The calcium salt of the acid is used to prevent the removal of calcium from the body.

The list of practical uses for chelate compounds is a long one and it is growing rapidly. Unfortunately, the basic knowledge of chelate chemistry has not been advanced as rapidly as the practical applications. No general theory of chelation has been developed by the academic chemist.

Trout and Erdmanis (1) and Trout and Gladding (2) have reported chelate compounds formed by the reaction of polyhydroxylamine hydrochloride compounds, such as 1,3 bis-[tris(hydroxymethyl)methylamino]-2-propanol dihydrochloride ("disec"), with the metal ions of the first transition series. It is likely that additional knowledge of the nature of chelation might be obtained by a study of the chelation reactions of compounds similar to "disec," which was reported by Pierce and Wotiz (3). These studies were made and the results are reported herein.

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(1) Velta Erdmanis, M.S. Thesis, University of Richmond (1955).
(2) J. B. Gladding, M.S. Thesis, University of Richmond (1955).
(3) Pierce and Wotiz, J. Am. Chem. Soc., <u>66</u>, 879 (1944).

DISCUSSION OF CHELATION

1. HISTORY

Chelate chemistry is an integral, although special part of coordination chemistry. Alfred Werner was the first chemist to give both the general and special fields scientific treatment. Werner (4) supplied the first satisfactory explanation of chelation and prepared the first chelate compounds identified as such. He prepared potassium dichloroacetylacetono platinite. Werner's conclusion that his compound was a chelate (cyclic structure) was based on large physical and chemical changes observed in metal ions (or atoms) when treated with what we now call a chelating agent. Color change was then, as now, among the most important changes observed.

Ley (5) first recognized the special properties of chelates in 1904. His work was based on the unusual color and low electrical conductivity of copper glycinate. A cyclic covalent structure was used to explain these phenomena. The deep blue color of the glycinate solution resembled the $Cu(NH_3)_4^{+2}$ complex and was quite different from the usual green color of such copper salts as the acetate. The low electrical conductivity observed indicated not only a stable chelate but a chelate of zero ionic charge.

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(4) Werner, Ber., 34, 2584 (1901).
(5) Ley, Ber., 42, 354 (1909).

Tschugaeff (6) studied the stability of ~~chelated~~ chelates of ions ~~by~~ with amino acids ~~with~~ containing different numbers of carbon atoms between the amino and carboxyl groups. He found that those compounds which formed chelates ~~rings~~ containing five or six membered rings were the most stable. This premise was generally accepted because it agreed with the pronounced stability of five and six membered organic ring compounds.

For a period of years after the work of Werner, Ley and Tschugaeff was reported, the theory of chelation was not appreciably advanced. In 1936 Pfeiffer (7,8) gave more solid evidence than had his predecessors concerning the structure of chelate compounds. He was also able to show that chelates containing asymmetric carbon atoms could be isolated in optically active forms. The isolation, purification, and analysis of these chelates by Pfeiffer and others gave definite proof of the existence of stable chelates and allowed one to draw conclusions concerning their structure.

The recent history of chelation may be divided into four categories, each of which will be treated briefly here. These fields are as follows: Quantitative treatment of chelate reactions, correlation of chelate chemistry with quantum chemistry, studies of chelate structure, and search for new chelating agents.

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(6) Tschugaeff, J. prakt. Chem., (2) 75, 153 (1902).
(7) Pfeiffer, Z. anorg. allgem. Chem., 230, 97 (1936).
(8) Pfeiffer, angew. Chem., 53, 933 (1940).

Bjerrum (9) in 1941 described a method for the calculation of equilibrium constants or chelate stability constants based on the law of mass action. Most of Bjerrum's work was with simple ammine complexes but his method is quite effective in the treatment of chelate stabilities. Simple pH titrations of the metal ion, chelating agent and chelate compound supply the data requisite for the calculation of stability constants. Bjerrum's method was given a thorough treatment recently by Erdmanis (10) in her thesis.

Turner and Anderson (11) have presented an alternate method for the determination of chelate stability constants based upon the color of the solution and on Beer's law. The formulas of chelates may be determined quantitatively by the method presented by Job (12) in 1936. This method will also receive further treatment later.

Rather complete quantitative treatment of chelate stabilities have been presented in recent years by Fernelius (13), Schwartzenbach (14), Verhoek (15), Jonassen (16) and others. The quantitative treatments used in most present publications are based on the classic work of Bjerrum.

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(9) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(10) Erdmanis, M.S. Thesis, University of Richmond (1955).

(11) Turner and Anderson, J. Am. Chem. Soc., 71, 913 (1949).

(12) Job, Ann. chim., (11) 6, 97 (1936).

(13) Hares, Fernelius and Douglas, J. Am. Chem. Soc., 78, 1816 (1956).

(14) Schwartzenbach, Kampitsch and Steiner, Helv. Chim. Acta, 28, 828 (1945).

(15) Carlson, McReynolds and Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

(16) Jonassen et al., J. Phys. Chem., 56, 16 (1952).

Pauling (17) and others have demonstrated the similarity between the covalent chelate bonds of the transition metals and the organic double bonds by calculation of bond orders.

The structure of chelates is discussed in considerable detail by Martell and Calvin (18). A large amount of work has been presented in this field by Bailar and others. Bailar (19) observed the Walden inversion in the conversion of optically active dichloro bis-ethylene diamine cobalt^3(CL) to the corresponding carbonato derivative. When the levo dichloro chelate was treated with aqueous potassium carbonate the dextro carbonato bis-ethylenediamine cobalt (CLT) was formed. However, when the solid levo dichloro chelate was pulverized in the absence of moisture with potassium carbonate and then water was added the resulting carbonato derivative had a levo rotation.

Many new chelating agents have been discovered in the intensive search carried out in the past fifteen years. Some of the most interesting complex compounds are those which employ carbon-carbon double bonds as the electron donor groups (Lewis Bases). D. F. Evans (20) has found that polystyrene forms a complex with silver chlorate. This complex is stable

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(17) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1939).

(18) Martell and Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, New York (1952).

(19) Bailar and Peppard, J. Am. Chem. Soc., 62, 820 (1940).

(20) Evans, J. Chem. Phys., 24, 6, 1244 (1956).

in both the solid and liquid phases. It is soluble in alcohol and insoluble in water. Evans does not call his compound a chelate. It is his belief that the Ag^+ ions are attached to the benzene rings, on the polystyrene chain, to form a rather unusual polyelectrolyte. A six membered ring chelate is possible with the silver bonded between the aromatic nuclei. The silver in this case would have a coordination number of 2 which is in accord with the normal coordination number for silver.

2. METAL IONS CHELATED

Most of the metals of the periodic table form chelate compounds. The transition metals form a large number of chelate compounds and are considered to have the strongest tendency for combining with electron donors. Recently some very stable chelate compounds have been made with the alkali metals and alkaline earths.

The factors affecting the tendencies for metals to combine with an electron donor are divided into two classes:

(a) Ionic forces--charge and radius of ion

(b) Relative tendency of metals to form homopolar bonds with the electron donor.

In the case of chelation other considerations, such as steric factors, complicate interpretation of experimental results.

It has been observed that there is a similarity between complex forming tendencies of metals in the vertical columns of the periodic table, with the metals of group eight and the rare earths as exceptions where horizontal similarities were found. Nyholm (21) has pointed out that these horizontal similarities apply only to simple salts of group eight metals and that in chelation the similarities are vertical ones. This postulate was demonstrated by the preparation of Fe^{+2}, Ru^{+2}, and Os^{+2} chelate compounds with o-phenanthroline which were quite similar.

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(21) Nyholm, Quart. Revs., 3, 321 (1949).

Mellor and Malby (22) have made an important contribution with their study of the effect of the metal ion upon chelate stability. By a study of the stability of chelate compounds formed by a number of bivalent ions with several different chelating agents, they were able to arrange the metal ions in a list of decreasing stabilities. The list they compiled follows:

$$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg$$

Other investigators such as Irving and Williams (23) have verified this relationship with tests using a number of different chelating agents.

Calvin and Melchior (24) discovered a relationship between ionization potential of the metal and chelate stability. Since the ionization of copper, nickel and cobalt involves the removal of an electron from the d orbital it is postulated that the energy released in replacing this electron would decrease in the order of $Cu > Ni > Co$. This is in the same order as the chelate stability constants observed. Calvin and Melchior therefore suggested that the d orbitals were involved in the formation of chelate compounds. They were not specific as to how d orbitals were involved.

When chelates are formed by ionic bonding the tendency

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(22) Mellor and Malley, Nature, 161, 436 (1948).
(23) Irving and Williams, Nature, 162, 746 (1948).
(24) Calvin and Melchior, J. Am. Chem. Soc., 70, 3240 (1948).

for chelate formation and hydration increases with increasing charge/radius ratio. Rare earth ions may be separated on the basis of charge/radius ratio by chelation with ethylenediamine tetraacetic acid. Plumb and Martell (25) found that selective chelation took place in the order of:

Y > Sm. > Nd. > Pr. > La.

This is also the order of increasing basicity and ionic radius.

Some chelating agents are specific for one or more metal ions and will not chelate with others. These ions and chelating agents are quite valuable in analytical work. The specificity in chelation is due to structural arrangements of the chelating agent and radius and charge of the metal ion. Little quantitative work has been done in this field.

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(25) Plumb, Martell and Bersworth, J. Phys. & Colloid Chem., 54, 1208 (1950).

3. CHELATING AGENTS

Almost any group containing an atom with unshared electrons may be a complexing agent although the degree to which they form complexes may vary tremendously. A chelating agent, however, must contain two or more Lewis bases or areas of high electron concentration so that a heterocyclic ring may be formed containing a metal ion or atom. Such ring forming groups are referred to as polydentate groups. Morgan and Drew (26) have referred to bidentate groups as chelate groups. They took the name chelate from the Greek word meaning claw, since the chelating agent wraps around the metal ion like the claws of a crab. The term "chelating agent" is now used for any polydentate compound.

The chelate compounds are most stable which contain five or six members including the metal ion, presumably because this structure is less strained than other forms.

Diehl (27) has listed many types of chelating agents. His list is far too voluminous for presentation here. However, it can be said that any organic compound containing two or more electron donor groups can form a chelate. The metal is usually bonded to nitrogen, oxygen or sulfur atoms. Chelating agents are frequently diacids, alpha-hydroxy acids,

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(26) Morgan and Drew, J. Chem. Soc., <u>117</u>, 1456 (1920).
(27) Diehl, Chem. Revs., <u>21</u>, 39 (1937).

diamides, amino acids, hydroxyl amines, 8-hydroxyquinolines, glyoximes, diamines, 1,2-glycols or disulfides.

A chelating agent is differentiated from a complexing agent by its polyfunctional nature and its stability. For example ethylamine forms a complex with Co^{+3} which is much less stable than the Co^{+3} chelate formed with ethylenediamine. Also neither phenol nor benzaldehyde form stable coordination compounds but when the two structures are combined in salicylaldehyde a bidentate chelating agent is produced which forms stable coordination compounds (chelates) with many ions.

It may be noted that the polyhydroxyl amine compounds used in the experimental work reported herein have many possible locations for metal bonding. These compounds are polydentate.

4. SURVEY OF CHELATION WITH AGENTS SIMILAR TO THE POLYHYDROXYLAMINES

The compound 1,3-bis[tris(hydroxymethyl)methylamino]-propane is typical of the polyhydroxylamine compounds studied in this work. Although no chelation work has been reported with this compound, much data has been presented concerning chelation studies made with similar compounds. Foremost among these compounds are the polyfunctional aliphatic amines and their derivatives. A survey is presented here of recent work reported in this field.

Carlson, McReynolds and Verhoek (28) reported a study of complexes formed between metal cations and amines which was directed toward the establishment of the overall equilibrium constant for the reaction

$$M + NA \rightleftharpoons MA_N$$

where: M = metal ion
N = number of ligands
A = ligand

The equilibrium constant for this reaction was called the complexity constant by Bjerrum. It was derived from the equation:

$$K_N = \frac{(MA_N)}{(M)(A)^N}$$

where: K_N = complexity constant
M = conc. of metal ion
A = conc. of ligand
MA_N = conc. of chelate

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(28) Carlson, McReynolds and Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

These investigators reported the results of a study of ethylenediamine and propylenediamine with copper, nickel, cadmium and zinc ions. They also made studies of the complexes of the silver ion with ethyl and diethyl-amine which will not be considered here.

The complexity constants obtained are tabulated below:

Ethylenediamine	Copper	Nickel	Zinc	Cadmium
K_N	19.60	18.06	12.09	12.09
Propylenediamine				
K_N	19.66	18.00	12.57	12.12

The work of Carlson, McReynolds and Verhoek showed the extreme stability of the cupric-ethylenediamine and propylenediamine complexes. Complex formation was found to begin at a free amine concentration of 10^{-12} molar and complexation was complete at 10^{-7} molar (pH approx. 5.5). It is interesting to note that these concentrations are similar to those found for the polyhydroxyl derivatives of ethylenediamine and propanediamine reported in this paper. The order of chelate stabilities reported by Carlson, McReynolds and Verhoek is in agreement with the relative chelate stabilities of metal ions previously reported by Mellor and Malley (29).

W. Conrad Fernelius is one of the most active contemporary

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(29) Mellor and Malley, Nature, 161, 436 (1948).

investigators in the field of chelation. In 1953 he, in conjunction with Ely Gonick and Bodie Douglas (30), reported a study of the chelation of copper, nickel, cobalt and zinc ions with several sulfur bearing amines. They reported formation and complexity constants at several temperatures for the chelates and were able to obtain thermodynamic functions such as free energy and entropy changes.

The general procedure used by these investigators in studying chelate formation involved the titration of a solution, 1 molar in neutral electrolyte (either KCl or KNO_3) and containing known amounts of metal salt and mineral acid. The titrant was either pure amine or a standardized aqueous solution of amine. In the case where the amine was in the form of the acid salt a weighed amount of salt was placed in the solution to be titrated with a standardized solution of sodium hydroxide. The latter technique was used in the titrations reported in this paper. The table below shows a comparison of the complexity constants obtained by Fernelius et al. for the sulfur bearing chelating agents with those of diamines.

Metal Ion	Chelating Agent	Complexity Constant at 30°C.
Ni^{++}	$CH_3SCH_2CH_2NH_2$	7.75
"	$H_2NCH_2CH_2NH_2$	18.06
Cu^{++}	$CH_3SCH_2CH_2NH_2$	10.68
"	$H_2NCH_2CH_2NH_2$	19.60

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(30) Gonick, Fernelius and Douglas, J. Am. Chem. Soc., <u>76</u>, 4671 (1954).

Considerably more data were given by Fernelius but the above is sufficient to show clearly that coordination through sulfur is not as strong as through nitrogen. (No data were given for the ferric ion which might not react in a similar manner.) This fact was further demonstrated by the failure to obtain complexes with certain sulfide amines while the corresponding imine compounds formed readily. The colors of the complexes formed between the various sulfide linkages are much the same as those formed with amines containing a secondary amino group in the place of the sulfur atom.

Hares, Fernelius and Douglas (31) have recently reported work to compare the relative stability of complex ions containing chelate rings of more than 5 members. An attempt was made to obtain formation constants of the complexes of Cu^{+2}, Ni^{+2}, Co^{+2} and Zn^{+2} ions with a series of polyamines. No formation constants could be obtained in the cases of 1,4-butanediamine, N,N-dimethyl-1,3-propanediamine, N-isopropyl-1,3-diamine and alpha-aminopropylmorpholine with any of the four metal ions studied because precipitation occurred before appreciable coordination took place. Data were obtained for all four metal ions only with 2,2-dimethyl-1,3-propanediamine and histamine. Incomplete data were obtained for the complexes of 3,3'-diaminodipropylamine, beta-aminoethylmorpholine and

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(31) Hares, Fernelius, and Douglas, J. Am. Chem. Soc., 78, 1816 (1956).

1,3-propanediamine because of precipitation with one or more of the metal ions. The work with the 1,3-propanediamine is interesting because of its similarity to 1,3-bis[tris(hydroxymethyl)methylamino]propane studied at the University of Richmond. The table below shows a comparison of the formation constants of several amine complexes studied by Fernelius, et al., with various bivalent metal ions at 30°C.

	Formation Constants with Metal Ions			
Amine	Cu^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}
3,3'-Diaminodipropylamine	14.25	9.09	6.63	--
1,3-Propanediamine	9.62	Precipitated		
2,2-Dimethyl-1,3-propanediamine	9.94	6.59	4.88	5.21
Histamine	9.60	6.87	5.34	--

Precipitation occurred most often for metal ions giving less stable complexes (Zn and Co) and for all four metal ions precipitation occurred more often at high temperatures where complexes were less stable. The considerable decrease in the stability of the complex as the size of the chelate ring increases from five to six members was indicated by the much higher stability of ethylenediamine chelates than for the propanediamine chelates. Only two molecules of 1,3-propanediamine were coordinated with the metal ions while three molecules of ethylenediamine and 1,2-propanediamine are coordinated by the same ions.

The separation of the amino groups by four carbon atoms as in 1,4-butanediamine resulted in precipitation before appreciable coordination occurred. Solid coordination compounds of copper with 1,4-butanediamine and hexamethylenediamine were obtained by Pfeiffer, and coworkers (32), in alcoholic solution but the compounds were unstable in water.

Additional data on similar compounds were published recently by Gonick, Fernelius and Douglas (33). This work is particularly interesting since it was done with 1,3-diamino-2-propanol which is very similar to 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol on which experimental work was done by Trout and Erdmanis (34) and Trout and Gladding (35). The same techniques were used in this work as in previously reported chelation studies by Fernelius, et al. The results of this work are shown below:

Chelating Agent	Metal Ion	Formation Constants
1,3-Diamino-2-propanol	Ni^{+2}	6.19
"	Co^{+2}	3.90
"	Zn^{+2}	4.60
1,3-Diaminopropane	Ni^{+2}	7.00

These results indicate that 1,3-diamino-2-propanol is a somewhat weaker base than 1,3-diaminopropane. This is in contrast to the results obtained at the University of Richmond with the polyhydroxylamines where the isopropanol diamine derivative was found to form more stable chelates than the diamino propane derivative.

The effect of steric hindrance on the chelating tendencies

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(32) P. Pfeiffer, A. Böhm and E. Schmitz, Naturwissenschaften, 35, 190 (1948).

(33) Gonick, Fernelius and Douglas, J. Am. Chem. Soc., 77, (1955).

(34) Erdmanis, M.S. Thesis, University of Richmond (1955).

(35) Gladding, M.S. Thesis, University of Richmond (1955).

of diamines with Cu^{+2} and Ni^{+2} was illustrated by Basolo and Merman (36). The stepwise formation constants were given for two metal ions with $RNHCH_2CH_2NH_2$, where R is H, methyl, ethyl, n-propyl, n-butyl and iso-propyl. Except for the n-butyl derivative there is a general decrease in complex stability with increase in the chain length of the straight chained alkyl groups. However, complexes with N-isopropylethylenediamine are less stable than those of the straight chained alkyl derivatives. Calculation of stability constants was made by the method of Bjerrum (37). The following results obtained by Basolo, et al. give the effect of steric hind~~e~~rance on the chelate stabilities of diamines:

Chelating Agent	Complexity Constants for Ni^{+2}	Cu^{+2}
Ethylenediamine	19.11	20.13
N-methylethylenediamine	15.11	19.11
N-ethylethylenediamine	14.08	18.57
N-n-propylethylenediamine	13.76	18.14
N-n-butylethylenediamine	14.49	18.21
N-i-propylethylenediamine	8.64	16.52

Although the complex stabilities, in general, decrease slightly from methyl to the n-propyl substituted derivatives, the complexes formed by n-butyl derivatives showed an increased stability. The enhanced stability at this point

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(36) Basolo and Mermann, J. Am. Chem. Soc., 74, 5243 (1952).
(37) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

may be attributed to the fact that a four carbon chain can coil itself around to shield the central atom and render it inaccessible to the solvent.

