made by adding an unknown excess of AO·HCl to a M^{+2} solution at *p*H 5 and titrating with OH^-. The end-point is sharp with Cu^{+2} but because the Ni^{+2} complexes form slowly it is better to add an excess of OH^- and back titrate with H^+. Zn(II), Pd(II) and Pt(II) interfere with the latter determination.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Stabilities and Absorption Spectra of Complexes of Some Divalent Metal Ions of the First Transition Series with the Thioglycolate Ion[1]

BY D. L. LEUSSING

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The metal ions Mn(II), Co(II), Ni(II) and Zn(II) have been found to react with the thioglycolate ion to form complexes of the type $M(SCH_2CO_2)$ and $M(SCH_2CO_2)_2^=$. The formation constants for these complexes were evaluated and their absorption spectra determined. The changes in the stabilities of the thioglycolato complexes in the series Mn(II) through Zn(II) were found to bear a close relationship to those observed for the oxygen and nitrogen ligands. The formation constants and absorption spectra show that the mercaptide group in the thioglycolate ion is able to exert a strong influence on the metal ion in a complex.

The thioglycolate ion has been found to react in solution with iron(II) to form the light red complex, $Fe(SCH_2CO_2)_2^=$.[2] In alkaline solutions containing the thioglycolate ion in low concentration, the yellow complex $Fe(OH)(SCH_2CO_2)^-$ also forms. The stability constants for these complexes were determined at an ionic strength of zero at 25° as, also, was the solubility product of the slightly soluble compound, $FeSCH_2CO_2$. Evidence was obtained that this latter compound is slow to precipitate and exists in super-saturated solution when the reactants are first mixed. Li and Manning[3] have reported the formation and stabilities of the zinc(II) thioglycolates, $ZnSCH_2CO_2$, and $Zn(SCH_2CO_2)_2^=$ at an ionic strength of 0.15 at 25°.

In order to obtain more information about the complexing of the mercaptide ion as reflected by that of the thioglycolate ion, the stabilities of the complexes with Mn(II), Co(II), Ni(II) and Zn(II) were evaluated and their absorption spectra determined in the present study. Copper(II) reacts rapidly with the thioglycolate ion to form copper(I) and the disulfide so the stabilities of the copper(II) complexes could not be obtained.

Experimental

Stock solutions, approximately 0.10 *M*, were prepared from reagent grade chemicals of $Ni(NO_3)_2$, $NiCl_2$, $MnCl_2$, $CoCl_2$ and $ZnCl_2$. The nickel nitrate solution was standardized with potassium cyanide according to the method of Kolthoff and Stenger.[4] The zinc chloride solution was prepared by dissolving a weighed amount of zinc in a known volume of standard hydrochloric acid. The final composition of this solution was 0.1000 *M* zinc chloride, 0.0407 *M* hydrochloric acid. The manganous chloride and cobaltous chloride solutions were standardized using disodium dihydrogen ethylenediaminetetraacetate.[5] The EDTA solution was standardized against the zinc chloride solution.

Eastman thioglycolic acid was purified as described previously.[6] Dilute stock solutions were freshly prepared from the purified reagent.

A 1.000 *M* potassium hydroxide solution was prepared from a British Drug Houses Concentrated Volumetric Solution. This solution was found to contain less than 0.2% carbonate by potentiometric titration.

The stability constants were determined using the *p*H-titration method.[7] In most of the experiments, solutions were prepared which contained 0.0100 *M* thioglycolic acid, 0.090 *M* KCl (or KNO_3) and 0.00200 *M* metal ion. These were titrated under an atmosphere of nitrogen with 1.000 *M* KOH using a micro-buret. Additional titrations were run with nickel(II) in 0.00100 and 0.00200 *M* thioglycolic acid and with zinc(II) in 0.00100 *M* thioglycolic acid. The potassium chloride concentration was increased accordingly. A Beckman Model G *p*H meter was used to determine the *p*H of the solutions during the titrations. The glass electrodes were calibrated against National Bureau of Standards buffers at an ionic strength of 0.10 at values of *p*H 1.52, 3.95, 6.85 and 9.20. A linear correction to the *p*H meter readings was assumed for intermediate values of *p*H.