Hans Jonassen (38), and coworkers, have studied chelates formed by Cu^{+2} and Ni^{+2} and diethylenetriamine. Once again using the classic method of Bjerrum, they determined complexity constants for the chelate compounds. Selected results from their work are shown below:

Metal Ion	Complexity Constant ~ 30°C.
Cu^{+2}	16.11
Ni^{+2}	10.81

It may be noted that the stabilities of the diethylenetriamine chelates are somewhat lower than with chelates formed by ethylenediamine but are considerably higher than with 1,3-propanediamine.

Although steric hindrance is an important factor in chelate stability some surprising chelates have been formed. For example, Hein and Müller (39) have reported stable coordination compounds formed by stilbenediamine with Ni^{+2}. Not only were they able to use stilbenediamine but many of its substitution products. No stability constants were reported by these investigators but they did recover and

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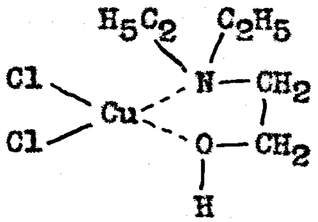
(38) Jonassen, Hurst, LeBlanc, J. Am. Chem. Soc., 72, 4968 (1950).
(39) Hein and Müller, Z. für anorg. Chem., 283, 176 (1956).

analyze the chelate compounds. In the case of the stilbenediamine a green chelate was obtained which could be separated into yellow and blue isomers.

Hein and Müller were also able to separate isomers from a number of substituted stilbenediamine-nickel chelates which will not be discussed here.

Hein and Beerstecher (40) have recently prepared chelate compounds by reacting N,N-disubstituted aminoethanol with Cu^{+2} ion. The chelate was formed by reacting $CuCl_2$ and pure dialkylaminoethanol in absolute alcohol. The reaction occurred in a 1:1 ratio to form a complex having the following structure, assigned by Hein (for the diethyl derivative):



It may be noted that chelation is postulated to occur through both the nitrogen and oxygen. A situation possible in the polyhydroxyamines under study by this writer.

Schwartzenbach and Anderegg (41) state that the ring forming (chelating) probabilities decrease rapidly from

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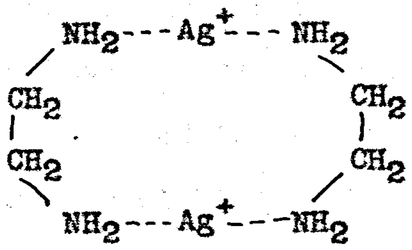
(40) F. Hein and W. Beerstecher, Z. für anorg. Chem., 282, 93 (1956).
(41) Schwartzenbach and Anderegg, Z. für anorg. Chem., 282, 286 (1956).

five member rings to nine or ten member rings where a minimum probability is reached, after which, as the number of possible ring members increase, the probability of cyclization increases, since the ring will be nearly unstrained. Also the activation energy required to open the heterocyclic chelate ring is about constant from five members on upward. Schwartzenbach raises the possibility of larger chelate rings actually being in solution but which may not be stable enough to be recovered per se. Relative stability constants were given for several silver-ethylenediamine chelates. The calculations by Schwartzenbach show an appreciable stability for a ten membered silver chelate of the following formula:



Schwartzenbach concludes that three membered rings have far too much strain to be stable and that little is known of four membered rings, although he does not preclude their possibility. Chelate rings containing silver and mercury are quite special since these ions do not form stable chelates containing five to seven members.

Nyman, Roe and Masson (42) investigated the complex

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(42) Nyman, Roe, and Masson, J. Am. Chem. Soc., 77, 4191 (1955).

compounds formed by Hg^{+2} with three different polyamines by polarographic means and found that the mercuric ion reacted with two molecules of ethylenediamine, 1,2-propanediamine, or diethylenetriamine. They got an indication of a different combination ratio at high ethylenediamine concentrations. They believe that a chelate containing four mols of ethylenediamine per Hg^{+2} was formed. This same possibility of higher ratio combinations was also found with the other polyamines tested.

Das Sarma and Bailar (43) have recently described the preparation of stable chelate compounds from bis-salicylaldehydetriethylenetetraamine and Co^{+3}, Co^{+2}, Fe^{+3}, Fe^{+2}, Al^{+3}, Cu^{+2}, Ni^{+2} and Pd^{+2}. The Schiff base offers six points of attachment (sexadentate). The octahedral complexes of Co^{+3}, Fe^{+3}, Al^{+3} were obtained in their optically active forms, but only two of the eight possible isomers were isolated. The copper compound, which is tetra-coordinated and planar, was obtained in optically active forms. Tentative structures of the complexes were described from the steric point of view and their infrared spectra. The Fe^{+3} compound is covalent with d^2sp^3 bonding. It also was resolved into optically active isomers.

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(43) Das Sarma and Bailar, J. Am. Chem. Soc., 77, 5477 (1955).

Since the work of Dwyer and Lions (44) it has been recognized that hexadentate ligands such as 1,8-bis-(salicylideneamino)-3,6-dithooctane (shown below) could span

$$\begin{array}{cccccc} HOC_6H_4 & CH{=}NCH_2CH_2 & NHCH_2CH_2 & NHCH_2CH_2 & N{=}CH & C_6H_4OH \\ (1) & (2) & (3) & (4) & (5) & (6) \end{array}$$

the octahedral positions around a metal ion. These proposed structures are shown using the ligand numbers indicated with the chelating agent formula.

Structures (B), (C) and (D) are strained structures, but in structure (A) the N-N-O bond angle is about 90°. It is highly probable that the structure (A) is the correct one for Dwyer's chelate compounds, as well as those reported by Das Sarma and Bailar.

The picture is slightly changed when the cupric ion is employed. Cupric chelates always show a Cu^{+2} coordination number of four and are planar in structure. Das Sarma and Bailar assume two protons to be replaced from hydroxyl groups and two of the four remaining nitrogens are coordinated to the cupric ion, thus giving a non electrolyte. The following structure was postulated:

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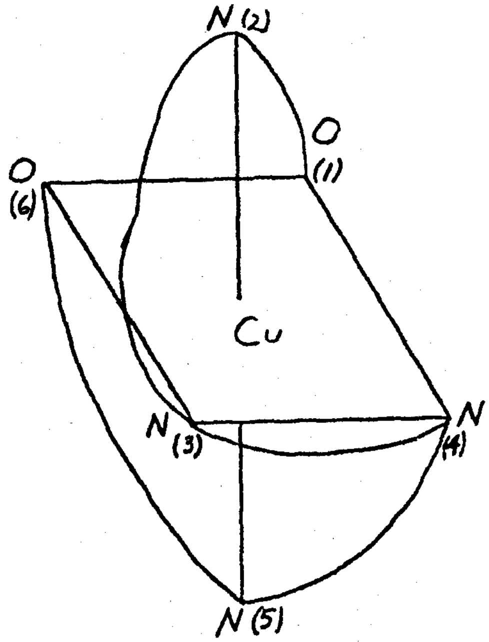
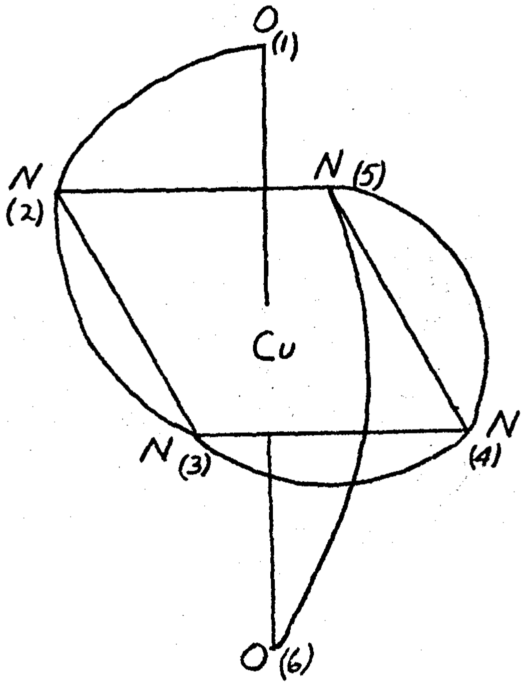
(44) Dwyer and Lions, J. Am. Chem. Soc., 69, 2917 (1947).

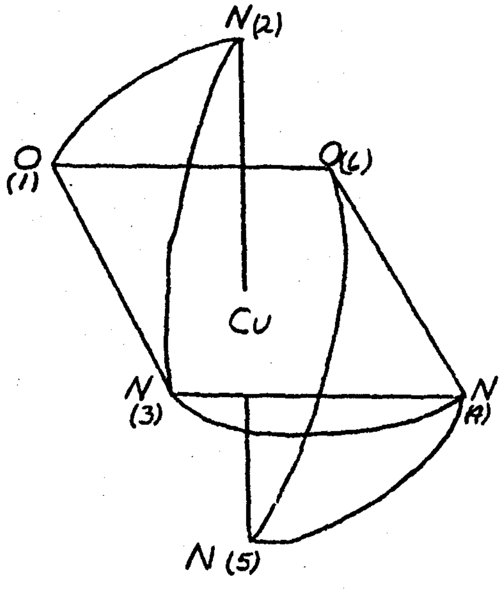
CHELATE STRUCTURES OF DWYER AND LIONS



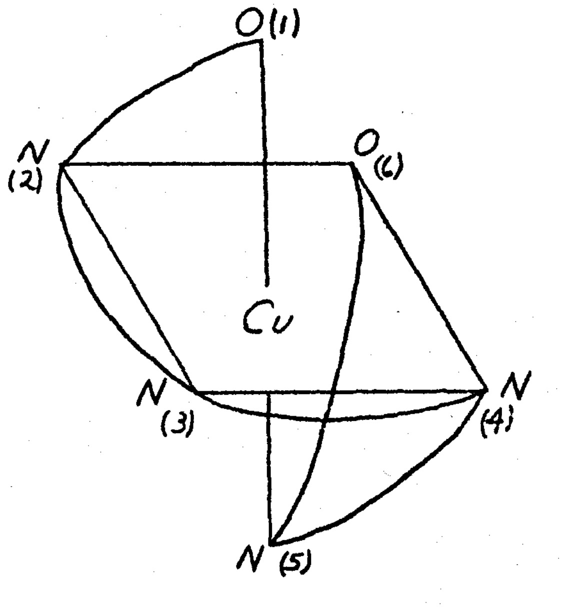
A



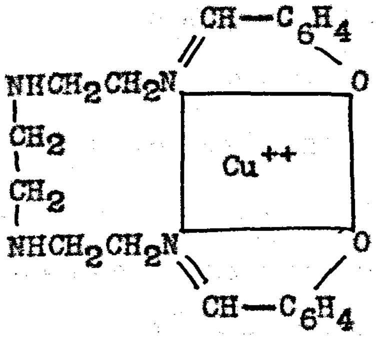
B



C



D



The spatial arrangement of the Zn^{+2}-glycine chelate was reported to be tetrahedral by Dickinson (45). Recent X-ray studies by Low indicate the chelate configuration to be planar about the central zinc ion.

Infrared studies by Sweeny, Curran and Quagliano (46) using the zinc chelate of glycine [bis-(glycino)-zinc monohydrate] are in accord with the evidence from the X-ray diffraction work, indicating a square planar configuration. They indicate that linear sp metal bond orbitals are involved in the nitrogen to metal bonds in this complex as well as in the copper and nickel complexes. As is to be expected, with bidentate ligands having as one coordinating center COO^-, one bond is essentially electrostatic ($COO^- --- Zn^{++}$).

Very stable chelate compounds were prepared and studied using N-hydroxyethylenediaminetetraacetic acid by Spedding, Powell, and Wheelwright (47). They reported stability

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(45) Dickinson, J. Am. Chem. Soc., 44, 774 (1922).
(46) Sweeney, Curran and Quagliano, J. Am. Chem. Soc., 77, 5508 (1956).
(47) Spedding, Powell, and Wheelwright, J. Am. Chem. Soc., 78, 34 (1956).

constants of the chelates formed with the rare earths and N-hydroxyethylene diaminetetraacetic acid by two independent methods. These constants could not be determined by direct pH titration because of the great stability of the chelates. In the first method used, the rare earth-HEDTA stability constants were calculated from measurements of the equilibrium constants of the competition reactions between HEDTA and triaminotriethylamine, for the rare earth and cupric ions. The second method used involved polarographic measurement of the amount of free copper ions liberated when equal molar quantities of the copper-HETDA complex and the rare earth ions were mixed together. A few representative complexity constants are shown below:

	Complexity Constants ~ 30°C.	
Metal Ion	By Potentiometric Method	By Polarographic Method
Sm^{+3}	15.15	15.3
Gd^{+3}	15.10	15.4
Dy^{+3}	15.08	15.3
Ho^{+3}	15.06	15.4
Er^{+3}	15.17	15.4
Tm^{+3}	15.38	15.5
Yb^{+3}	15.64	15.8

There is no significant variation in the stabilities of the rare earth-HEDTA complexes, which means that no separation of these elements could be obtained by ion exchange elution with HEDTA as the eluting agent. The hydroxyethylenediaminetetraacetic acid is interesting because the free acid is considerably more soluble than the common ethylenediaminetetraacetic acid.

Das Sarma (48) and Bailar (49) are studying the structure of diamines, amino acids, and dicarboxylic acid chelates by resolution of optically active forms.

The vast contemporary activity in the field of chelation indicates that this field is in its golden age. Major attention is devoted to the polyfunctional aliphatic amines. Whereas, our experimental work has been directed toward the amino alcohols the preponderance of the work in the field has been with the amino acids. This is quite logical since the amino acids have already demonstrated considerable commercial value as chelating agents.

It seems profitable to present a condensation of the contemporary achievements with chelating agents similar to the polyhydroxyamines under study at the University of Richmond. This is presented in the form of a list, which follows:

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(48) Das Sarma, J. Am. Chem. Soc., 78, 892 (1956).
(49) Das Sarma and Bailar, J. Am. Chem. Soc., 78, 895 (1956).

1. Very stable chelates are prepared with ethylenediamine and propylenediamine and the metal ions of the transition series. The concentrations of ligand and pH where chelation occurs are similar to those found in our studies with the polyhydroxylamines.
2. The coordination (chelation) of the transition metals through sulfur (and oxygen) is much weaker than through nitrogen. The colors are the same through either linkage.
3. There is a considerable decrease in chelate stability as the chelate ring increases from five to six to seven members.
4. 1,3-diamino-2-propanol is a weaker chelating agent than 1,3-diaminopropane. This is in contrast to our results with similar polyhydroxylamine compounds.
5. Steric hindrance has an appreciable effect on chelate stability. In going from unsubstituted ethylenediamine through N-isopropylethylenediamine, chelate stability decreases markedly.
6. Chelate stability with transition metals is lower for diethylenetriamine than for ethylenediamine but higher than those of 1,3-propanediamine.
7. Chelates of transition metals and highly hindered stilbenediamine (and its derivatives) were prepared, recovered and analyzed. Optically active isomers were resolved.

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8. Chelate between Cu^{+2} and alkyl disubstituted aminoethanol involved coordination through both the nitrogen and oxygen atoms.
9. Chelate rings with three members are not possible, and none with four have been reported although they may exist. Chelate compounds with ten or more members are possibly obtained in solution but decompose on recovery. A stable ten member ring chelate was reported from Ag^{+} and ethylenediamine.
10. High ratios of ligand to metal ion cause high chelating ratio between ethylenediamine and Hg^{+2}. Chelate ratios as high as 4 to 1 were obtained.
11. Stable chelates were formed with sexadentate bis-salicylaldehydetriethylenediamine and the transition elements. The Fe^{+3} chelate contained $\underline{d}^2\underline{sp}^3$ bonding.
12. Sexadentate chelating agents can span the six positions around metal ions.
13. Zinc and copper chelates with glycine were proven to be planar in structure by X-ray and infrared studies. One bond is between nitrogen and metal and involves the $\underline{s}$ and $\underline{p}$ orbitals of the metal. The other bond is an electrostatic bond between the metal and the carboxyl group.
14. There is no appreciable difference between the stabilities of the rare earth chelates with hydroxyethylenediaminetetraacetic acid. The hydroxy acid is more soluble in water than the free unsubstituted amino acid.

DISCUSSION OF POLYHYDROXYLAMINE COMPOUNDS

Polyfunctional compounds are interesting because of their ability to react and give compounds with widely varying properties. The ethanolamines, for example, have found wide acceptance in the chemical industry. The commercial synthesis of tris-(hydroxymethyl)-amino methane by the Commercial Solvents Corp. (50) has opened the way to a series highly polar amino alcohols. Tris-(hydroxymethyl)-amino methane (henceforth designated "Tris") was first synthesized by Piloty and Ruff (51) by the reduction of tris-(hydroxymethyl)-nitromethane which was prepared by Henry (52). Henry prepared the nitromethane derivative by reacting formaldehyde with nitromethane.

A series of polyhydroxylamine compounds, having two polyhydroxylamine groups on the molecule, were prepared by Pierce and Wotiz (53) in 1944. These symmetrical polyhydroxydisecondary amines were usually prepared by heating "Tris" with a dihalide, in most cases a dibromide. A series of asymmetrical diamines, all derivatives of 2-propanol, were prepared by reacting a secondary amine with epichlorohydrin. In these preparations an excess of hydrogen halide

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(50) Gabriel, Ind. Eng. Chem., 32, 891 (1940).
(51) Piloty and Ruff, Ber., 30, 1665, 2062 (1897).
(52) Henry, Bull. soc. chim., (3) 13, 1001 (1895).
(53) Pierce and Wotiz, J. Am. Chem. Soc., 66, 879 (1944).

was added to convert all of the free bases to their halide salts. Purification of the reaction products was effected usually by fractional crystallization. A list of several of the compounds reported by Pierce and Wotiz (54) follows:

$(HOCH_2)_3CNHCH_2CH_2NHC(CH_2OH)_3 \cdot 2HBr$

$(HOCH_2)_3CNH(CH_2)_3NHC(CH_2OH)_3 \cdot 2HBr$

$(HOCH_2)_3CNH(CH_2)_6NHC(CH_2OH)_3 \cdot 2HBr$

$(HOCH_2)_3CNHCH_2CHOHCH_2NHC(CH_2OH)_3 \cdot 2HCl$

The polyhydroxyamines prepared by Pierce and Wotiz are characterized by their white crystallinity, high water solubility, insolubility in alcohol and other non-polar solvents, and their chemical stability. Pierce and Wotiz noted a tendency for some of these compounds to hold ferric, bismuth and other metallic hydroxides in solution.

It was on the basis of this observation that Trout and Erdmanis (55) and Trout and Gladding (56) made a study of the chelation of the transition metal ions with "disec," $(HOCH_2)_3CNHCH_2CHOHCH_2NHC(CH_2OH)_3 \cdot 2HCl$. These investigators found "disec" to be an effective chelating agent for the bivalent ions of the transition metals and fair in its chelate stability with the ferric ion.

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(54) Pierce and Wotiz, J. Am. Chem. Soc., 73, 2594 (1951).
(55) Erdmanis, M.S. Thesis, University of Richmond (1955).
(56) Gladding, M.S. Thesis, University of Richmond (1955).

These compounds seemed to offer a convenient route to the study of chelation. This author, therefore, prepared a series of polyhydroxyamine hydrochlorides, some of which had been reported by Pierce and Wotiz and some of which were new compounds, and studied their chelation reactions with the ions of the first transition series. The methods of synthesis and purification used were much akin to those employed by Pierce and Wotiz and are discussed under the "Experimental Methods" portion of this paper.

EXPERIMENTAL

1. PREPARATION OF CHELATING AGENTS

The chelating agents studied were prepared and purified by methods similar to those used by Pierce and Wotiz (57, 58). Organic polyhalides were reacted in a refluxing ethanol medium with trishydroxymethylamino methane to give the corresponding polyhydroxyamine hydrochloride derivatives. The polyhydroxyamine hydrochlorides formed were white crystalline solids, quite soluble in water and insoluble in alcohol, acetone or hydrocarbons.