To calculate the results obtained in the moderately alkaline range, it was necessary to make a correction for unreacted hydroxide. The relation between the concentration of free hydroxide and the measured *p*H of the solutions was obtained by titrating the 1.000 *M* potassium hydroxide into 0.100 *M* potassium chloride. The product $a_H M_{OH}$ was found to have the value $12.3 \pm 0.2 \times 10^{-15}$ in the range *p*H 9.90 to 11.90. Assuming that γ_{OH} is equal to γ_H and using the value 0.63 for $\gamma_H\gamma_{OH}/a_{H_2O}$[8] the activity product of water is calculated to be 9.7×10^{-15}, which is in good agreement within an error of 0.02 *p*H unit with the accepted value of 10.08×10^{-15}. The value of γ_{OH} equal to 0.76 given by Kielland[9] gives a value of 9.3×10^{-15}.

The ionization constants of thioglycolic acid were determined by titrating 5.02×10^{-3} *M* thioglycolic acid in 0.100 *M* potassium chloride with the standard potassium hydroxide. The constants so obtained were converted to molarity constants using a value of the activity coefficient of hydrogen ion equal to 0.83.[9] The molarity constants were calculated to be 3.83×10^{-4} and 6.35×10^{-11} for K_1 and K_2. The titration curve calculated using the above values agreed excellently within the error of the measurements with that observed when the appropriate corrections were made for the concentration of free hydrogen or hydroxide ions in the solution.

The titration curves in the presence of the divalent metal ions showed the formation of mono- and bis-thioglycolato complexes, designated hereafter as MRS and $M(RS)_2^=$ where $RS^=$ refers to the divalent thioglycolate ion. The complexes presumably are chelates and the water molecules occupying the remaining coördination positions of the metal ion are assumed without writing them in the formula. The

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[1] Financial assistance for this work was made available by a grant from the National Science Foundation.

[2] D. L. Leussing and I. M. Kolthoff, THIS JOURNAL, **75**, 3904 (1953).

[3] N. C. Li and R. A. Manning, *ibid.*, **77**, 5225 (1955).

[4] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd Rev. Ed., Interscience Publishers, Inc., New York, N. Y., 1947.

[5] G. Schwarzenbach, "Die Komplexometrische Titrationen," Ferdinand Enke, Stuttgart, 1955.

[6] D. L. Leussing and I. M. Kolthoff, *J. Electrochem. Soc.*, **100**, 334 (1953).

[7] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

[9] J. Kielland, THIS JOURNAL, **59**, 1675 (1937).

mono-complexes precipitated when higher concentrations of metal ion were used, but under the final conditions chosen the precipitation was slow and no precipitate was noted during the titration.

A Cary Model 14 Spectrophotometer was used to obtain the absorption spectra of the complexes. The spectra were determined on solutions in which conditions were such that either MRS or $M(RS)_2^=$ was calculated to be the predominant species. For the spectra in the visible, determinations were made using 1.00 to 5.00 cm. cells on solutions in which the total metal ion concentration was varied from 0.0010 to 0.0050 *M* in the various experiments. Air had to be rigorously excluded from the solutions containing the complexes of Mn(II), Fe(II) and Co(II) as these are easily oxidized to more intensely absorbing species. To exclude air, the spectra were determined using absorption cells which were equipped with Teflon plugs. These held self-sealing Buna N stoppers. The cells were flushed with nitrogen and then filled with solution by means of hypodermic needles inserted through the self-sealing stoppers.

The spectra in the ultraviolet region were determined using solutions of 0.0040 *M* thioglycolic acid, 0.0020 *M* metal-(II) chloride and 0.0050 *M* KOH in 0.100 cm. cells. This gave solutions containing 0.0010 *M* MRS. In the case of zinc sufficient extra base was added to neutralize the hydrochloric acid present.

Bis mercapto complexes of Ni(II) have been shown to be diamagnetic,[10,11] while those of Co(II) were found to have the quartet ground state.[11] In the present study the bis-thioglycolato complex of Fe(II) was found to be paramagnetic and that of Ni(II) was found to be diamagnetic using the Gouy method. The spectra indicate that in the present case the Co(II) thioglycolates have the quartet ground state.

Results and Discussion

The titration curves in the presence of the metal ions gave no indication of complex formation during the titration of the first (the carboxylic) hydrogen of thioglycolic acid. Strong complex formation was evident during the titration of the second (mercaptan) hydrogen. Only the formation of two complexes MRS and $M(RS)_2^=$ but no higher complexes was indicated. The over-all molar formation constants, Q_{f1} and $Q_{f1}Q_{f2}$, were evaluated from the titration curves and are presented in Table I. The titration curves in which smaller amounts of thioglycolic acid were used gave constants in agreement with these. Theoretical titration curves calculated from the constants agreed well with those observed.

TABLE I

THE FORMATION CONSTANTS OF THE THIOGLYCOLATES

	Q_{f1}	$Q_{f1}Q_{f2}$
Mn^{++}	2.4×10^4	3.6×10^7
Fe^{++a}	....	1.7×10^{10}
Co^{++}	6.9×10^5	1.4×10^{12}
Ni^{++}	9.5×10^6	3.4×10^{13}
Zn^{++b}	7.2×10^7	1.1×10^{15}

[a] From ref. 2. [b] Li and Manning[3] report values of 2.8×10^7 and 2.6×10^{14}.

The formation constants for the thioglycolates are significantly greater than those compiled[12] for the glycinates and are considerably greater than those for the malonates and oxalates. Another feature is that the zinc(II) thioglycolates are appreciably more stable than those of nickel(II). This is a departure from the usual stability relationships noted for oxygen and nitrogen donors.[12a,13] In order to assess the factors involved, the approximate crystal-field stabilization in the complexes was evaluated using the method presented by George.[14] In this method the free energies of formation of a series of complexes are corrected for the hydration energies of the metal ions so that, essentially, in the series a comparison is made for the energies of the reactions

$$M_g^{++} + nL_{aq} \longrightarrow ML_{naq}$$

For the divalent metal ions the monotonic increase in the stability of the complexes with decreasing radius of the metal ion is approximated as a linear function passing through the points for the corrected free energies of formation for the Mn(II) and Zn(II) complexes where no crystal field stabilization occurs. The crystal field stabilization for the other transition metal ion complexes is taken as the difference between their corrected energies and that corresponding to the linear function. George has shown that with oxygen and nitrogen ligands the maximum stabilization in the divalent ions occurs approximately with nickel. Also, he has shown that the value of this maximum stabilization was found to be proportional to the difference, Δ, between the corrected free energies fort he manganese(II) and zinc(II) reactions. The treatment of George was repeated in the present study for a number of complexes using the Benjamin and Gold[15] hydration energies. It was found that the stabilizations for the complexes of the other divalent transition metals are also nearly proportional to the value of Δ. The general effect is illustrated in Fig. 1 where the proportionality constants are also given. In this figure the data are presented relative to a value of Δ equal to unity. The circles represent the average values calculated from the formation constants reported in the literature.

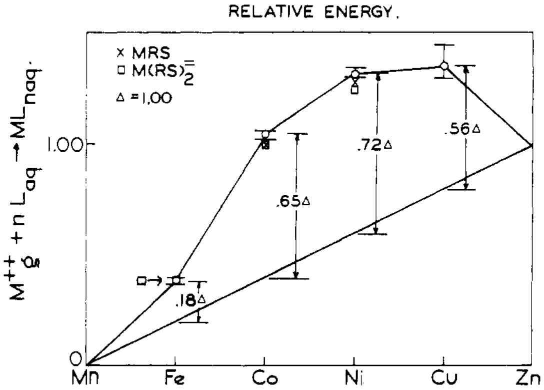

Fig. 1.—A comparison of the relative crystal field stabilizations in the thioglycolato complexes with those in the oxygen and nitrogen complexes. The circles represent the averages of values calculated from the heats of hydration of the ions (ref. 15) and the formation constants for pyridine$_1$, en$_1$, en$_2$, salicylaldehyde$_1$, salicylaldehyde$_2$, oxalate$_1$, malonate$_1$, histidine$_1$, glycine$_1$, glycine$_2$ (refs. 12a, b). The limits represent the range of these values.

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(10) J. J. Draney and M. Cefola, THIS JOURNAL, **76**, 1975 (1954).