The yields of the polyhydroxyamines from "tris" and the polyhalides were nearly quantitative, except in the case of the propanone derivative where the yield was only 21 per cent of theoretical. Considerable tar was formed in this reaction. The preparations of 1,2,3-tris[tris(hydroxymethyl)methylamino]-propane trihydrochloride, and 1,3-bis[tris(hydroxymethyl)-methylamino]-2-propanone have not been reported in the literature. The table below shows the reactions employed in the preparations of the chelating agents studied.

Since all of the polyhydroxyamine compounds were similar only the preparation of 1,2;3-tris[tris(hydroxymethyl)methylamino]propane trihydrochloride will be described here in

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(57) Pierce and Wotiz, J. Am. Chem. Soc., 66, 879 (1944).
(58) Pierce and Wotiz, J. Am. Chem. Soc., 73, 2594 (1951).

SYNTHESES OF CHELATING AGENTS

2)

$2NH_2C(CH_2OH)_3 + ClCH_2CH_2Cl \rightarrow (HOH_2C)_3CNHCH_2CH_2NHC(CH_2OH)_3 \cdot 2HCl$

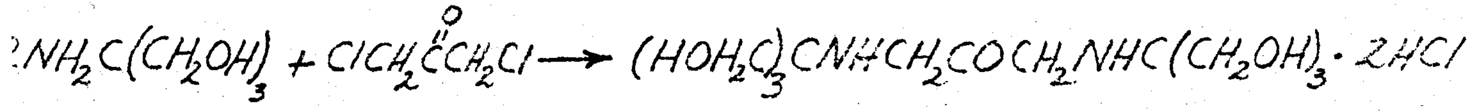
1, 2-BIS [TRIS (HYDROXYMETHYL) METHYLAMINO]
ETHANE DIHYDROCHLORIDE

?

$3NH_2C(CH_2OH)_3 + ClCH_2CHClCH_2Cl \rightarrow (HOH_2C)_3CNHCH_2CHNHC(CH_2OH)_3CH_2NC(CH_2OH)$

$\cdot 3HCl$

1, 2, 3-TRIS [TRIS (HYDROXYMETHYL) METHYLAMINO]
PROPANE TRIHYDROCHLORIDE



$2NH_2C(CH_2OH)_3 + ClCH_2\overset{O}{\overset{\|}{C}}CH_2Cl \rightarrow (HOH_2C)_3CNHCH_2COCH_2NHC(CH_2OH)_3 \cdot 2HCl$

1,3-BIS [TRIS (HYDROXYMETHYL) METHYLAMINO]-2-
PROPANONE DIHYDROCHLORIDE

$2NH_2C(CH_2OH)_3 + ClCH_2CHOHCH_2Cl \rightarrow (HOH_2C)_3CNHCH_2CHOHCH_2NHC(CH_2OH)_3 \cdot 2HCl$

1, 3-BIS [TRIS (HYDROXYMETHLYL) METHYLAMINO]-2-
PROPANOL DIHYDROCHLORIDE

$2NH_2C(CH_2OH)_3 + ClCH_2CH_2CH_2Cl \rightarrow (HOH_2C)_3CNHCH_2CH_2CH_2NHC(CH_2OH)_3 \cdot 2HCl$

1, 3-BIS [TRIS (HYDROXYMETHYL) METHYLAMINO]
PROPANE DIHYDROCHLORIDE

detail.

A mixture of 45.8 grams of trishydroxymethylamino methane (3/8 mol.) and 18.5 grams of 1,2,3-trichloropropane (1/8 mol.) were refluxed for one hour in 300 ml. of 95 per cent ethanol. Then 50 per cent aqueous potassium hydroxide was added to bring the solution pH up to 9.5. The mixture was allowed to reflux again until the pH fell to about 8 when more potassium hydroxide was added. This procedure was continued over a period of seven hours until the pH ceased to drop, indicating that the reaction was complete. 100 ml. 37 per cent hydrochloric acid was added to the cooled solution causing precipitation of inorganic salts. These salts were removed by filtration and were discarded.

The filtrate was vacuum evaporated until it became a tacky, viscous liquid. Three hundred milliliters of warm absolute ethanol was added to the mixture causing a precipitation of the polyhydroxyamine hydrochlorides along with some inorganic salts which had not been previously removed. The filtrate was evaporated and reprecipitated by the above method and the precipitate was combined with the original organic precipitate.

The combined precipitate was then dissolved in hydrochloric acid and water. The solution was vacuum evaporated until viscous and precipitated by the addition of hot absolute ethanol. This procedure was repeated again and the final precipitate was filtered and vacuum dried at 50°C. for

16 hours. The yield of 1,2,3-tris[tris(hydroxymethyl)-methylamino]propane trihydrochloride was 50.6 grams. The reaction was probably quantitative with the 20 per cent loss coming in the purification steps.

The compounds prepared, as above, were analyzed for hydroxyl and chloride groups by standard methods. The gravimetric method given by Pierce and Haenisch (59) gave good agreement with theoretical. This method involved the precipitation of the chloride as silver chloride. The hydroxyl content was determined by the method of Ogg and Willits (60) described by Siggia (61) in his textbook. This method is based on the acylation of the hydroxyl groups by acetic anhydride to give the ester. One mol. of the acetic anhydride was reacted by each amino and hydroxyl group. Good agreement with theory was given in each case except "disec" where a dark reaction product was formed which gave low results.

An attempt was made to analyze for carbonyl in the case of the propanone derivative by reacting with 2,4-dinitrophenylhydrazine to give the corresponding insoluble hydrazone. No such precipitation could be obtained. A study of

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(59) Pierce and Haenisch, "Quantitative Analysis," Wiley, New York (1948).

(60) Ogg, Porter, and Willits, Ind. Eng. Chem., Anal. Ed., 17, 394-397 (1945).

(61) Siggia, "Quantitative Organic Analysis via Functional Groups," Wiley, New York (1951).

the infrared spectrum of this compound made for the author by R. L. Levins (62) showed the normal absorption peak for carbonyl to be shifted downward indicating that the compound may be in the enol form or that the carbonyl is tied up by hydrogen bonding with one of the many hydroxyl groups in its vicinity.

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(62) R. L. Levins, Private Communication, Oct. 12, 1955.

2. PREPARATION OF CHELATE COMPOUNDS

The chelate compounds were formed by adding the chelating agent (polyhydroxyamine hydrochloride) to an aqueous solution of cupric nitrate, or other transition metal nitrates, and sodium nitrate. The acidity of the solution was then adjusted to a point where chelation occurred by the addition of 1 molar aqueous sodium hydroxide. In the final chelate mixture the concentrations were as follows:

$NaNO_3$ - 0.100 M
$Cu(NO_3)_2$ - 0.010 M
Ch. Agent - 0.010 M

These concentrations were varied somewhat but no metal ion concentrations above 0.02 M were used.

In all the quantitative work, such as pH titrations, spectrophotometric studies and Job's method determinations, the hydrochloride salts of the polyhydroxyamine compounds were used. The free base, supplied by J. S. Pierce (63) was used in the work where the copper chelate was prepared in methanol and recovered by precipitation with diethyl ether.

When a solution containing 5 grams of the "disec" free base in methanol was reacted with an equi-molar amount of $Cu(NO_3)_2$ a royal blue colored chelate solution was formed.

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(63) J. S. Pierce, Private Gift and Communication, June 22, 1956.

The chelate was much more soluble in methanol than was the "disec" free base so it could be evaporated down to a volume of 25 ml. without precipitation. Either dioxane or diethyl ether when added caused the chelate compound to precipitate out of solution, while acetone did not.

For the recovery, ether was used as the precipitant. After seven precipitations from methanol the chelate compound remained a heavy royal blue oil. This oil was recovered and vacuum dried at 50°C. overnight. After drying the chelate was a hard plastic-like blue solid which picked up moisture on standing in air to return to a thick blue liquid material.

3. METHODS OF DETECTION AND STUDY OF CHELATE COMPOUNDS

Martell and Calvin (64) give an excellent summary of the methods for the detection and study of chelate compounds in their book. The isolation, purification and analysis of pure chelate compounds was considered by Pfeiffer (65) to be conclusive in deciding whether a compound was a chelate. This method was used in the experimental chelation program at the University of Richmond by this author in one case but seems rather difficult and involved for the amount of information it discloses.

An important method for detecting chelate formation is the alteration of normal chemical reactions in solution. The fact that metal ions in solution do not undergo their normal reactions is a good indication that they are not present. Ley (66) used this method when he observed that the copper-glycine chelate did not hydrolyze in water while the weaker copper-alanine chelate did. We have used this method of observation in our work where we found that the cupric ion when chelated with several of the strong chelating agents did not precipitate even in concentrated aqueous sodium hydroxide but it did precipitate as the hydroxide

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(64) Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York (1952).
(65) Pfeiffer, Golther and Angern, Ber., 60B, 305 (1927).
(66) Ley, Ber., 42, 354 (1909).

with the weaker agents such as 1,3-bis[tris(hydroxymethyl)-methylamino]-2-propanone.

Color and absorption spectra are perhaps the most obvious methods for chelation detection. This method of study lends itself well to both qualitative and quantitative work and was used throughout the study of chelation with the polyhydroxylamines. Foley and Anderson (67) have used this treatment in their work with uranyl-sulfosalicylic acid chelation studies. Various other investigators have used this method with success.

Electrical conductance was used by the early investigators in this field since the disappearance of ions in complex formation could cause an appreciable change in the conductance of the solution. The contemporary workers in this field use the method very little and it seemed of no value in the work with polyhydroxyamine chelates since the material was highly ionic.

Most chelates occur as a result of the replacement of one or more usually weak protons on the chelating agent by a metal ion. Chelation is then accompanied by a decrease in the pH of the reaction mixture. It can be further concluded that the greater the tendency for the metal to combine, the greater the drop in pH. This constitutes a simple method

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(67) Foley and Anderson, J. Am. Chem. Soc., 71, 909 (1949).

of testing for chelation and for the determination of the relative stabilities of chelates. This method lends itself to the quantitative treatment of chelation data better than any other method of treatment and, as such, is more used by contemporary workers than any other method. It was the primary tool used in the study of the polyhydroxyamine-transition metal chelates. Bjerrum (68) did the classic work with this treatment of chelates.

Other methods found useful in the study of chelate compounds are as follows: optical activity, solubility, reaction rates studies, X-ray diffraction studies, infrared spectra and magnetic susceptibility measurements. The latter three methods seem applicable to the study of the polyhydroxyamine chelates but were not used for various reasons.

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(68) Bjerrum and Anderson, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen (1945).

4. STABILITY CONSTANTS

Much of the recently reported chelation data has been treated by means of the classic method of Bjerrum (69) in which stepwise formation constants were calculated. This is a technically sound approach and has been covered in some detail by Martell and Calvin (70); Carlson, McReynolds and Verhoek (71); and Erdmanis (72). For the complicated system of the polyhydroxyamine chelates, the treatment implies quite excessive accuracy. An overall complexity constant such as the 19.60 reported by Fernelius for the Cu^{++}-ethylenediamine chelate would require extreme accuracy in titration and pH measurement.

It seemed more prudent to work with what Bjerrum called the complexity constant which is simply the overall equilibrium constant for the chelation reaction. For the reaction

$$M + NA \rightleftharpoons MA_N$$

where:
M = central ion
N = number of coordinating ligands
A = coordinating ligand
MA_N = coordinatively saturated chelate

$$K_N = \frac{(MA_N)}{(M)(A)^N}$$

where:
MA_N = activity of the saturated chelate
M = activity of the uncomplexed metal ion
A = activity of the uncomplexed ligand
N = number of ligands

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(69) Bjerrum ~~and Andersen~~, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen (1945). 1941

(70) Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York (1952).

(71) Carlson, McReynolds and Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

(72) Erdmanis, M.S. Thesis, University of Richmond (1955).

All of the experimental work was done with a large excess of ionic strength (0.1 molar $NaNO_3$ compared to 0.01 molar for chelate) so that the activity coefficients should not vary appreciably in the reaction. It was, therefore, possible to substitute concentrations in the equilibrium expression without introducing appreciable error.

The concentrations requisite for the calculations were obtained from the known concentrations of ligand and metal ion charged and from the pH titration curves. Since in each case the chelation of the metal ions resulted in the displacement of two protons from the ligand, the concentration of saturated chelate could be determined by the difference in the amount of sodium hydroxide required to produce the same pH in the pure ligand and the chelated solution. The concentrations of the ligand and the metal ion at equilibrium were obtained by subtracting the concentration of saturated chelate from the original concentrations of the ligand and ion. The constants thus obtained are shown below:

Ligand	Metal Ion	Complexity Constant $\sim \log K_s$
1,2,3-tris[tris(hydroxymethyl)-methylamino]propane	Mn^{+2}	2.24
same	Co^{+2}	5.65
same	Cu^{+2}	(approx.) 10.00
1,2-bis[tris(hydroxymethyl)-methylamino]ethane	Cu^{+2}	2.52
1,3-bis[tris(hydroxymethyl)-methylamino]-2-propanone	Cu^{+2}	2.57

It may be noted that the order of stabilities in the case of the 1,2,3-propanetriamine derivative chelates are in agreement with those listed by Mellor and Malley (73, 74). The above stability constants confirm the fact, previously surmised from other qualitative observations, that the 1,2,3-propanetriamine derivative is, by far, the strongest chelating agent prepared. It was not possible to obtain stability constants for all the chelating agents or metal ions tested because of precipitation of the metallic ion as the hydroxide before appreciable coordination occurred. For example, none of the agents tested chelated the ferric ion, except "disec." This is interesting since the stability constant for the "disec"-copper chelate, reported by Erdmanis (75), was of the same order of magnitude (6.45) as that of the 1,2,3-propanetriamine derivative. Yet "disec" chelated iron, although weakly, while the 1,2,3-propanetriamine derivative did not. This suggests that a completely different mechanism is involved in the chelation of the ferric and cupric ions by the polyhydroxyamines. Since the secondary alcohol group on the 2-carbon is the only feature which "disec" has which is not contained in at least some of the other polyhydroxyamine compounds (which did not chelate

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(73) Mellor and Malley, Nature, <u>159</u>, 370 (1947).
(74) Mellor and Malley, Nature, <u>161</u>, 436 (1948).
(75) Erdmanis, M.S. Thesis, University of Richmond (1955).

the ferric ion), one surmises that the secondary alcohol group is involved in the chelation of iron.

5. POTENTIOMETRIC TITRATIONS

When chelation occurs there is a displacement of one or more protons from the chelating agent by the metal ion. This causes a change in the hydrogen ion concentration of the solution. The drop in pH was used in a quantitative treatment of the chelation data. This work was described in the preceding section of this thesis.

It was not possible to treat all of the chelates quantitatively since some precipitated before appreciable coordination occurred. However, these experiments were evaluated qualitatively as competitive reactions between the OH^- and the chelating agent for the metal ion. The potentiometric titrations are discussed in the following section for the several metal ions tested with each chelating agent.

(a) 1,2-Bis[tris(hydroxymethyl)methylamino]-ethane - Cu^{++}

The pH titration curve with the above chelate and aqueous sodium hydroxide is shown on Figure 1 and the table of experimental data is shown on Table 1. The titrations of the $Cu(NO_3)_2$ solution and the free ligand are shown on Tables 2 and 3, respectively.

It was noted that chelation began at a pH of about 5. The color of the chelate compound was blue until it was made just basic. The color then changed to violet. Precipitation of cupric hydroxide occurred when the solution was made more basic (about pH 9). pH titrations (not shown) using Fe^{+3} ions

FIGURE 1

1,2 BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]ETHANE – Cu^{++} CHELATE

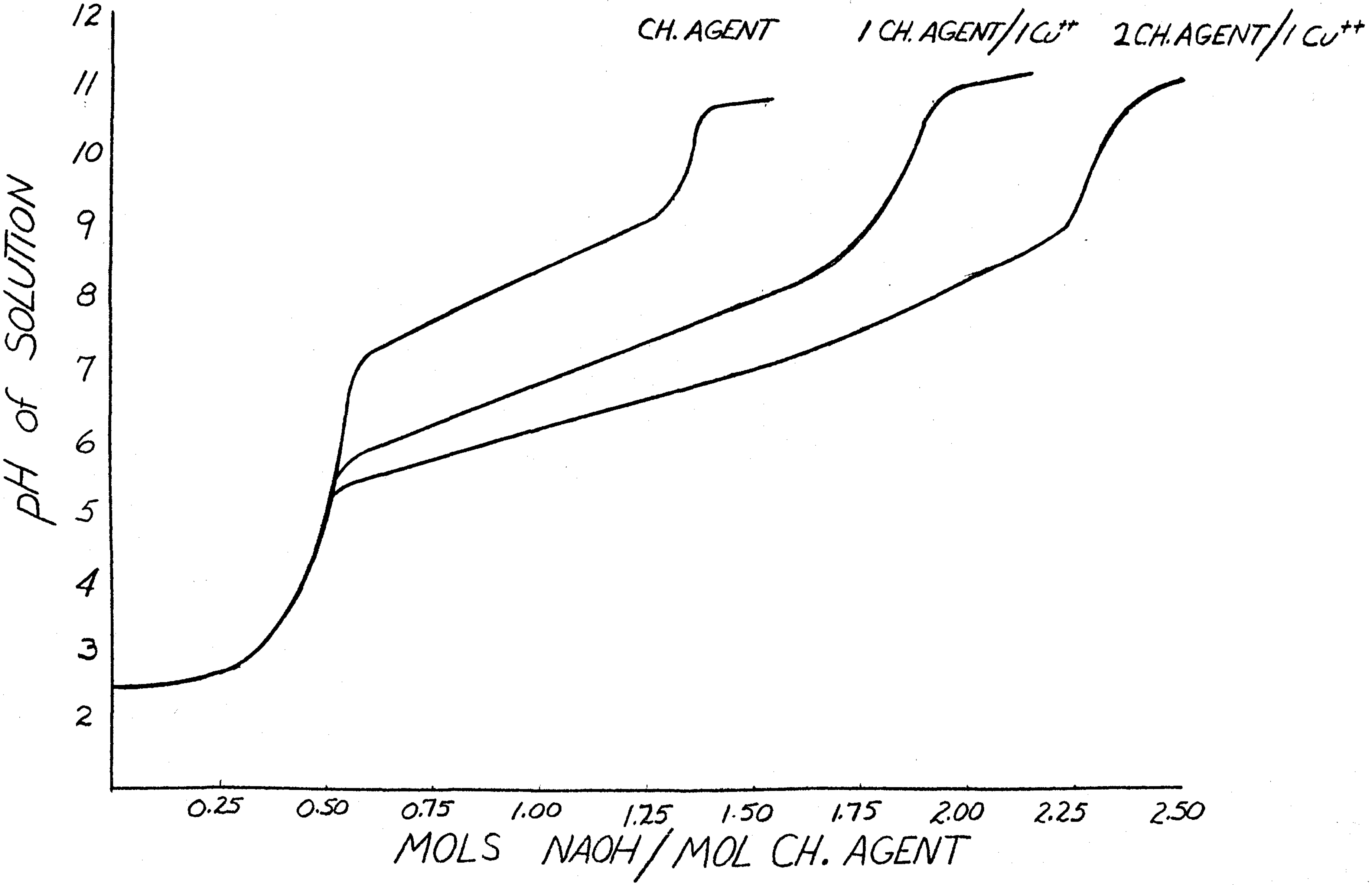

TABLE 1

TITRATION OF 1,2-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]ETHANE WITH NaOH

20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
70 ml. Distilled Water

1.000 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	2.39	0.54	6.89
0.06	2.40	0.60	7.30
0.10	2.45	0.80	7.91
0.14	2.49	0.91	8.13
0.20	2.56	1.00	8.31
0.26	2.69	1.13	8.70
0.30	2.79	1.19	8.89
0.36	3.01	1.25	9.15
0.42	3.50	1.28	9.41
0.45	4.25	1.34	10.19
0.48	5.00	1.38	10.61
0.50	6.00	1.47	10.82
0.52	6.50	1.54	11.00

TABLE 2

TITRATION OF $Cu(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Cu(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
70 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH
0.00	4.49
0.02	5.31 pptation.
0.12	5.62
0.35	5.91

TABLE 3

TITRATION OF 1,2-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-ETHANE-$Cu(NO_3)_2$ WITH NaOH

A	B
20 ml. 0.500 M $NaNO_3$	20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent	20 ml. 0.100 M Chelating Agent
10 ml. 0.100 M $Cu(NO_3)_2$	10 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water	50 ml. Distilled Water

1.000 M NaOH

A		B	
ml. NaOH	pH	ml. NaOH	pH
0.00	2.40	0.00	2.36
0.10	2.45	0.09	2.42
0.14	2.49	0.16	2.50
0.20	2.59	0.30	2.77
0.36	3.01	0.36	3.05
0.40	3.39	0.41	3.50
0.44	3.79	0.48	4.96
0.46	4.25	0.50	5.30
0.50	5.00	0.53	5.51
0.53	5.55	0.71	5.89
0.60	5.80	0.81	6.03
0.72	6.11	0.95	6.21
0.80	6.25	1.11	6.40
0.93	6.50	1.21	6.53
1.06	6.85	1.31	6.70
1.14	7.00	1.41	6.84
1.30	7.42	1.48	7.00
1.40	7.70	1.61	7.20
1.59	8.21	1.73	7.51
1.68	8.50	1.85	7.78
1.77	9.30	1.91	7.96
1.81	9.95	2.01	8.22
1.86	10.50	2.11	8.64
1.89	10.70	2.15	9.21
2.02	10.95	2.19	9.72
		2.25	10.23
		2.38	10.80

resulted in no coordination, but rather rapid precipitation of ferric hydroxide. On the basis of the pH titrations, one concludes that this polyhydroxy derivative of ethylenediamine is a rather weak chelating agent.