(11) J. M. White, T. J. Weismann and N. C. Li, *J. Phys. Chem.*, **61**, 126 (1957).

(12) (a) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952; (b) Chr. K. Jorgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

(13) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

(14) P. George, *Rec. trav. chim.*, **75**, 671 (1956).

(15) L. Benjamin and V. Gold, *Trans. Faraday Soc.*, **50**, 797 (1954).

The limits give the range of the literature values. With copper, the tetragonality effects (the tendency to form square-planar complexes) are seen to cause a much greater spread of values than with the other metal ions.

The relative values of the crystal-field stabilization were calculated in the same manner from the equilibrium constants of the thioglycolato complexes. These results also are presented in Fig. 1. It is seen that the thioglycolato complexes behave almost the same as the oxygen and nitrogen donors, although their stabilization with cobalt and nickel is slightly less. It is not to be expected that the values for $Ni(RS)_2^=$ would agree very closely as the ground state of Ni(II) is different in the bis-thioglycolato complex than it is in the other nickel complexes, but in Fig. 1 the departure is seen to be not considerable. Some effect in going to the next row in the periodic table is to be expected but, at present, it cannot be stated by how much the lower cobalt and nickel values are a general reflection of this change in ligand. At least part of the difference may be ascribed, also, to the large values of Δ in the thioglycolato complexes. The values of Δ equal to 52.3 and 58.3 kcal. for the mono- and bis-thioglycolates are about the largest that can be calculated from the relatively meager data in the literature concerning the stabilities of both Mn(II) and Zn(II) complexes with a given ligand. The large values of Δ indicate that the stabilities of the thioglycolato complexes are more dependent upon the radius of the coördinated metal ion than those of the other ligands compared in Fig. 1.

The spectra of the complexes are characterized by intense absorption in the ultraviolet and weaker absorption in the visible. The spectra of the cobalt complexes are presented in Fig. 2 and those of nickel in Fig. 3. The spectra of CoRS and NiRS do not bear close resemblance to the spectra of the aquo ions which have maxima at 1,250, 625 and 505 mμ in the case of $Co(H_2O)_6^{++}$[16] and 1,180, 740, 650 and 395 mμ in the case of $Ni(H_2O)_6^{++}$.[16b,17]

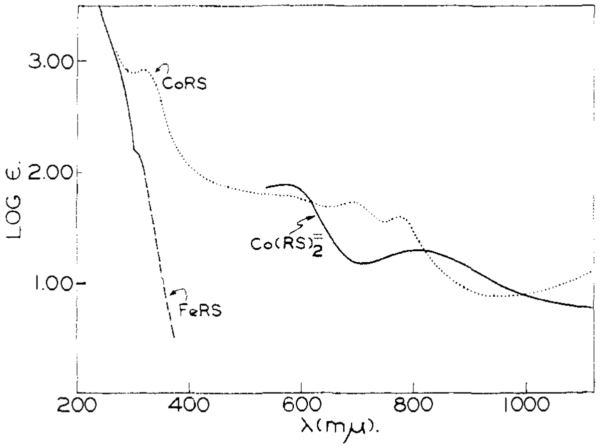

Fig. 2.—The absorption spectra of the thioglycolato complexes of iron(II) and Co(II).

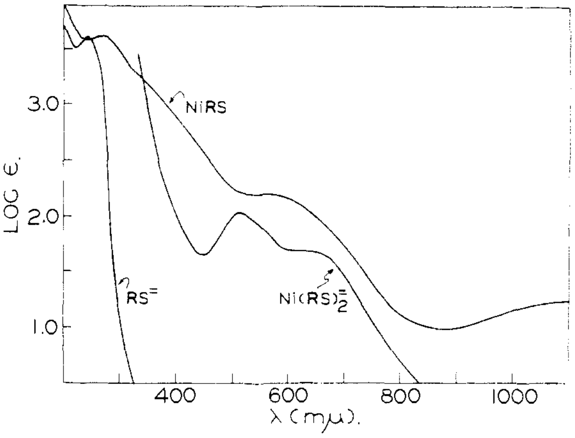

Fig. 3.—The absorption spectra of the thioglycolate ion and its nickel(II) complexes.