(b) 1,2,3-Tris[tris(hydroxymethyl)methylamino]-propane - Cu^{+2}

pH titrations made in this study using aqueous sodium hydroxide ~~is~~ are shown on Figure 2. Experimental data ~~is~~ are shown on Tables 4, 5 and 6. This was a very stable chelate compound when either the 1:1 or 2:1 ratio of ligand to cupric ion was used. No sign of precipitation was noted after this material was stored for six months in concentrated sodium hydroxide.

are

(c) 1,2,3-Tris[tris(hydroxymethyl)methylamino]-propane - Co^{++}

This chelate was studied by means of potentiometric titrations with aqueous sodium hydroxide. The titration curve for the 1:1 ligand to metal ion ratio is shown on Figure 3 while the experimental data is shown on Table 7. A stable chelate was formed with Co^{++} at about pH 6.0 which was reddish yellow in color. As the chelate solution was made more basic the color darkened. No precipitation was noticeable immediately after the titration was completed. After setting a week at pH 11.5 the cobaltous ion precipitated as the hydroxide.

1,2,3 TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE—Cu^{++} CHELATE

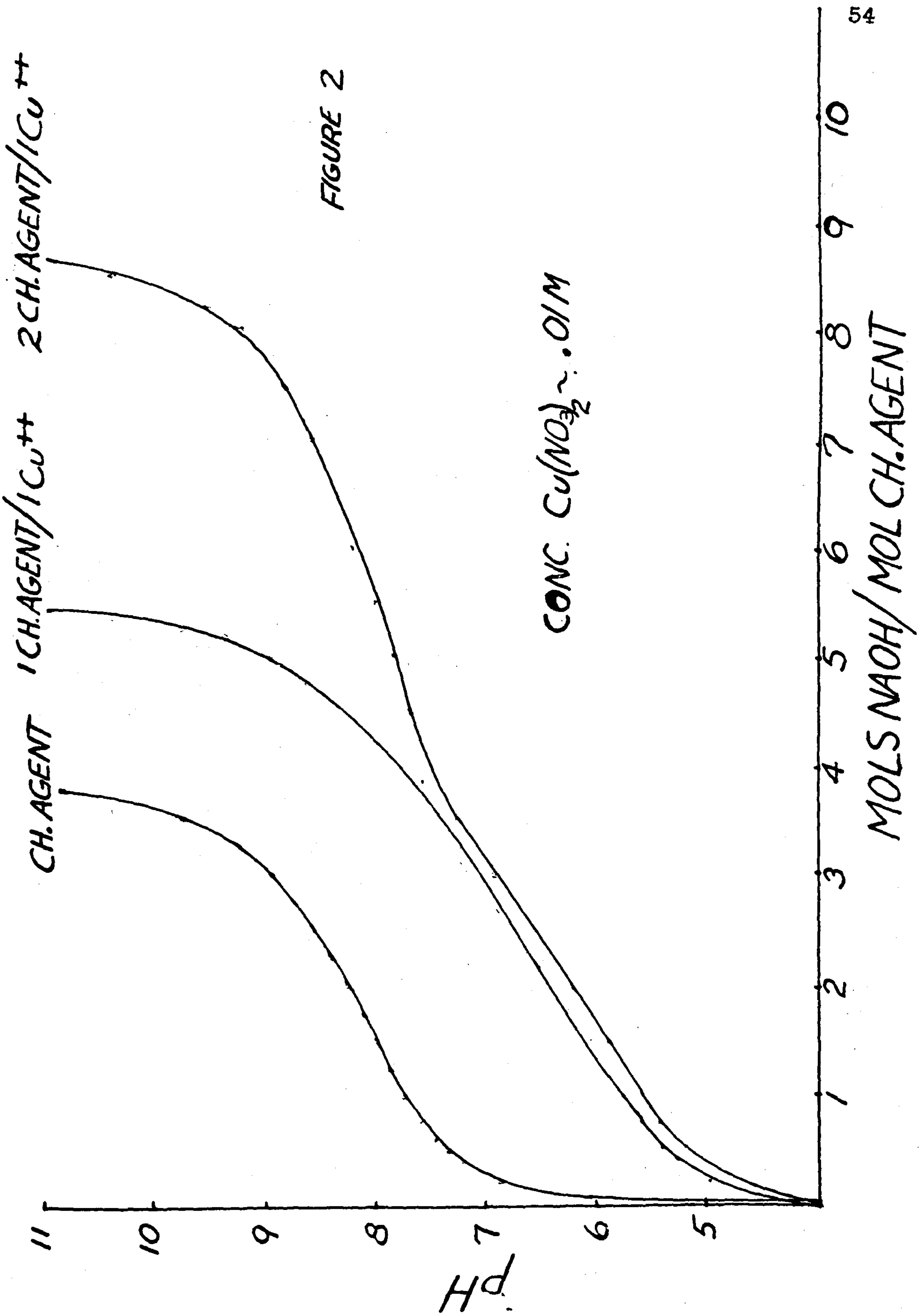

FIGURE 2

TABLE 4

TITRATION OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-PROPANE WITH NaOH

10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
70 ml. Distilled Water

1.050 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	5.13	2.64	8.66
0.04	6.06	2.91	8.88
0.075	6.33	3.17	9.11
0.14	6.68	3.25	9.26
0.17	6.79	3.36	9.50
0.20	6.87	3.46	9.75
0.27	7.02	3.57	10.18
0.32	7.11	3.64	10.48
0.36	7.18	3.73	10.86
0.57	7.42	3.80	11.06
0.71	7.55	3.91	11.25
0.81	7.62	4.00	11.40
1.00	7.74	4.22	11.60
1.23	7.89	4.55	11.71
1.37	7.96	4.85	11.78
1.73	8.14	5.00	11.80
1.86	8.21	6.00	11.94
2.31	8.46		

TABLE 5

TITRATION OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-PROPANE-$Cu(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar Chelating Agent
10 ml. 0.100 Molar $Cu(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.050 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	3.89	0.77	5.63
0.05	4.50	0.82	5.69
0.09	4.66	0.90	5.72
0.12	4.79	0.97	5.78
0.18	4.94	1.09	5.84
0.20	5.00	1.13	5.88
0.215	5.06	1.19	5.90
0.248	5.13	1.26	5.96
0.290	5.19	1.50	6.09
0.31	5.21	1.65	6.16
0.36	5.29	1.78	6.22
0.40	5.31	1.93	6.31
0.45	5.39	2.13	6.49
0.51	5.45	2.37	6.64
0.55	5.48	2.50	6.73
0.60	5.51	2.60	6.84
0.63	5.52	2.75	6.96
0.66	5.56	2.93	7.13
0.70	5.60	3.23	7.39

TABLE 5 (CONTINUED)

ml. NaOH	pH
3.35	7.50
3.79	7.80
4.07	8.00
4.19	8.09
4.35	8.20
4.63	8.49
4.81	8.64
4.91	8.79
5.02	8.91
5.05	9.03
5.06	9.15
5.12	9.42
5.18	9.69
5.24	10.21
5.27	10.48
5.33	10.80
5.40	11.00
5.51	11.21
5.67	11.40
5.85	11.55
6.05	11.65
6.86	11.84
7.28	11.89
7.88	11.96
8.41	12.00
9.34	12.05
10.01	12.10
15.00	12.23

TABLE 6

TITRATION OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-PROPANE-$Cu(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Cu(NO_3)_2$
20 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
50 ml. Distilled Water

1.050 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	3.72	1.82	6.12
0.04	4.09	2.09	6.27
0.10	4.45	2.25	6.39
0.14	4.51	2.56	6.60
0.17	4.65	2.74	6.74
0.26	4.86	2.97	6.92
0.33	4.97	3.28	7.15
0.44	5.14	3.54	7.30
0.49	5.21	3.78	7.41
0.54	5.29	4.14	7.60
0.61	5.32	4.64	7.75
0.70	5.41	5.08	7.90
0.76	5.50	5.40	8.15
0.92	5.58	6.88	8.53
1.05	5.68	7.40	8.79
1.16	5.73	7.62	8.90
1.38	5.88	7.90	9.15
1.63	6.00	8.08	9.31

TABLE 6 (CONTINUED)

ml. NaOH	pH
8.25	9.64
8.38	9.96
8.40	10.40
8.57	10.70
8.66	11.03
8.78	11.21
8.96	11.48
9.27	11.70

FIGURE ~ 3

1,2,3 TRIS [TRIS (HYDROXYMETHYL) METHYLAMINO] PROPANE ~ Co^{++} AND Mn^{++} CHELATES

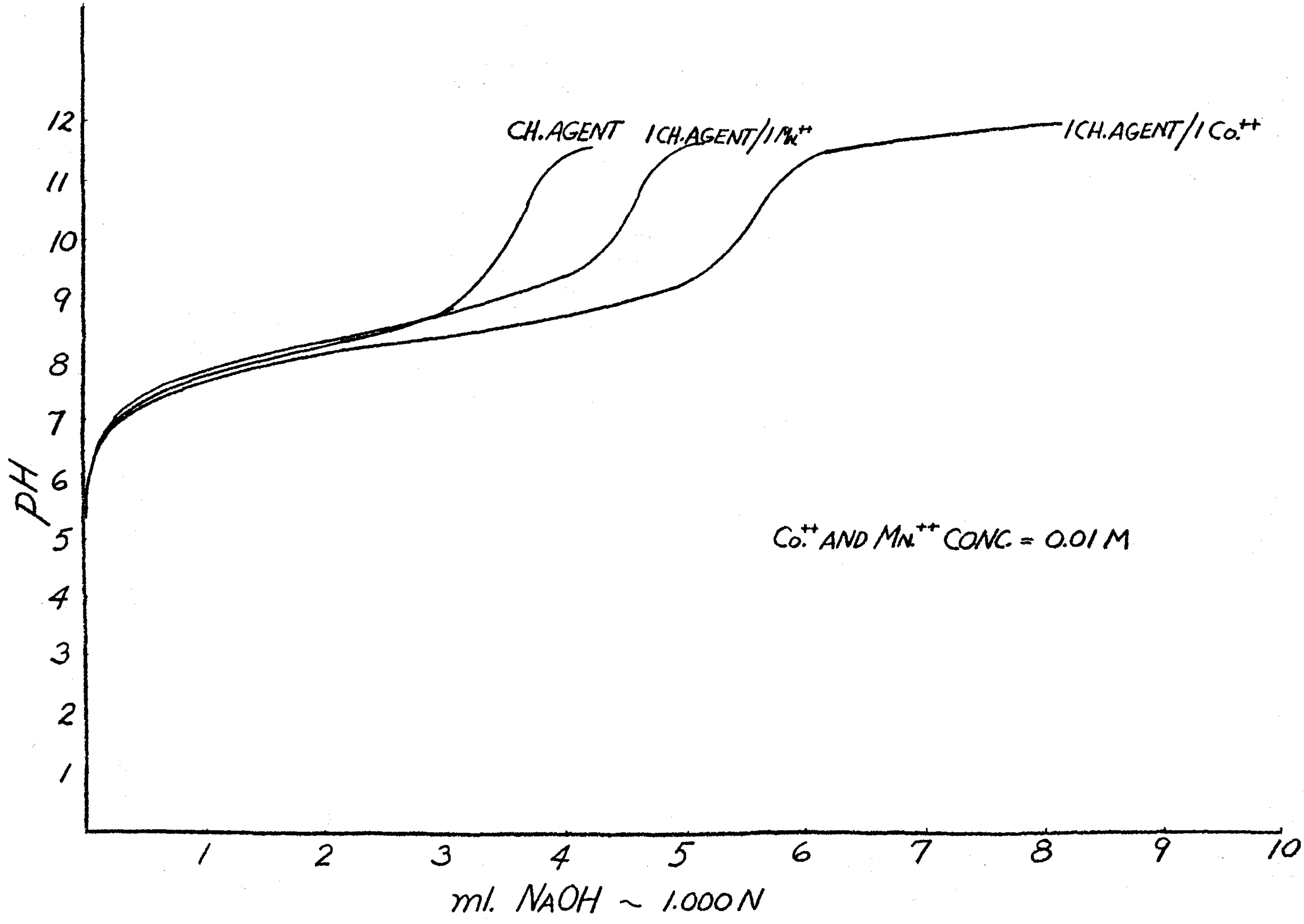

TABLE 7

TITRATION OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Co(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Co(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water 1.000 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	5.81	1.80	8.07
0.06	6.55	1.95	8.11
0.14	6.70	2.07	8.15
0.19	6.80	2.44	8.25
0.24	6.91	2.60	8.30
0.28	7.00	2.70	8.32
0.34	7.08	3.03	8.41
0.40	7.15	3.32	8.50
0.52	7.30	3.86	8.70
0.60	7.39	4.02	8.75
0.78	7.51	4.35	8.91
0.90	7.61	4.51	9.00
1.00	7.69	4.75	9.15
1.11	7.71	4.80	9.20
1.20	7.79	5.00	9.30
1.34	7.85	5.08	9.41
1.47	7.91	5.24	9.51
1.60	8.00	5.29	9.66

TABLE 7 (CONTINUED)

ml. NaOH	pH	
5.46	10.01	
5.52	10.25	
5.59	10.45	
5.65	10.70	
5.74	10.85	
5.83	11.06	
5.93	11.20	
6.21	11.44	
6.66	11.67	pptation.
8.65	12.00	

(d) 1,2,3-Tris[tris(hydroxymethyl)methylamino]-propane - Mn^{++}

The potentiometric titration curve of the 1,2,3-propane triamine derivative is shown on Figure 3 and experimental data is shown on Table 8. Precipitation of the chelate occurred at pH 9.0. This indicates the chelate to be rather unstable since the solubility product of $Mn(OH)_2$ had not been greatly exceeded.

(e) 1,2,3-Tris[tris(hydroxymethyl)methylamino]-propane - Fe^{+3}

No chelate was formed between the ferric ion and the 1,2,3-propane triamine derivative. This is clearly demonstrated by the pH titration curves shown on Figure 4 and the titration data on Table 9. It is notable that this compound, which was the most powerful agent tested for the chelation of the bivalent transition metals, had no tendency to complex the ferric ion.

(f) 1,3-Bis[tris(hydroxymethyl)methylamino]-2-propanone - Cu^{+2}

The 1:1 chelate precipitated near neutral. The titration curves are shown on Figure 5 and the data are shown on Tables 10 and 11. The chelate formed at about pH 5. It was blue but turned to a violet color at pH 7, as the other cupric chelates with the polyhydroxyamines. Under strongly basic conditions precipitation of cupric hydroxide occurred. The 2-propanone derivative did not form coordination compounds of detectable stability with the ferric ion or with the ions

TABLE 8

TITRATION OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Mn(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Mn(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.000 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	6.00	1.92	8.29
0.08	6.55	2.36	8.50
0.24	7.11	2.66	8.65
0.28	7.20	3.16	8.90
0.38	7.31	3.31	9.00 pptation.
0.48	7.44	3.64	9.18
0.62	7.60	3.93	9.41
0.72	7.69	4.18	9.60
0.80	7.72	4.39	10.01
1.01	7.89	4.51	10.55
1.29	8.01	4.62	10.90
1.51	8.14		

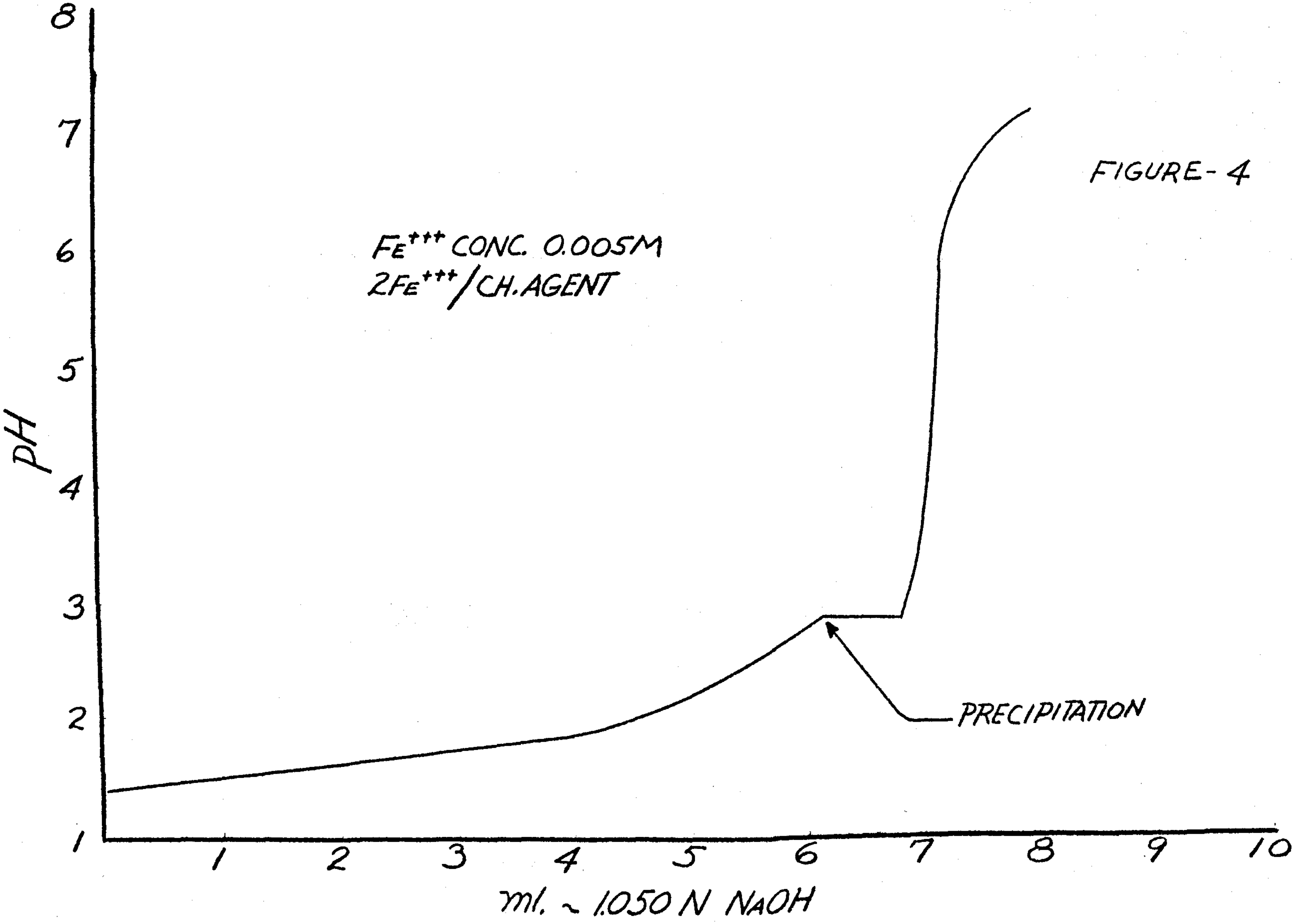

FIGURE- 4

Fe^{+++} CONC. 0.005M
$2Fe^{+++}$/CH. AGENT
PRECIPITATION
pH
1
2
3
4
5
6
7
8
1
2
3
4
5
6
7
8
9
10
ml. ~ 1.050 N NaOH

TABLE 9

TITRATION OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-PROPANE-Fe(NO_3)$_3$ WITH NaOH

10 ml. 0.050 Molar Fe(NO_3)$_3$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.050 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	1.31	6.47	2.85
0.92	1.42	6.80	2.85
4.70	2.00	6.86	3.30
5.00	2.12	7.02	4.33
5.61	2.44	7.04	4.89
5.86	2.62	7.12	5.79
5.97	2.73	7.14	6.18
6.17	2.84	7.25	6.42
6.18	2.84	7.40	6.62
6.34	2.85	7.44	6.80

FIGURE 5

1,3 BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-2-PROPANONE ~ Cu^{++} CHELATE

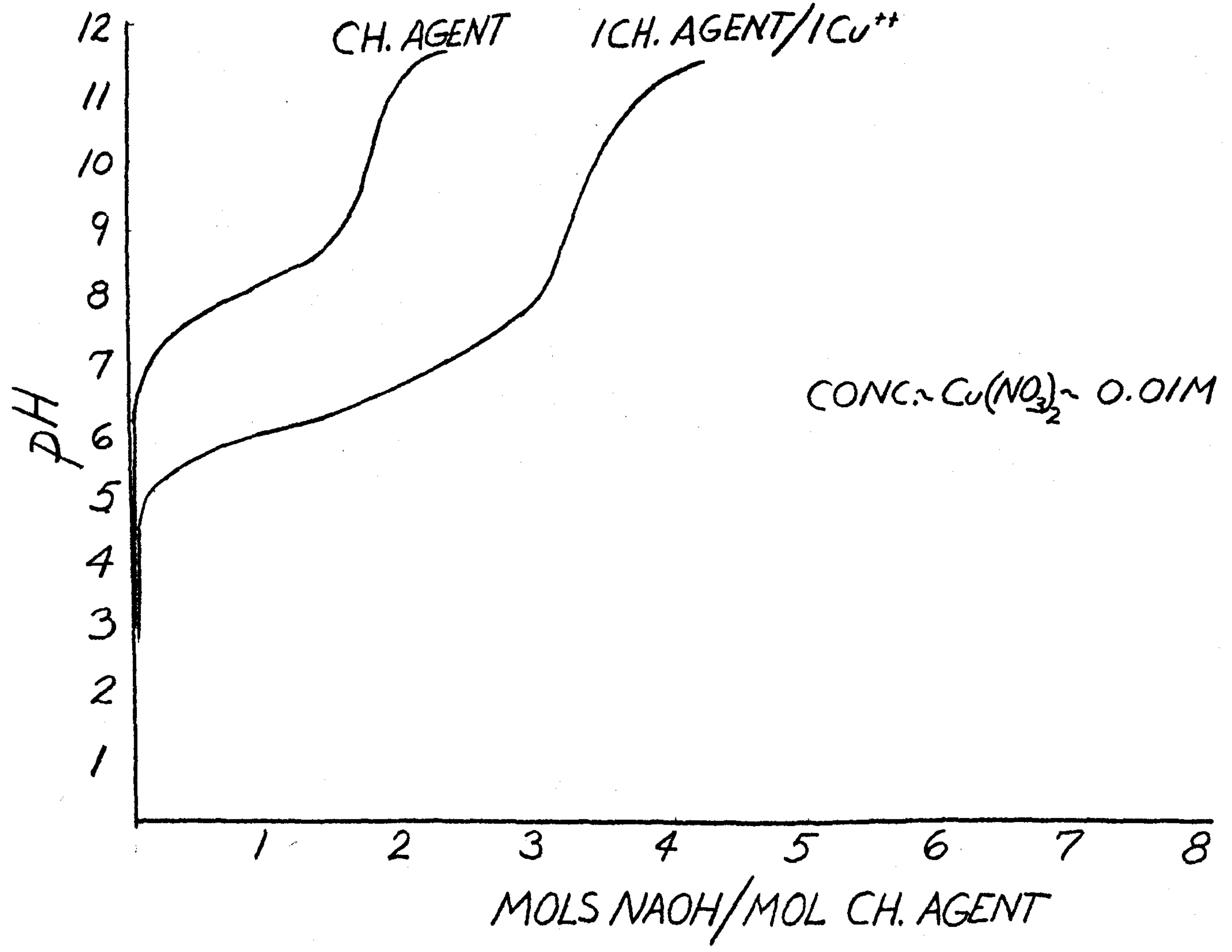

TABLE 10

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-2-PROPANONE WITH NaOH

10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
70 ml. Distilled Water

1.000 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	4.05	0.84	8.00
0.04	5.26	0.93	8.12
0.06	6.28	1.18	8.38
0.10	6.59	1.30	8.50
0.12	6.82	1.52	8.81
0.16	6.98	1.62	9.05
0.20	7.22	1.69	9.30
0.24	7.24	1.76	9.69
0.28	7.30	1.84	10.35
0.36	7.44	1.90	10.80
0.50	7.69	1.98	11.03
0.70	7.86		

TABLE

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-2-PROPANONE $Cu(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar Chelating Agent
10 ml. 0.100 Molar $Cu(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.000 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	3.69	1.00	5.91
0.01	3.79	1.18	6.02
0.02	4.28	1.44	6.19
0.07	4.61	1.53	6.24
0.10	4.81	1.66	6.36
0.14	4.96	1.76	6.48
0.18	5.07	1.91	6.61
0.22	5.15	2.02	6.70
0.29	5.30	2.11	6.80
0.32	5.36	2.20	6.90
0.40	5.44	2.28	7.00
0.47	5.51	2.54	7.30
0.61	5.65	2.70	7.44
0.68	5.80	2.77	7.61 pptation.
0.82	5.81		

of the rare earths. This is seen in the titration data shown on Tables 12 and 13.

(g) 1,3-Bis[tris(hydroxymethyl)methylamino]propane

The above chelating agent was used in a number of potentiometric studies using 0.01 molar agent and metal ion strengths, as in the other chelation studies. The chelate with cupric ion formed at a pH of approximately 5, and was royal blue in color. The color changed to purple at pH 7. It was stable in rather basic solutions although some precipitation occurred after several weeks storage in strong base when a 2:1 ligand to Cu^{+2} ratio was used. Precipitation occurred with the 1:1 chelate at pH9. These effects are shown by data on Tables 14, 15 and 16.

Green chelates were prepared with the 1,3-propanediamine derivative and the Ni^{+2} ion which precipitated as the $Ni(OH)_2$ upon standing for a period of a week in strong base. The titration data for the 2:1 and 1:1 chelates are shown on Tables 17, 18 and 19.

Tables 20, 21 and 22 show potentiometric titrations of $Zn(NO_3)_2$-1,3-bis[tris(hydroxymethyl)methylamino]propane solutions. Precipitation of the zinc occurred in each case with no appreciable chelate formation. Similar results were obtained in titrations using the ferric and manganous ions. These results are shown on Tables 23 and 24.

The results shown on Table 25 indicate that a reasonably stable chelate is formed by 1,3-bis[tris(hydroxymethyl)-

TABLE 12

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-2-PROPANONE-$Fe(NO_3)_3$ WITH NaOH

10 ml. 0.050 Molar $Fe(NO_3)_3$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.000 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	1.40	5.54	1.99
0.01	1.40	5.68	2.02
0.02	1.40	6.00	2.15
1.12	1.42	6.25	2.24
1.24	1.43	6.52	2.38
1.36	1.45	6.64	2.46
1.57	1.47	6.84	2.55
1.88	1.50	6.96	2.64
2.08	1.50	7.20	2.18
2.28	1.52	7.44	2.45
2.75	1.55	7.49	2.80
3.70	1.65	7.63	2.80
4.01	1.69	7.80	2.88
4.28	1.72	7.92	2.95
4.53	1.76	8.04	3.10
4.73	1.80	8.16	3.40
5.00	1.86	8.24	3.90
5.34	1.91	8.29	5.30 pptation.

TABLE 13

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-2-PROPANONE-RARE EARTH NITRATE WITH NaOH

10 ml. 0.1 Molar Rare Earth Nitrate
20 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
50 ml. Distilled Water

1.000 N NaOH

ml. NaOH	pH
0.00	4.42
0.02	5.65
0.08	6.50
0.11	6.90
0.14	7.12
0.17	7.24
0.30	7.58
0.46	7.73
0.49	7.82
0.56	7.90
0.76	8.04
0.96	8.20
1.10	8.25
1.30	8.30 pptation.
1.92	8.19
2.38	8.31

TABLE 14

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE WITH NaOH

10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
70 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00		1.65	8.66
0.04	6.75	2.00	8.90
0.13	7.00	2.40	9.13
0.17	7.05	2.68	9.30
0.23	7.25	2.94	9.55
0.35	7.42	3.25	9.80
0.54	7.74	3.43	10.05
0.65	7.90	3.58	10.36
1.00	8.20	3.69	10.75
1.15	8.31	3.85	11.00
1.34	8.49	4.00	

TABLE 15

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Cu(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Cu(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	3.00	2.10	6.51
0.02	3.30	2.24	6.75
0.04	3.50	2.40	6.93
0.055	3.62	2.55	7.19
0.19	4.16	2.68	7.39
0.24	4.52	2.84	7.60
0.28	4.75	3.01	8.09
0.32	4.85	3.40	8.29
0.36	5.00	3.65	8.50
0.42	5.10	3.85	8.70
0.45	5.20	4.05	8.89
0.55	5.32	4.20	9.01 pptation.
0.64	5.42	4.51	9.39
0.82	5.60	4.79	9.50
1.07	5.80	4.95	9.71
1.44	6.02	5.00	9.72
1.79	6.25		

TABLE 16

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Cu(NO_3)_2$ WITH NaOH

5 ml. 0.100 Molar $Cu(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
65 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	3.31	1.86	8.11
0.03	3.50	2.04	8.36
0.09	4.00	2.14	8.44
0.13	4.28	2.33	8.70
0.16	4.69	2.55	8.89
0.19	4.90	2.76	9.05
0.26	5.24	3.02	9.26
0.30	5.35	3.25	9.49
0.42	5.64	3.48	9.71
0.63	5.90	3.67	9.94
0.92	6.31	3.82	10.05
1.01	6.50	3.97	10.61
1.18	6.80	4.09	10.90
1.24	6.96	4.22	11.20
1.39	7.30		
1.52	7.59		
1.68	7.88		

TABLE 17

TITRATION OF $Ni(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Ni(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
70 ml. Distilled Water 0.981 N NaOH

ml. NaOH	pH
0.00	5.70
0.03	7.24
0.06	7.82
0.09	8.02 pptation.
0.34	8.15
0.59	8.24
0.87	8.30
1.17	8.38
1.42	8.51
1.63	8.71
1.73	8.90
1.81	9.35
1.85	10.24
1.91	10.50
2.00	10.81

TABLE 18

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Ni(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar Chelating Agent
5 ml. 0.100 Molar $Ni(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
65 ml. Distilled Water

0.981 N NaOH

ml. NaOH	pH
0.00	4.80
0.04	5.68
0.08	5.88
0.12	6.02
0.14	6.12
0.18	6.24
0.21	6.42
0.24	6.56
0.34	6.89
0.44	7.14
0.62	7.42
0.75	7.60
0.88	7.75
1.10	7.98
1.24	8.10
1.43	8.24
1.72	8.46
1.95	8.60
2.17	8.73
2.45	8.90
2.70	9.02
3.00	9.19
3.20	9.30
3.58	9.51
3.87	9.74
4.04	9.92
4.18	10.04
4.33	10.25
4.43	10.48
4.59	10.80
4.80	11.00

TABLE 19

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Ni(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar Chelating Agent
10 ml. 0.100 Molar $Ni(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

ml. NaOH	pH	ml. NaOH	pH
0.00	4.79	2.08	8.39
0.04	5.28	2.33	8.50
0.06	5.51	2.57	8.66
0.12	5.88	2.88	8.80
0.18	6.11	3.16	8.95
0.22	6.20	3.45	9.12
0.28	6.47	3.71	9.24
0.36	6.71	4.03	9.46
0.47	6.97	4.34	9.65
0.61	7.14	4.60	9.86
0.80	7.42	4.78	10.01
1.03	7.69	4.92	10.20
1.28	7.89	5.01	10.36
1.53	8.08	5.12	10.58
1.77	8.25		

TABLE 20

TITRATION OF $Zn(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Zn(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
70 ml. Distilled Water

0.986 N NaOH

ml. NaOH	pH	
0.00	5.51	
0.03	6.50	
0.08	7.12	pptation.
0.27	7.23	
0.73	7.60	
1.24	7.75	
1.87	8.20	
2.02	10.00	
2.05	10.48	
2.13	10.61	

TABLE 21

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Zn(NO_3)_2$ WITH NaOH

5 ml. 0.100 Molar $Zn(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
65 ml. Distilled Water

0.986 N NaOH

ml. NaOH	pH
0.00	5.96
0.06	6.39
0.09	6.52
0.14	6.78
0.20	6.92
0.23	7.01
0.29	7.12
0.34	7.26
0.52	7.42
0.61	7.50 pptation.
1.12	7.81
1.78	8.25
2.08	8.61
2.62	8.86
2.80	9.01
3.02	9.19
3.59	9.39
3.88	9.55
4.05	9.68
4.25	9.86

TABLE 22

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Zn(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar $Zn(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

0.986 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	4.91	0.76	7.30 pptation.
0.02	5.59	1.18	7.51
0.04	5.99	1.68	7.68
0.09	6.20	2.22	7.89
0.12	6.40	2.77	8.15
0.15	6.51	3.07	8.38
0.23	6.75	3.36	8.58
0.25	6.81	3.64	8.76
0.35	7.00	3.91	8.90
0.42	7.15	4.22	9.08
0.45	7.18	4.58	9.30
		5.00	9.51

TABLE 23

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Fe(NO_3)_3$ WITH NaOH

10 ml. 0.100 Molar Chelating Agent
10 ml. 0.100 Molar $Fe(NO_3)_3$
20 ml. 0.500 Molar $NaNO_3$
60 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	1.11	5.60	2.41
0.12	1.12	5.76	2.52
1.04	1.15	5.81	2.55
2.00	1.24	5.90	2.62
2.61	1.30	6.01	2.65
3.89	1.51	6.17	2.75
4.40	1.65	6.35	2.75 pptation.
4.68	1.75	6.45	2.82
4.83	1.81	6.52	2.82
5.00	1.91	6.60	3.01
5.06	1.96	6.64	3.30
5.21	2.05	6.68	3.50
5.30	2.14	6.70	3.86
5.43	2.24	6.72	4.35

TABLE 24

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Mn(NO_3)_2$ WITH NaOH

5 ml. 0.100 Molar $Mn(NO_3)_2$
10 ml. 0.100 Molar Chelating Agent
20 ml. 0.500 Molar $NaNO_3$
65 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH
0.00	3.50
0.06	6.41
0.09	6.59
0.12	6.86
0.16	7.05
0.20	7.22
0.26	7.39
0.30	7.48
0.36	7.59
0.44	7.74
0.59	7.94
0.68	8.04
0.86	8.23
1.02	8.39
1.17	8.50
1.27	8.60
1.45	8.70
1.63	8.81 pptation.

TABLE 25

TITRATION OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-$Co(NO_3)_2$ WITH NaOH

10 ml. 0.100 Molar Chelating Agent
5 ml. 0.100 Molar $Co(NO_3)_2$
20 ml. 0.500 Molar $NaNO_3$
65 ml. Distilled Water

1.00 N NaOH

ml. NaOH	pH	ml. NaOH	pH
0.00	4.50	1.86	8.70
0.04	6.10	2.20	8.93
0.10	6.46	2.62	9.21
0.19	6.85	2.80	9.41
0.28	7.00	3.22	9.65
0.35	7.16	3.44	9.90
0.64	7.65	3.60	10.15
0.81	7.89	3.74	10.36
1.06	8.10	3.82	10.60
1.31	8.32	3.92	10.90
1.61	8.53	4.09	11.15

methylamino] propane + Co^{+2} . This chelate, formed at a pH of approximately 6, had a reddish yellow color which darkened as the solution was made more basic. The chelate was stable in strong base for a week--no precipitate of the hydroxide occurred.

The potentiometric titrations offered a quick and reasonably accurate method of testing for chelate formation.

6. ABSORPTION SPECTRA

Werner (76) recognized that a characteristic color is one of the most important features of chelate compounds, and used the absorption spectra to distinguish between free metal ions and their chelate compounds. The free metal ions and the free polyhydroxyamine ligands have very little light absorbance in the region of 300 to 900 millimicrons light wave length while the absorbance is very strong for the chelate compounds in this region. This fact indicated that this method should be a good one for detecting the presence of the chelate compound.

This method was used to show the formation of the 1,2,3-tris[tris(hydroxymethyl)methylamino]propane - Cu^{+2} chelate. This work is illustrated by the spectrophotometric study shown on Figure 6. It is shown that little light absorbance occurs at pH 2.5 indicating little or no chelation and just slightly more at pH 5.0. When a pH of 6.5 is reached the absorbance is very high meaning that chelation is essentially complete. At a pH of 8.5 the maximum light absorbance is about the same. The degree of chelation is essentially equal to that at pH 6.5. The wave length at which maximum light absorbance occurred decreased appreciably

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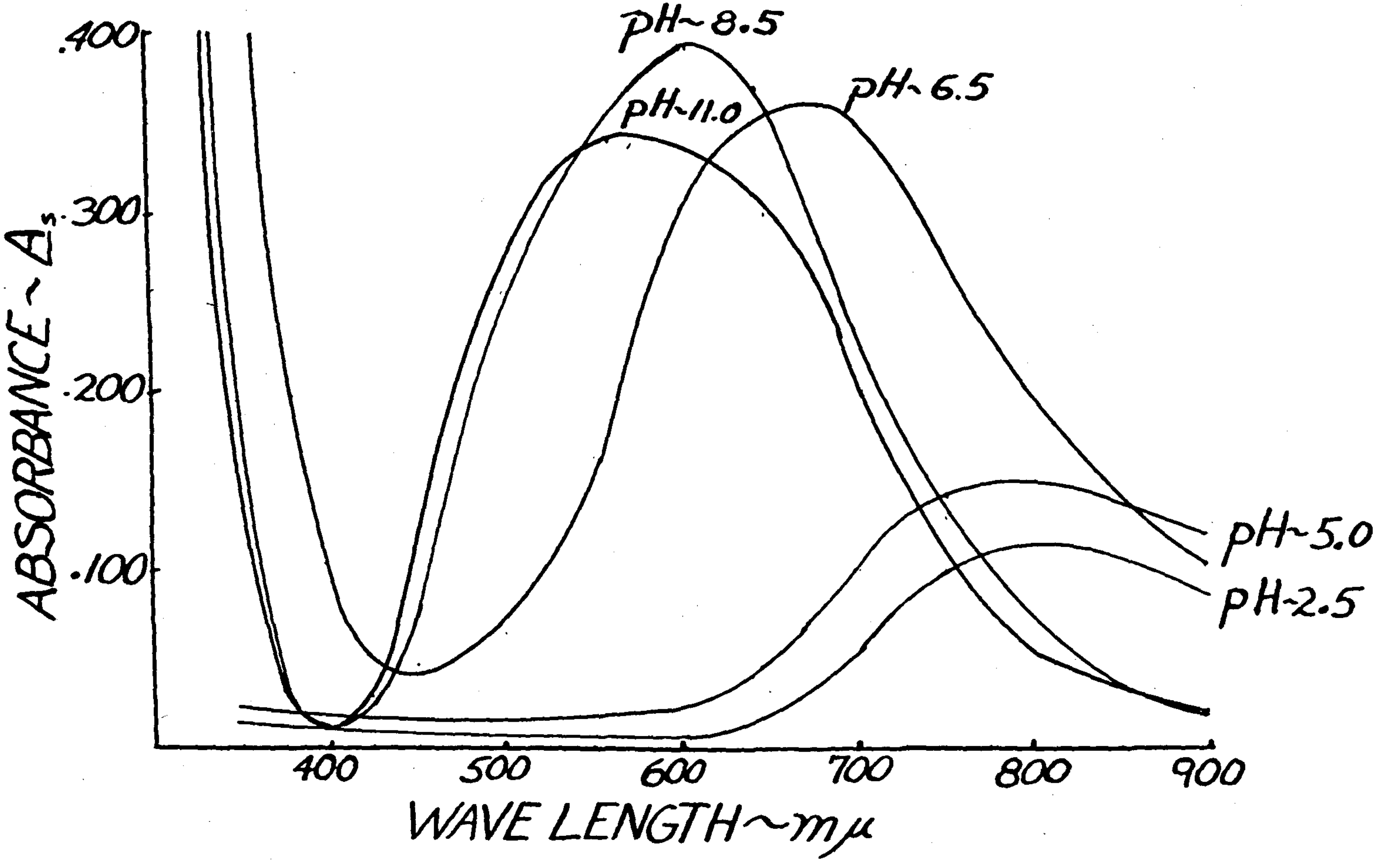
(76) Werner, Ber., 34, 2584 (1901).