If the divalent thioglycolate ion and water were close together in the Fajans–Tsuchida spectrochemical series[18] then the rule of "average environment" would apply and general conformity to the Orgel diagram[19] would be observed with a shift of the bands of the aquo ions to shorter wave lengths in the thioglycolato complexes. However, the spectra show splitting of the bands as would be expected in an unsymmetric, rhombic, field.[18,20] The band maximum of CoRS which lies in the near-infrared could not be located with certainty but lies somewhere between 1200 and 1300 mμ. The two bands in this same complex which are seen at 776 and 690 mμ are not expected on the basis of the Orgel diagram but may be due to a very large splitting of the first excited level (as given in the diagram of reference 16a), or these may be due to spin-forbidden bands which are observed in the unsymmetric field. With the addition of the second thioglycolate ion, a decided shift to shorter wave lengths can be noted.

Similar arguments can be stated for the spectrum of NiRS which, also, shows a considerable over-lap of bands. The spectrum of $Ni(RS)_2^=$ is typical of that expected for a square-planar diamagnetic nickel(II) complex. Its red color indicates that it lies near the paramagnetic-diamagnetic border.[20]

The spectra of the nickel(II) thioglycolates resemble closely those in the visible for the cysteine and cysteine methyl ester complexes of nickel(II) presented by White, Manning and Li.[21] This shows that it is the common mercaptide ion which has by far the predominant influence on the nickel(II) ion in these complexes. The absorption maximum of the mono-methylcysteinate complex is at a slightly shorter wave length than that of the mono-thioglycolato complex. This shift can be explained by the substitution of a coördinated $-NH_2$ group (in methyl cysteinate) for a $-CO_2^-$ (in thio-

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(16) (a) C. J. Ballhausen and C. K. Jorgensen, *Acta Chem. Scand.*, **9**, 397 (1955); (b) C. K. Jorgensen, Report to the Xth Solvay Council. Brussels, May 1956.

(17) C. K. Jorgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(18) F. Basolo, C. J. Ballhausen and J. Bjerrum, *ibid.*, **9**, 810 (1955).

(19) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(20) (a) C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat fys. Medd.*, **29**, No. 8 (1955); (b) C. J. Ballhausen and C. K. Jorgensen, *ibid.*, **29**, No. 14 (1955).

(21) J. M. White, R. A. Manning and N. C. Li, This Journal, **78**, 2367 (1956).

glycolate). The shift is in the expected direction according to the relative positions of these groups in the spectrochemical series.

The mercaptide ion exhibits an intense band in the ultraviolet which has been identified by Orgel[22] as a charge-transfer transition. In the divalent thioglycolate ion the maximum of this band occurs at 245 mμ (see Fig. 3). In the complexes, CoRS and NiRS, this band is seen to become broadened and shifted to longer wave lengths. With FeRS the shift is not as great but even here a slight overlap into the visible region occurs. The FeRS spectrum also shows a d-level transition in the region 975–950 mμ with an extinction coefficient equal to six.

The spectrum of MnRS shows no absorption in the visible regions under the present experimental conditions. The beginning of a band is observed in the same region in which the free divalent thioglycolate ion absorbs, however. Because of the appreciable dissociation of the complex an interpretation of the results is difficult.

The spectrum of ZnRS shows no absorption until about 250 mμ where the beginning of a band having a maximum at shorter wave lengths is observed. The excess RSH^- ion present in the solution, also, contributes greatly to the absorption in this same region. No attempt was made to resolve the spectrum into that of its components because the resulting spectrum of ZnRS would be obtained from the difference of large numbers.

The spectral changes of the mercaptide ion absorption band in the series of thioglycolato complexes run somewhat parallel to those observed by Katzin[23] for the iodide ion. The charge-transfer bands of the iodide ion are shifted to longer wave lengths on complexing with cobalt(II) and nickel(II), but in the lower complexes of zinc(II) a shift to shorter wave lengths occurs.