FIGURE 6

1,2,3TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE-
Cu⁺⁺ CHELATE



when the solution pH was increased from 6.5 to 8.5. This effect indicates some change in the composition of the compound. Job's method discussed in the next section indicated a 1:1 chelate ratio at both pH's. The exchange of OH^- groups for water of hydration molecules on the copper ion might well be responsible for this effect. The color of the chelate solution at pH 6.5 was blue and at pH 8.5 it was violet. When more base was added and the pH increased to 11 no shift was noted (from the 8.5 pH) in the wave length of maximum light absorbance. The absorbance was slightly lower at pH 11, probably due to the considerable dilution of the solution by sodium hydroxide solution.

Spectrophotometric studies are shown on Figures 7, 8, 9 and 10 for the following chelates, respectively:

(a) 1,2-bis[tris(hydroxymethyl)methylamino]-ethane - Cu^{+2}

(b) 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanone - Cu^{+2}

(c) 1,3-bis[tris(hydroxymethyl)methylamino]-propane - Cu^{+2}

(d) 1,3 bis[tris(hydroxymethyl)methylamino]-propane - 2 Cu^{+2} and 2 Co^{+2}

These studies were made at pH's of 6.5 and 8.5 except in the case of the cobalt chelate which was studied at pH 7.

It is interesting to note that with each chelate studied the wave length giving maximum light absorbance at pH 8.5 was

FIGURE 7

1,2-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO] ETHANE–Cu^{++} CHELATE

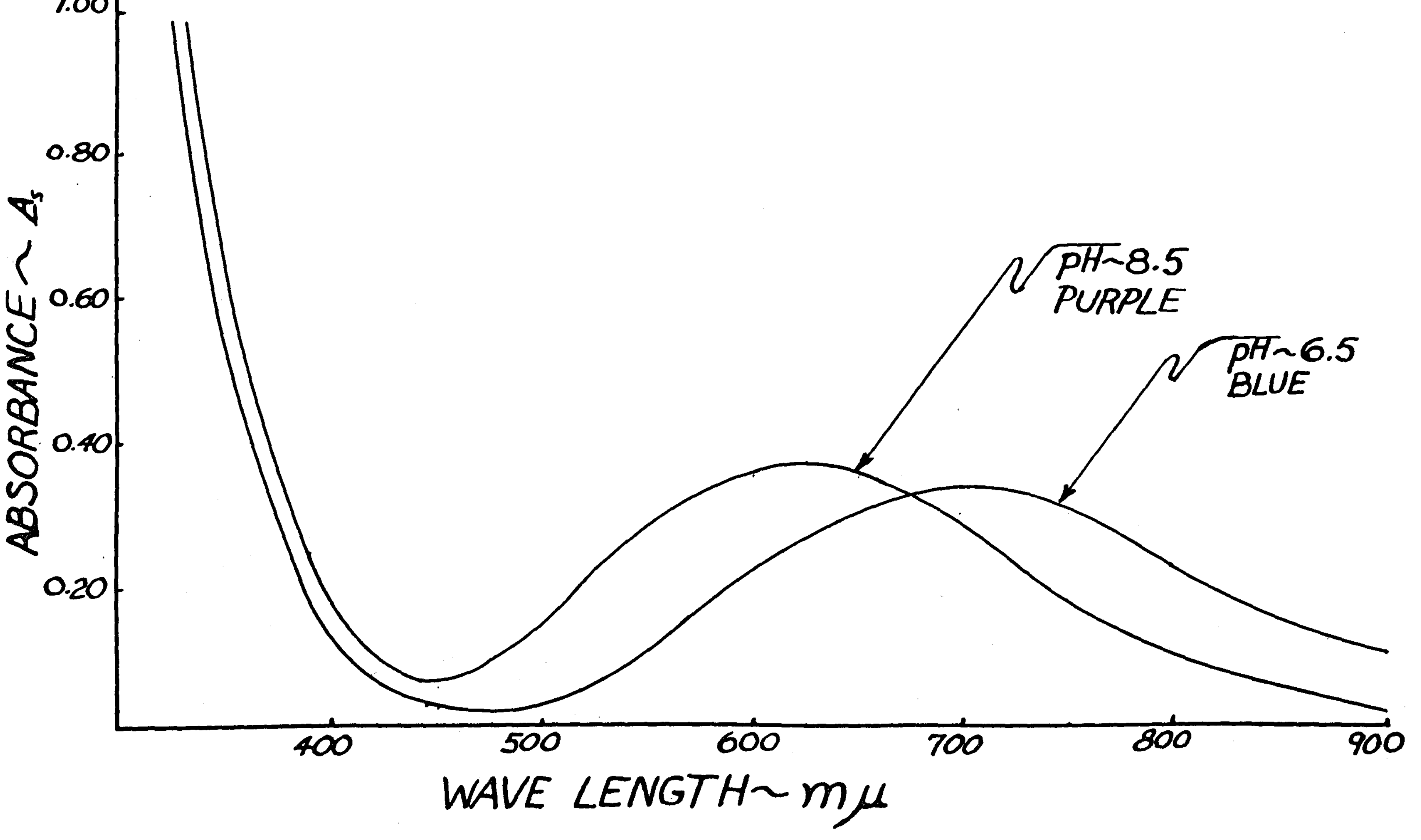


FIGURE 8

1,3 BIS[TRIS(HYDROXYMETHYL)METHYLAMINO] PROPANONE~ Cu^{++} CHELATE

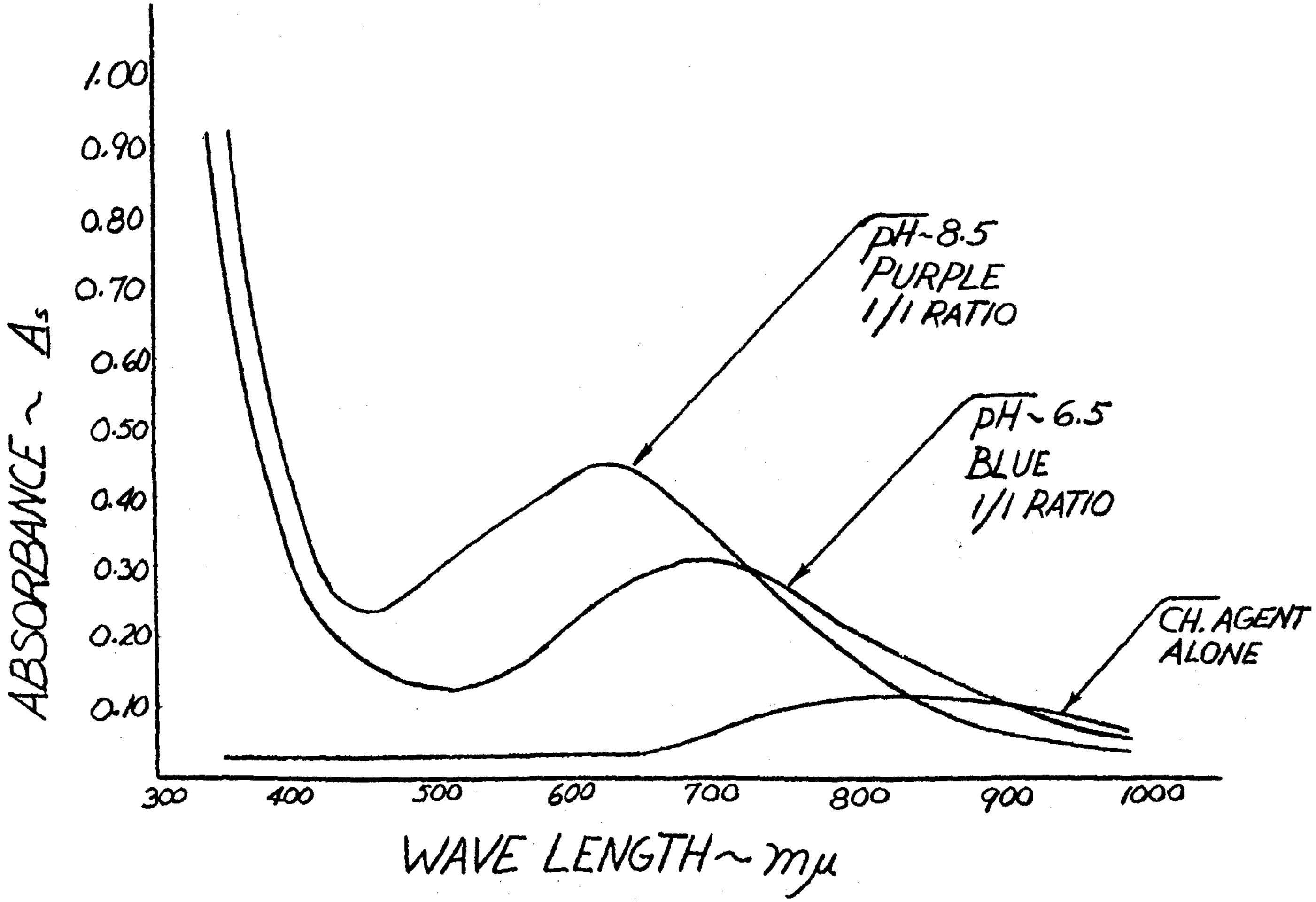
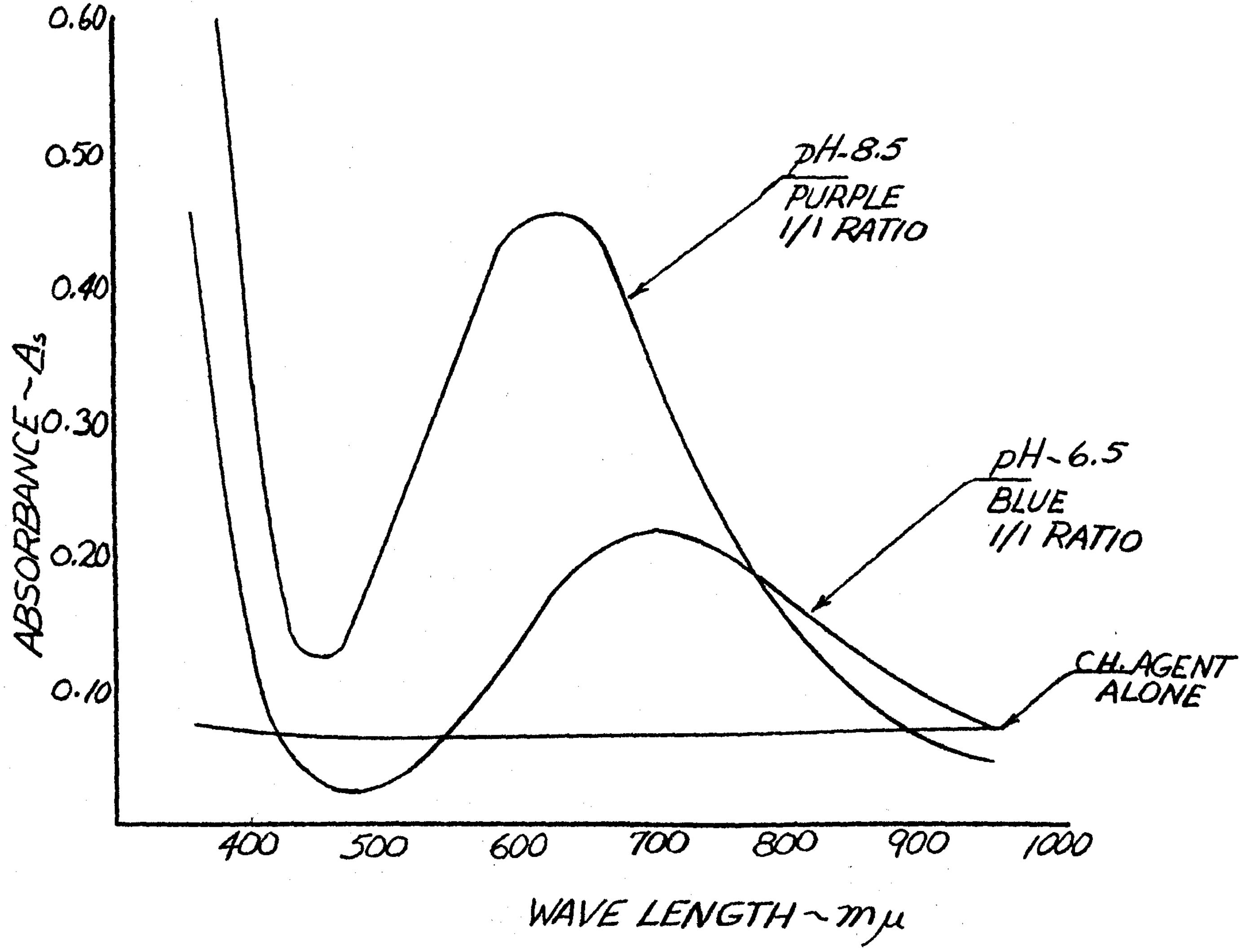


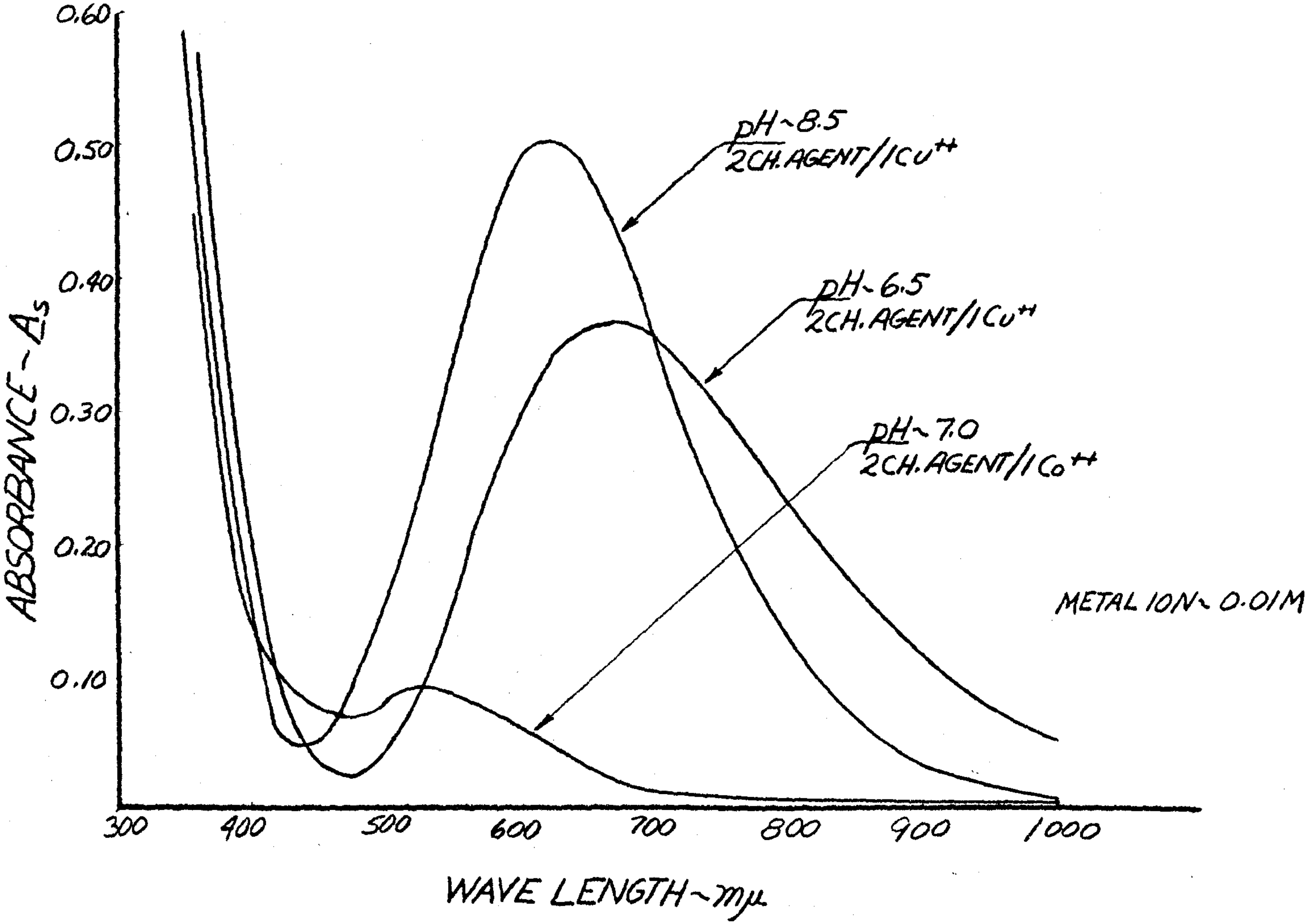
FIGURE 9

1,3 BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE ~ Cu^{++} CHELATE



[redacted]

1,3 BIS[TRIS(HYDROXYMETHYL) METHYLAMINO] PROPANE ~ Cu^{++} AND Co^{++} CHELATES



50 to 70 millimicrons lower than the one at pH 6. This is another way of stating that the chelates were blue at pH 6.5 and violet at pH 8.5.

Experimental data taken in this work is shown on Tables 26, 27, 28, 29 and 30.

TABLE 26

DETERMINATION OF CHELATE RATIO OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE AND $Cu(NO_3)_2$ BY JOB'S METHOD

(1) 20 ml. 0.500 M $NaNO_3$
20 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 6.5

(2) 20 ml. 0.500 M $NaNO_3$
15 ml. 0.100 M $Cu(NO_3)_2$
5 ml. Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(3) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M $Cu(NO_3)_2$
10 ml. 0.100 M Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(4) 20 ml. 0.500 M $NaNO_3$
5 ml. 0.100 M $Cu(NO_3)_2$
15 ml. 0.100 M Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(5) 20 ml. 0.500 M $NaNO_3$
20 ml. 0.100 M Chelating Agent
60 ml. Distilled Water

WAVE LENGTH Millimicrons	ABSORBANCE 1	2	3	4	5
360	Precipitation		0.447	0.125	0.002
520	Precipitation		0.093	0.038	0.006
620	Precipitation		0.371	0.160	0.007
720	Precipitation		0.358	0.177	0.010

RESULTS WITH ABOVE COMPOSITIONS
ADJUSTED TO pH 8.5

WAVE LENGTH Millimicrons	1	2	3	4	5
360	Precipitation		0.089	0.055	0.002
520	Precipitation		0.275	0.150	0.006
620	Precipitation		0.346	0.184	0.007
720	Precipitation		0.170	0.091	0.010

TABLE 27

DETERMINATION OF CHELATE RATIO OF 1,3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]PROPANE AND $Cu(NO_3)_2$ BY JOB'S METHOD

(1) 20 ml. 0.500 M $NaNO_3$
20 ml. 0.100 M Chelating Agent
60 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
3 ml. 0.100 M $Cu(NO_3)_2$
17 ml. 0.100 M Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(3) 20 ml. 0.500 M $NaNO_3$
6 ml. 0.100 M $Cu(NO_3)_2$
14 ml. 0.100 M Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(4) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M $Cu(NO_3)_2$
10 ml. 0.100 M Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(5) 20 ml. 0.500 M $NaNO_3$
8 ml. 0.100 M Chelating Agent
12 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 6.5

(6) 20 ml. 0.500 M $NaNO_3$
6 ml. 0.100 M Chelating Agent
14 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 6.5

(7) 20 ml. 0.500 M $NaNO_3$
3 ml. 0.100 M Chelating Agent
17 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 6.5

WAVE LENGTH	ABSORBANCE						
Millimicrons	1	2	3	4	5	6	7
650	0.012	0.092	0.134	0.189	Precipitation		
680	---	0.084	0.141	0.210	Precipitation		

TABLE 27 (CONTINUED)

RESULTS WITH ABOVE COMPOSITION ADJUSTED TO pH 8.5

WAVE LENGTH	ABSORBANCE						
Millimicrons	1	2	3	4	5	6	7
620	0.012	0.152	0.288	0.394	Precipitation		
650	---	0.135	0.264	0.380	Precipitation		

TABLE 28

LIGHT ABSORBANCE OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)-METHYLAMINO]PROPANE-$Cu(NO_3)_2$ CHELATES

(1) Standard
20 ml. 0.500 M $NaNO_3$
80 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
10 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 2.5

(3) SAME COMPOSITION AS (2)
MADE TO pH 5.0

(4) SAME COMPOSITION AS (2)
MADE TO pH 11.0

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
360	0.000	0.020	0.064
370	0.000	0.018	0.034
380	0.002	0.017	0.025
390	0.004	0.016	0.022
400	0.005	0.016	0.023
410	0.006	0.015	0.024
420	0.005	0.015	0.028
430	0.005	0.015	0.036
440	0.006	0.013	0.047
450	0.006	0.013	0.065
460	0.006	0.013	0.093
470	0.006	0.013	0.125

TABLE 28 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE		
	2	3	4
480	0.006	0.013	0.165
490	0.007	0.013	0.209
500	0.007	0.013	0.248
510	0.006	0.013	0.280
520	0.006	0.012	0.304
530	0.006	0.012	0.320
540	0.006	0.012	0.330
550	0.006	0.014	0.341
560	0.006	0.015	0.345
570	0.008	0.018	0.345
580	0.006	0.018	0.350
590	0.007	0.022	0.350
600	0.010	0.024	0.347
610	0.013	0.030	0.343
625	0.018	0.038	0.329
650	0.027	0.054	0.290
675	0.044	0.075	0.236
700	0.084	0.098	0.182
750	0.100	0.135	0.101
775	0.111	0.144	0.071
800	0.119	0.147	0.053
850	0.115	0.138	0.028
900	0.105	0.120	0.019
950	0.089	0.101	0.015

TABLE 29

LIGHT ABSORBANCE OF 1,3-BIS[TRIS(HYDROXYMETHYL)-METHYLAMINO]2-PROPANONE-$Cu(NO_3)_2$ CHELATES

(1) Standard
20 ml. 0.500 M $NaNO_3$
80 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M $Cu(NO_3)_2$
70 ml. Distilled Water

(3) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M $Cu(NO_3)_2$
10 ml. 0.100 M Chelating Agent
60 ml. Distilled Water
MADE TO pH 6.5

(4) SAME COMPOSITION AS (3)
MADE TO pH 8.5

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
355	0.016	0.738	0.920
365	0.015	0.608	0.759
375	0.014	0.409	0.620
385	0.013	0.395	0.506
400	0.012	0.297	0.384
410	0.012	0.251	0.324
420	0.012	0.218	0.280
430	0.012	0.194	0.254
440	0.012	0.175	0.240
450	0.012	0.160	0.236
460	0.012	0.149	0.244
470	0.012	0.140	0.252

TABLE 29 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE		
	2	3	4
480	0.012	0.132	0.269
490	0.012	0.130	0.288
500	0.012	0.130	0.304
510	0.012	0.130	0.318
520	0.012	0.132	0.330
530	0.012	0.139	0.345
540	0.012	0.146	0.359
550	0.012	0.154	0.374
560	0.013	0.168	0.384
570	0.015	0.181	0.399
580	0.016	0.196	0.412
590	0.017	0.213	0.424
600	0.018	0.229	0.430
610	0.023	0.244	0.435
625	0.027	0.266	0.442
635	0.031	0.276	0.430
650	0.035	0.288	0.414
675	---	0.305	0.374
700	---	0.302	0.324
725	0.088	0.287	0.274
750	0.104	0.262	0.223
800	0.117	0.206	0.145

TABLE 29 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
850	0.112	0.149	0.096
900	0.100	0.104	0.065
950	0.087	0.074	0.048

TABLE 30

LIGHT ABSORBANCE OF 1,3-BIS[TRIS(HYDROXYMETHYL)-METHYLAMINO]PROPANE-$Cu(NO_3)_2$ CHELATE

(1) Standard
20 ml. 0.500 M $NaNO_3$
80 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
70 ml. Distilled Water

(3) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
10 ml. 0.100 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 6.5

(4) SAME COMPOSITION AS (3)
MADE TO pH 8.5

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
360	0.072	0.455	0.880
365	0.071	0.395	0.773
370	0.070	0.349	0.688
375	0.069	0.304	0.595
380	0.068	0.267	0.528
385	0.068	0.230	0.454
390	0.068	0.200	0.400
395	0.067	0.171	0.345
400	0.067	0.145	0.298
410	0.067	0.106	0.227
420	0.066	0.075	0.178
430	0.066	0.055	0.147

TABLE 30 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE		
	2	3	4
440	0.065	0.037	0.129
450	0.064	0.027	0.124
460	0.063	0.021	0.127
470	0.063	0.019	0.135
480	0.062	0.019	0.158
490	0.063	0.022	0.181
500	0.062	0.025	0.206
520	0.062	0.040	0.264
540	0.062	0.062	0.324
560	0.063	0.089	0.376
580	0.063	0.119	0.424
600	0.063	0.148	0.451
620	0.063	0.172	0.455
640	0.063	0.195	0.452
660	0.062	0.205	0.425
680	0.062	0.219	0.382
700	0.068	0.220	0.335
725	0.069	0.216	0.281
750	0.068	0.204	0.228
775	0.070	0.186	0.184
800	0.070	0.168	0.148
850	0.071	0.128	0.097
900	0.071	0.096	0.067
950	0.071	0.069	0.048

7. JOB'S METHOD

Job (77, 78) developed a simple method to determine the composition of chelate compounds in solution, which is called the method of continuous variation. This method is based on the fact that, for a constant total concentration of metal and chelating agent, the concentration of chelate is greatest when the metal and chelating agent are present in the same ratios in which they exist in the chelate compound.

Since light absorbance is a good indication of chelate concentration, it is the measure most often used in Job's method, although other physical measurements such as refractive indices might be used. Thus in the work reported herein, light absorbance was plotted against R, where R equals ratio of metal ion to metal ion plus ligand. Therefore, an R value of 0.5 would indicate an ion to ligand ratio of 1 to 1. Figures 11, 12 and 13 show Job's method studies on the following chelates:

(a) 1,2-bis[tris(hydroxymethyl)methylamino]-ethane - Cu^{+2}

(b) 1,2,3-tris[tris(hydroxymethyl)methylamino]-propane - Cu^{+2}

(c) 1,3-bis[tris(hydroxymethyl)methylamino]-propane - Cu^{+2}

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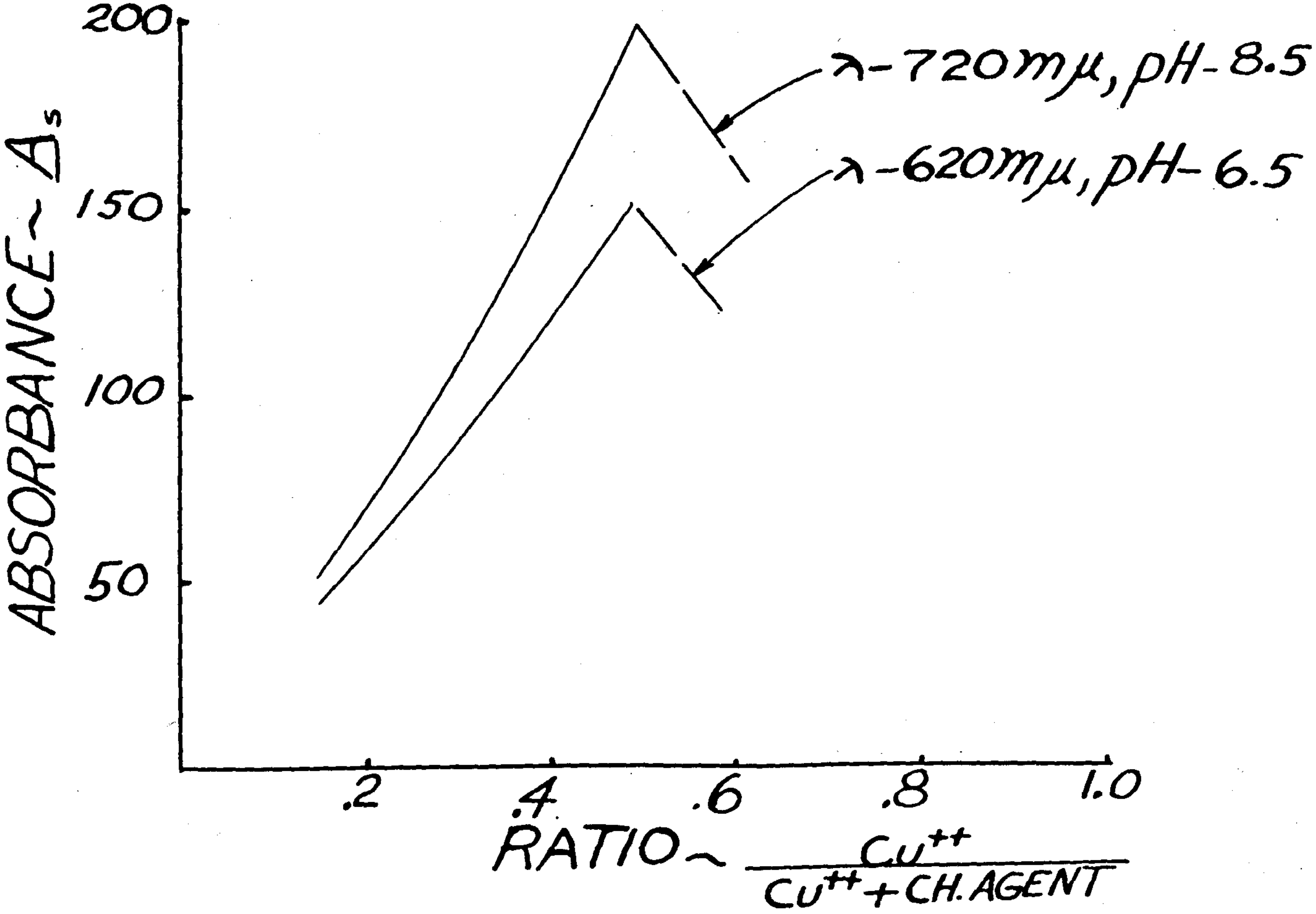
(77) Job, Ann. chim., (10)9, 113 (1928).
(78) Job, Ann. chim., (11)6, 97 (1936).

FIGURE II

1,2 BIS[TRIS(HYDROXYMETHYL)METHYLAMINO] ETHANE—Cu^{++} CHELATE



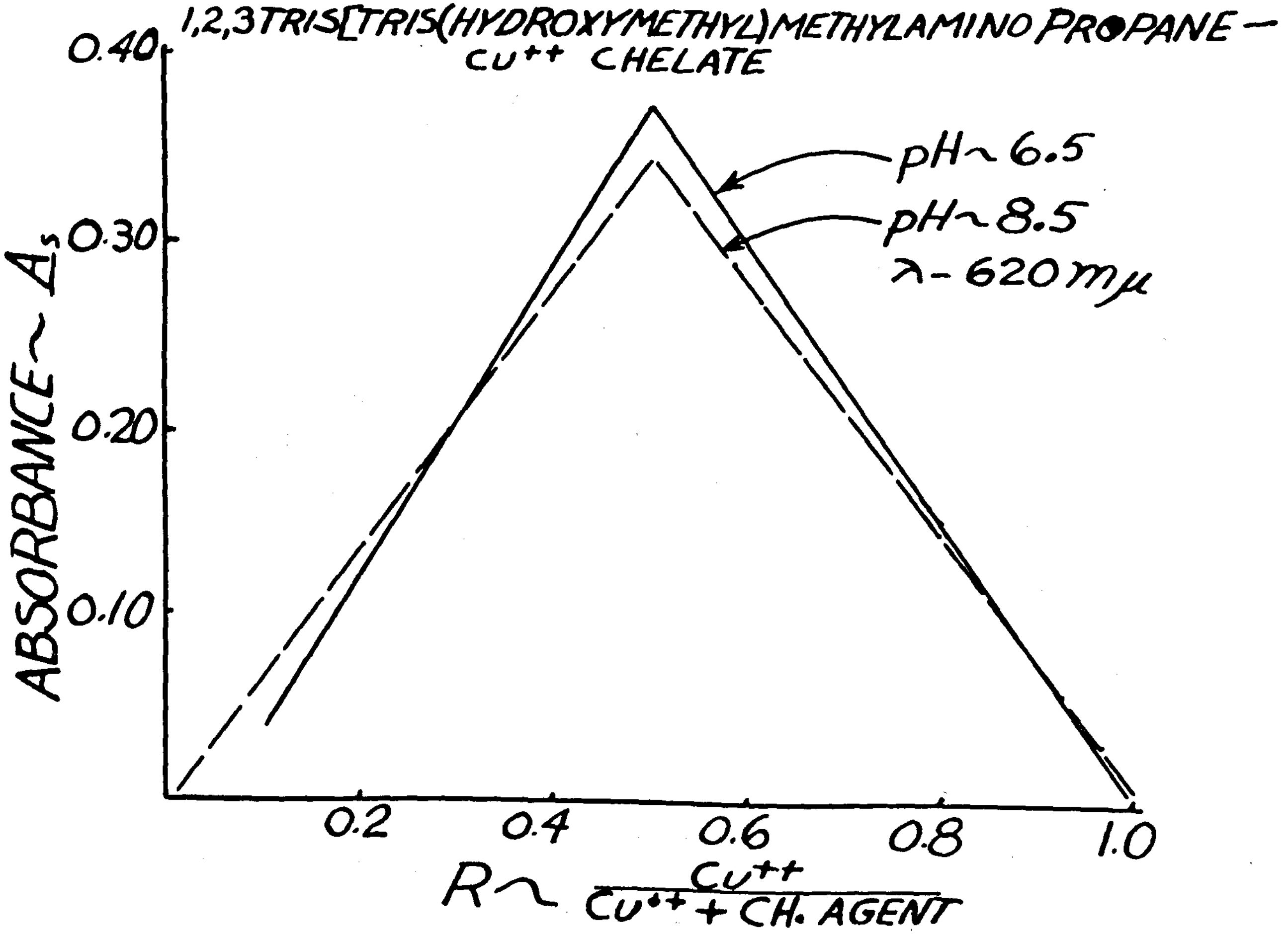
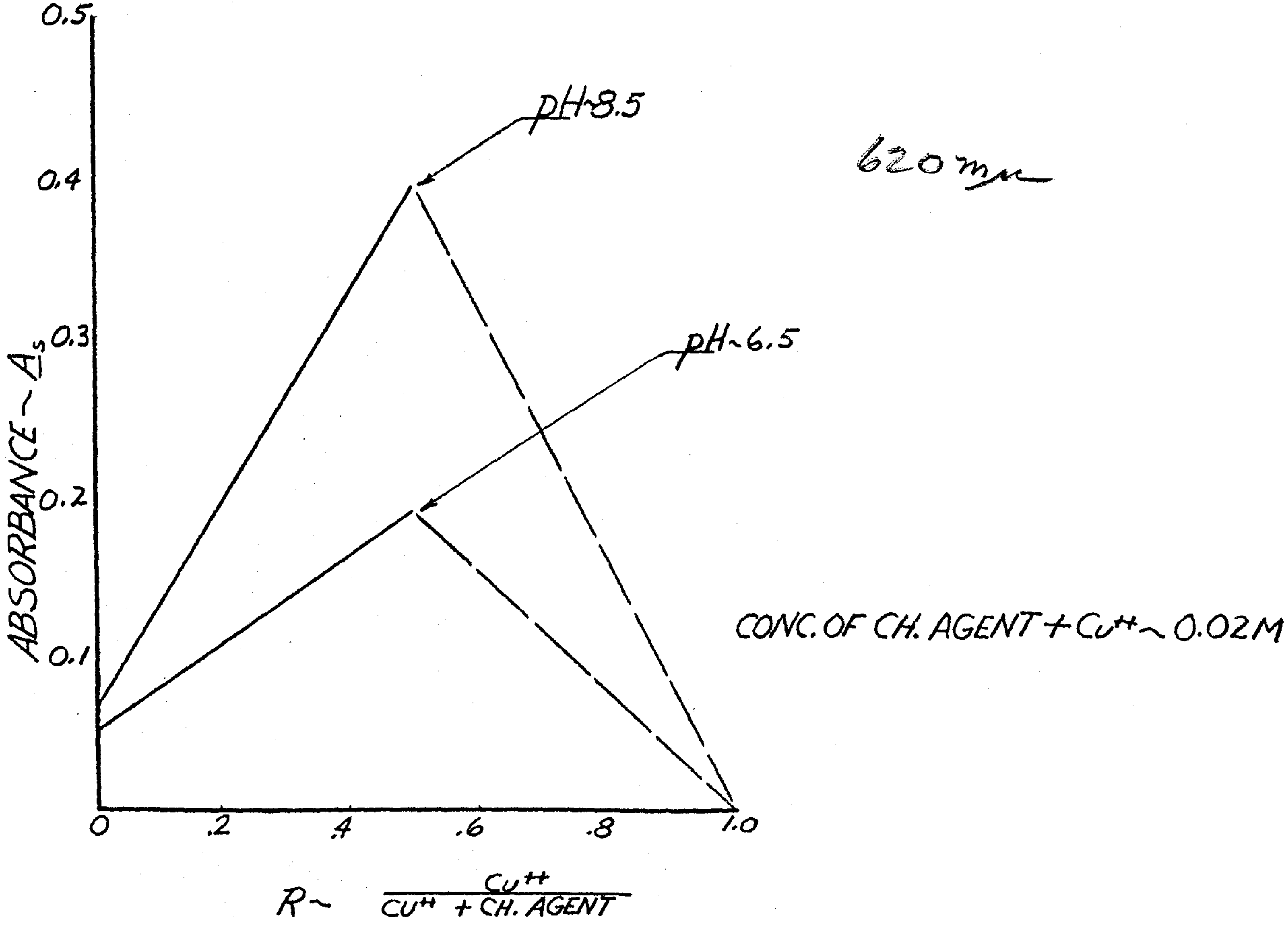

1,2,3TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO PROPANE—
Cu++ CHELATE
pH~6.5
pH~8.5
λ-620 mμ
ABSORBANCE ~ A_s
0.40
0.30
0.20
0.10
0.2
0.4
0.6
0.8
1.0
$R \sim \frac{Cu^{++}}{Cu^{++} + CH.\ AGENT}$

FIGURE 12

FIGURE ~13

1,3 BIS[TRIS(HYDROXYMETHYL)METHYLAMINO] PROPANE~ Cu^{++} CHELATE

JOB'S METHOD



The experimental data from these studies are shown on Tables 31, 32, 33 and 34.