The oxidation of the metal ion brings about a shift of the charge-transfer band of the thioglycolate to even longer wave lengths. With $\mathrm{Fe(III)OH(RS)_2^{=2}}$ the maximum occurs at 535 mμ with a shoulder at 410 mμ, and with Co(III)[24] the maximum occurs at 362 mμ with a shoulder at 450 mμ. This shift to longer wave lengths upon oxidizing the metal ion is a reflection of the greater ease with which these trivalent metal ions can accept an electron from the coördinating thioglycolate ion than can the corresponding divalent metal ions. In the latter case the transfer of electrons to the metal ions occurs less readily because highly unstable monovalent metal ions are formed.

The stability and spectra data show that the mercaptide ion exerts a strong influence upon the central metal ion of a complex. The influence can be expressed quantitatively by the value of the term *Dq* in the Orgel diagram.[19] The lack of symmetry in the present complexes precludes the accurate evaluation of *Dq* for the mercaptide ion, but it can be stated that its value is fairly large.

Whether the strong effect of the mercaptide is primarily an electrostatic one or a covalent one is not evident at the present. In the spectrochemical series the increase in *Dq* is in the order in which increased covalent bonding is expected.[25] The thioglycolate ion, on the other hand, is able to exert a strong electrostatic field. Most likely, both effects play large roles in bringing about the stability of the complexes.

[22] L. E. Orgel, *Quart. Revs.*, **8**, 422 (1954).

[23] L. I. Katzin, *J. Chem. Phys.*, **20**, 1165 (1952); **23**, 2055 (1955).

[24] Prepared by the air oxidation of the CoRS solution used in the ultraviolet studies.

[25] L. E. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WEST VIRGINIA UNIVERSITY]

Metal Ion Complexes of 2-(2-Aminoethylamino)-ethanol. Reaction of the Copper(II) Complexes with Sodium Hydroxide[1,2]

BY JAMES L. HALL AND WARREN E. DEAN

RECEIVED JANUARY 2, 1958

In solution 2-(2-aminoethylamino)-ethanol, $H_2N(CH_2)_2NH(CH_2)_2OH$, (hydroxyethyl-ethylenediamine, abbreviated hn or hen-OH) forms complexes with copper(II) ion in the ratio Cu(II):hn of 1:1 and 1:2. The reaction of these complexes with further amine and with sodium hydroxide in solution has been studied by spectrophotometric, conductometric and potentiometric methods. The 1:1 complex, $\mathrm{Cu(hn)^{+2}}$, reacts with one equivalent of sodium hydroxide to form $\mathrm{Cu(hen\text{-}O^-)^{+1}}$ and with two equivalents of sodium hydroxide to form $\mathrm{[Cu(hen\text{-}O^-)(OH)]^0}$ which is quite stable in solution. The 1:2 complex reacts with hydroxyl radical from excess amine or from sodium hydroxide to form $\mathrm{[Cu(hn)(hen\text{-}O^-)]^{+1}}$, assuming the formation of a five-coördinate copper(II) ion. The 1:2 complex also reacts with excess amine to form $\mathrm{Cu(hn)_3^{+2}}$ for which five-coördinate copper(II) ion is again assumed. In strongly basic solution both of these latter complexes lose amine molecules to form $\mathrm{[Cu(hen\text{-}O^-)(OH)]^0}$.

Introduction

Breckenridge[3] prepared the crystalline compounds $\mathrm{Cu(hn)_2Cl_2}$, $\mathrm{Cu(hn)_2Br_2}$ and $\mathrm{[Cu(hn)Cl]Cl\cdot{}^1/_2H_2O}$ by reaction in 95% ethanol of the appropriate copper salt and 2-(2-aminoethylamino)-ethanol, $H_2N(CH_2)_2NH(CH_2)_2OH$, (hydroxyethyl-ethylenediamine, abbreviated hn or hen-OH). Harvey, Tewksbury and Haendler[4] made a spectrophotometric study of copper(II) acetate and hydroxyethyl-ethylenediamine mixtures. Analysis by the method of continuous variations[5] indi-

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[1] Sponsored by the Office of Ordnance Research, U. S. Army.

[2] Presented before the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., Nov. 14 to 16, 1957.

[3] J. G. Breckenridge, *Can. J. Research*, **26B**, 11 (1948).

[4] J. L. Harvey, C. I. Tewksbury and H. M. Haendler, THIS JOURNAL, **71**, 3641 (1949).

[5] W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941).