It is evident, from the sharp peaks obtained at an R of 0.5, that chelation of the polyhydroxyamines with the ions of the first transition metals occurs in a one to one ratio. This was true with either pH 6.5 or 8.5, blue color or violet and in the rather limited concentration variations covered. In all cases when excess Cu^{+2} (over a 1:1 ratio) was added, precipitation of cupric hydroxide occurred. With the strong chelating agent 1,2,3-tris[tris(hydroxymethyl)-methylamino]propane precipitation occurred very slowly and only with rather high Cu^{+2} to ligand ratios.

TABLE 31

DETERMINATION OF CHELATE RATIO OF 1,2-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]ETHANE AND $Cu(NO_3)_2$ BY JOB'S METHOD

(1) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
70 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
2 ml. 0.100 M $Cu(NO_3)_2$
8 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 6.5

(3) 20 ml. 0.500 M $NaNO_3$
4 ml. 0.100 M $Cu(NO_3)_2$
6 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 6.5

(4) 20 ml. 0.500 M $NaNO_3$
5 ml. 0.100 M $Cu(NO_3)_2$
5 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 6.5

(5) 20 ml. 0.500 M $NaNO_3$
6 ml. 0.100 M $Cu(NO_3)_2$
4 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 6.5

(6) 20 ml. 0.500 M $NaNO_3$
8 ml. 0.100 M $Cu(NO_3)_2$
2 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 6.5

(7) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M $Cu(NO_3)_2$
ADJUSTED TO pH 6.5

WAVE LENGTH	ABSORBANCE						
Millimicrons	1	2	3	4	5	6	7
360	0.000	0.040	0.094	0.132	Precipitation		
650	0.000	0.075	0.115	0.137	Precipitation		
720	0.000	0.071	0.122	0.150	Precipitation		

TABLE 31 (CONTINUED)

RESULTS WITH ABOVE COMPOSITIONS
ADJUSTED TO pH 8.5

WAVE LENGTH Millimicrons	ABSORBANCE 1	2	3	4	5	6	7
360	0.000	0.016	0.048	0.265	Precipitation		
650	0.000	0.086	0.149	0.196	Precipitation		
720	0.000	0.056	0.106	0.162	Precipitation		

(8) 20 ml. 0.500 M $NaNO_3$
3 ml. 0.100 M $Cu(NO_3)_2$
7 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 8.5

(9) 20 ml. 0.500 M $NaNO_3$
3.5 ml. 0.100 M $Cu(NO_3)_2$
6.5 ml. Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 8.5

(10) 20 ml. 0.500 M $NaNO_3$
4.5 ml. 0.100 M $Cu(NO_3)_2$
5.5 ml. 0.100 M Chelating Agent
70 ml. Distilled Water
ADJUSTED TO pH 8.5

WAVE LENGTH Millimicrons	ABSORBANCE 8	9	10
360	0.024	0.026	0.062
620	0.112	0.110	0.153
720	0.079	0.079	0.111

TABLE 32

LIGHT ABSORBANCE OF 1,2-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]ETHANE-$Cu(NO_3)_2$ CHELATES

(1) 20 ml. 0.500 M $NaNO_3$
80 ml. Distilled Water

(2) 10 ml. 0.1045 M $Cu(NO_3)_2$
20 ml. 0.500 M $NaNO_3$
70 ml. Distilled Water

(3) 10 ml. 0.1045 M $Cu(NO_3)_2$
20 ml. 0.500 M $NaNO_3$
20 ml. 0.100 M Chelating Agent
50 ml. Distilled Water
ADJUSTED TO pH 6.5

(4) SAME COMPOSITION AS (3)
ADJUSTED TO pH 8.5

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
320	0.007	1.48	1.70
330	0.007	1.20	1.48
340	0.018	0.823	0.972
350	0.006	0.563	0.657
360	0.008	0.434	0.513
370	0.008	0.320	0.380
380	0.006	0.234	0.275
390	0.009	0.165	0.192
400	0.010	0.120	0.135
420	0.009	0.057	0.061
440	0.008	0.022	0.044
460	0.008	0.011	0.067

TABLE 33

LIGHT ABSORBANCE OF 1,2,3-TRIS[TRIS(HYDROXYMETHYL)-METHYLAMINO]PROPANE-$Cu(NO_3)_2$ CHELATES

(1) Standard
20 ml. 0.500 M $NaNO_3$
80 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.104 M $Cu(NO_3)_2$
70 ml. Distilled Water

(3) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
70 ml. Distilled Water

(4) 20 ml. 0.500 M $NaNO_3$
10 ml. 0.100 M Chelating Agent
10 ml. 0.104 M $Cu(NO_3)_2$
60 ml. Distilled Water
MADE TO pH 6.5

(5) SAME COMPOSITION AS (4)
MADE TO pH 8.5

WAVE LENGTH	LIGHT ABSORBANCE			
Millimicrons	2	3	4	5
340	0.016	0.002	0.900	0.420
350	0.008	0.000	0.611	0.191
360	0.004	0.002	0.423	0.090
370	0.002	0.002	0.295	0.050
380	0.001	0.001	0.215	0.037
390	0.001	0.001	0.158	0.025
400	0.000	0.001	0.116	0.021
410	0.000	0.000	0.088	0.022
420	0.000	0.000	0.067	0.027
430	0.000	0.000	0.054	0.038

TABLE 33 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE			
	2	3	4	5
440	0.000	0.000	0.047	0.054
450	0.000	0.000	0.042	0.078
460	0.000	0.000	0.041	0.110
470	0.000	0.000	0.044	0.146
480	0.000	0.000	0.049	0.185
490	0.000	0.000	0.057	0.224
500	0.000	0.000	0.067	0.258
520	0.000	0.000	0.100	0.305
540	0.000	0.002	0.135	0.338
560	0.000	0.002	0.193	0.362
580	0.004	0.003	0.244	0.381
600	0.008	0.003	0.294	0.390
625	0.014	0.004	0.337	0.384
650	0.026	0.005	0.362	0.349
675	0.040	0.006	0.363	0.295
700	0.064	0.006	0.345	0.235
725	0.082	0.006	0.315	0.183
750	0.098	0.006	0.275	0.137
800	0.115	0.006	0.204	0.075
850	0.109	0.005	0.138	0.039
900	0.098	0.005	0.100	0.021
950	0.083	0.005	0.070	0.014

TABLE

LIGHT ABSORBANCE OF 1,3-BIS[TRIS(HYDROXYMETHYL)-METHYLAMINO]PROPANE-$Cu(NO_3)_2$ CHELATE

(1) Standard
20 ml. 0.500 M $NaNO_3$
80 ml. Distilled Water

(2) 20 ml. 0.500 M $NaNO_3$
20 ml. 0.100 M Chelating Agent
10 ml. 0.100 M $Cu(NO_3)_2$
50 ml. Distilled Water
MADE TO pH 6.5

(3) SAME COMPOSITION AS (2)
MADE TO pH 8.5

(4) 20 ml. 0.500 M $NaNO_3$
20 ml. 0.100 M Chelating Agent
10 ml. 0.100 M $Cu(NO_3)_2$
50 ml. Distilled Water
MADE TO pH 7.0

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
360	0.635	0.569	0.447
365	0.522	0.452	0.363
370	0.455	0.388	0.316
375	0.407	0.330	0.276
380	0.356	0.281	0.245
385	0.313	0.239	0.218
390	0.275	0.201	0.196
395	0.240	0.170	0.176
400	0.204	0.140	0.158
405	0.175	0.116	0.144

TABLE 34 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
410	0.149	0.097	0.131
415	0.124	0.080	0.117
420	0.104	0.065	0.107
425	0.087	0.056	0.101
430	0.074	0.050	0.095
435	0.060	0.045	0.088
440	0.050	0.044	0.083
445	0.041	0.044	0.079
450	0.030	0.046	0.075
455	0.029	0.050	0.071
460	0.026	0.056	0.069
465	0.024	0.064	0.067
470	0.025	0.074	0.067
475	0.025	0.084	0.068
480	0.026	0.096	0.068
490	0.034	0.122	0.072
500	0.046	0.153	0.079
510	0.062	0.188	0.086
520	0.082	0.223	0.090
540	0.135	0.304	0.088
550	0.163	0.341	0.081
570	0.221	0.413	0.071
580	0.248	0.440	0.068

TABLE 34 (CONTINUED)

WAVE LENGTH Millimicrons	LIGHT ABSORBANCE 2	3	4
590	0.276	0.468	0.067
600	0.301	0.488	0.065
625	0.344	0.500	0.052
635	0.358	0.496	---
650	0.366	0.475	0.035
675	0.371	0.425	0.019
685	0.399	0.368	0.014
700	0.359	0.356	0.009
725	0.335	0.290	0.004
750	0.305	0.229	0.001
775	0.267	0.173	0.000
800	0.231	0.131	0.000
850	0.165	0.074	0.000
900	0.116	0.035	0.000
950	0.080	0.022	0.000
1000	0.056	0.011	0.003

STRUCTURE OF POLYHYDROXYAMINE CHELATES

In every chelate compound made using the polyhydroxyamines and the bivalent transition metal ions, the chelating agent behaved as a bidentate compound. The bidentate nature was indicated by the fact that two protons were displaced in the reaction. Chelation of the transition metal ions by the polyhydroxyamines seems to fall into two categories. First, the general case, occurs where the bidentate agent chelates in a one to one ratio with Cu^{+2}, Ni^{+2}, Co^{+2}, and Mn^{+2} ions. Two protons are displaced in this reaction. Fernelius, et al. (79) have shown that chelates bonded through nitrogen are considerably more stable than those which are bonded through sulfur (or oxygen). The ferric ion was not used in this work and may behave differently. Where the bivalent ions have a choice of bonding through the oxygen or nitrogen, as in the polyhydroxyamines, it is logical to assume that they would bond through the nitrogens, thereby giving the structure of highest stability with five or six membered rings, depending upon whether the chelating agent is an ethane or propane derivative. It has also been shown that the copper forms a square planar chelate with the cupric ion in the center. The The structure postulated for case one is shown on Figure 14. The chelating agent used in the example is 1,2,3-tris[tris-

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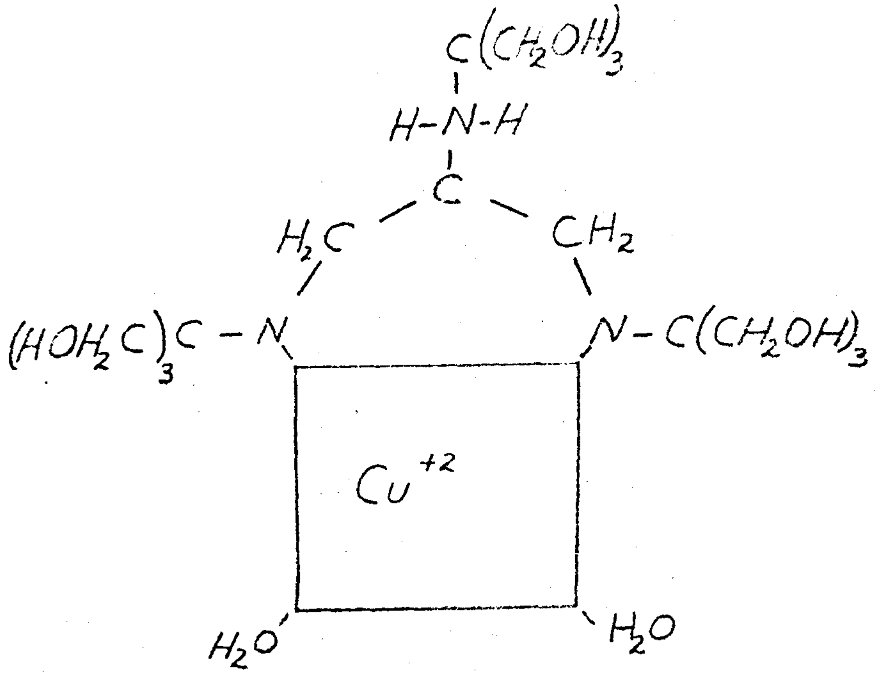
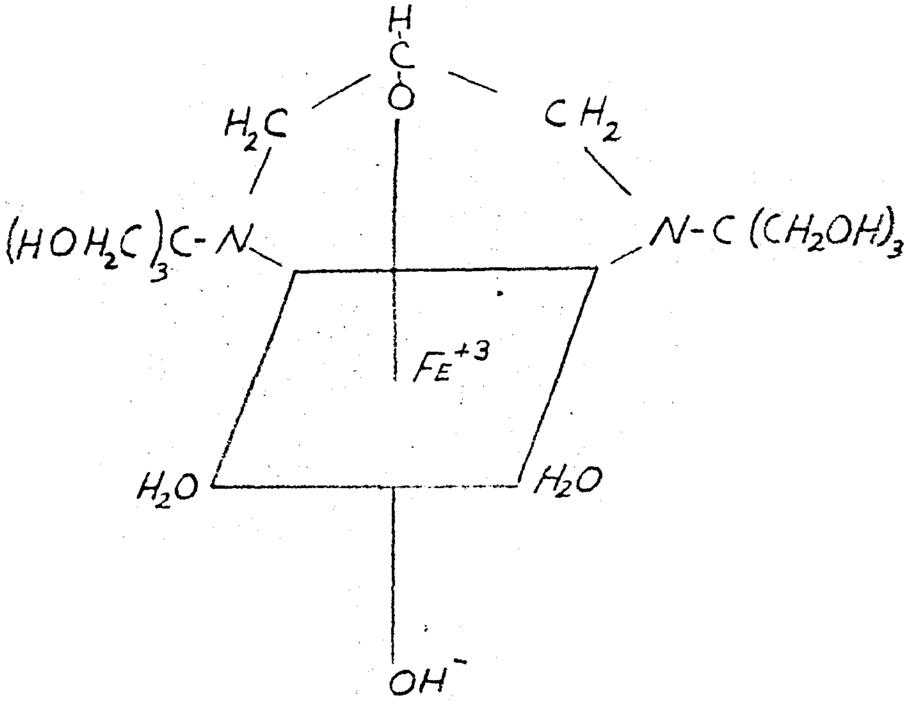
(79) Hares, Fernelius and Douglas, J. Am. Chem. Soc., 78, 1816 (1956).



CASE

,3-TRIS[TRIS(HYDROXYMETHYL)METHYLAMINO] PROPANE– Cu^{+2} CHELATE



CASE 2

3-BIS[TRIS(HYDROXYMETHYL)METHYLAMINO]-2-PROPANOL – Fe^{+3} CHELATE

FIGURE 14

(hydroxymethyl)methylamino]propane and the metal ion is Cu^{+2}.

In the second case (the special one), the ferric ion is chelated by 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol. The major work in this field was done by Gladding (80), who has proposed three possible structures for the "disec"-ferric ion chelate. The ferric ion was found to displace three protons from the ligand. The structures proposed by Gladding therefore involve chelation by terdentate agents. The structures proposed are bonded as follows:

(a) Through the two secondary amine groups and the oxygen of the secondary alcohol group.

(b) Through the two secondary amine groups and the oxygen of one of the primary alcohol group.

(c) Through the oxygens of three primary alcohol groups of one of the polyhydroxyamine groups.

The proposals (b) and (c) are untenable since chelating agents similar in nature and containing the functional groups and structure requisite for forming chelate structures such as (b) and (c) do not form stable chelates with ferric ion. 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol ("disec") is the only agent which chelated iron although other polyhydroxyamines (notably the 1,2,3-propane triamine derivative) gave comparable stability constants with the bivalent

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(80) J. B. Gladding, M.S. Thesis, University of Richmond (1956).

transition metal ions. This suggests a completely different mechanism of chelation in the special case of the chelation of ferric ion by "disec." Structure (a) proposed by Gladding, involving bonding through the secondary amines and secondary alcohol groups seems to fit all experimental requirements. This structure is shown on Figure 14 and contains two five membered rings.

SUMMARY

Cu^{+2} forms stable chelates with the following polyhydroxyamine compounds: 1,2,3-tris[tris(hydroxymethyl)-methylamino]propane, 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol, 1,3-bis[tris(hydroxymethyl)methylamino]propane, 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanone and 1,2-bis[tris(hydroxymethyl)methylamino]ethane. These compounds are listed in order of decreasing chelate stability. The solid Cu^{+2} - 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol chelate was recovered and purified. It was non-crystalline, and deliquescent. This chelate was soluble in water, methanol, ethanol and acetone and insoluble in diethyl ether, dioxane and hydrocarbons.

Stable chelates containing Co^{+2} were produced with 1,2,3-tris[tris(hydroxymethyl)methylamino]propane, 1,3-bis[tris-(hydroxymethyl)methylamino]-2-propanol and 1,3-bis[tris(hydroxymethyl)methylamino]propane. These compounds were less stable than the Cu^{+2} chelates.

Mn^{+2} gave a rather weak chelate compound when reacted with 1,2,3-tris[tris(hydroxymethyl)methylamino]propane while Fe^{+3} produced no chelate when reacted with polyhydroxyamine compounds not containing the secondary alcohol group.

The Ni^{+2} ion formed a chelate with the 1,3-propanediamine derivative. No chelates were formed by the rare earth ions with the polyhydroxyamine compounds.

Stability constants were obtained for several of the polyhydroxyamine chelate compounds. A list of them follows:

Ligand	Metal Ion	Complexity Constant ~ log K_s
1,2,3-tris[tris(hydroxymethyl)-methylamino]propane	Mn^{+2}	2.24
same	Co^{+2}	5.65
same	Cu^{+2}	approx.10.00
1,2-bis[tris(hydroxymethyl)-methylamino]ethane	Cu^{+2}	2.52
1,3-bis[tris(hydroxymethyl)-methylamino]-2-propanone	Cu^{+2}	2.57

Structures are proposed for the general case of the polyhydroxyamine compounds with the bivalent transition metal ions, and the structures, proposed by Gladding, for the ferric ion - "disec" chelate are commented upon.

APPENDIX

ACKNOWLEDGEMENTS

Major credit for this work belongs to Dr. W. E. Trout, Jr. His suggestions, advice and encouragement were of great value in the formulation of this program and in the interpretation of the results. The counseling of Dr. J. Stanton Pierce, on the preparation of the polyhydroxyamines, was both generous and wise. His gift of the "diseo" free base was gracious and helpful. Dr. W. Allan Powell frequently offered sound advice on the analysis of these compounds. Helpful suggestions were made by Dr. James E. Worsham, Jr. on the treatment of this work from the standpoint of physical chemistry.

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AUTOBIOGRAPHY

I, William Percy Moore, Jr., was born February 28, 1924 in Salisbury, North Carolina. In 1940 I graduated from Boyden High School in Salisbury. From 1940 to 1944 I attended North Carolina State College, where I received a B.S. in Chemical Engineering.

After graduation I was employed by the Tennessee Eastman Corporation at Oak Ridge, Tennessee as a Process Engineer in a plant producing Uranium (235) which was used in the initial atomic explosion. The period of my employment with Eastman covered the years of 1944 and 1945.

In September 1945 I joined the Phillips Petroleum Company at Phillips, Texas, as a Research Chemical Engineer. There, I participated in the development of a process for the production of butadiene from butane.

Since January 1946 I have been associated with the Research Department of the Nitrogen Division of Allied Chemical and Dye Corporation at Hopewell, Virginia. At present I am a Senior Research Chemist (Project Leader). My major interest has been in acetylene and carbon monoxide chemistry.

I was married to Anne Rosser Swart in 1944. We now have two sons and reside in Chester, Virginia.