will escape entirely. This last point was proved in an experiment where guest-free Dianin's compound, after being exposed at 100° for five days to one atmosphere of sulfur hexafluoride, took up only a trace of the gas.

The enumerated experimental observations are adequately explained in accordance with the assumption that the thermal decomposition of the sulfur hexafluoride clathrate proceeds only by sublimation of the host component. Since in all the experiments of this investigation there was hindrance to the escape of Dianin's compound (at least because of the bulk of the sample), the evolution of sulfur hexafluoride also was suppressed as a result, these effects increasing with increasing sample size and pressure. However, the suppression of sulfur hexafluoride evolution occurs to a lesser extent than that of Dianin's compound because the formation of an effective protective coating occurs only as a result of the decomposition of clathrate. Therefore, the total weight ratio of evolved sulfur hexafluoride to evolved Dianin's compound is always greater than the ratio of these components and increases with increasing external pressure or increasing sample size, since the major effect of these two factors is to suppress the escape of Dianin's compound. However, this ratio should decrease with increasing decomposition time as was generally, but not always, observed. A decomposing sample decreases in size (thereby facilitating the evolution of Dianin's compound) and acquires a more effective protective coating, which in turn suppresses the evolution of sulfur hexafluoride. Reduction of the ratio of sulfur hexafluoride to Dianin's compound in a decomposing sample is not a factor because this ratio was always close to the original ratio, the greatest decrease observed being 12%.

The complicating features that surround the proposed sublimation mechanism tie in with the powdered nature of the samples. However, since information was not obtained on the geometry of the particles composing the powders, a strict kinetic analysis of the analytical data could not be made.

Acknowledgments.—The authors wish to express their sincerest thanks to C. W. Lewis, International Resistance Corporation, 401 North Broad Street, Philadelphia, Pa., for his helpful discussions and suggestions throughout the entire project, to W. M. Hickam for the mass spectrometer analyses and to J. H. Lady for the infrared spectra determinations.

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

Metal Ion Complexes of N,N′-Bis-(2-hydroxyethyl)-ethylenediamine. Reaction of the Copper(II) Complexes with Sodium Hydroxide[1]

BY JAMES L. HALL AND WARREN E. DEAN

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In solution N,N′-bis-(2-hydroxyethyl)-ethylenediamine, $\mathrm{HO(CH_2)_2NH(CH_2)_2NH(CH_2)_2OH}$,[2] forms complexes with copper(II) ion in the ratio Cu(II):hen(OH)$_2$ of 1:1 and 1:2. The reaction of these complexes with more amine and with sodium hydroxide in solution has been studied by spectrophotometric and conductometric methods. The 1:1 complex, Cu[hen(OH)$_2$]$^{+2}$, reacts with an equivalent amount of sodium hydroxide to form Cu[hen(OH)(O$^-$)]$^{+1}$ and with two equivalents of sodium hydroxide to form Cu[hen(O$^-$)$_2$]^0. These latter two complexes may be formed partially by action of an excess of the amine. By comparison with the copper(II) complexes of ethylenediamine, a monoalkanol-substituted ethylenediamine and a tetraalkanol-substituted ethylenediamine, it is shown that the range of *p*H over which the 1:2 complexes are stable decreases with the degree of alkanol substitution. The 1:1 complexes are more stable as the degree of substitution is increased, but this evidently is due to the increased opportunity for formation of chelate rings involving the hydroxyl oxygen atoms.

Introduction

Previous reports from this Laboratory have described the copper(II) complexes of a monoalkanol-substituted ethylenediamine,[3] 2-(2-aminoethylamino)-ethanol (hydroxyethylethylenediamine) and of a tetralkanol-substituted ethylenediamine,[4] N,-N,N′,N′-tetrakis-(2-hydroxypropyl)-ethylenediamine. The present study of the copper(II) complexes of N,N′-dihydroxyethylethylenediamine was undertaken with the expectation that a comparison of the three systems would lead to some generalizations relating the degree of alkanol substitution of the ethylenediamine molecule to the type of complexes formed under various degrees of alkalinity.

No previous detailed studies of the metal-ion complexes of hen(OH)$_2$ have been reported. Martell, Chaberek, Courtney, Westerback and Hyytiainen[5] have reported the results of titration with strong base of 1:1 mixtures of copper(II) nitrate and this amine, giving the formation constant of the 1:1 complex and the equilibrium constant for the reaction of the 1:1 complex with strong base. More recently, in a report made after completion of the present work, Courtney, Gustafson, Chaberek and Martell[6] have shown that 1:1

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[1] Sponsored by the Office of Ordnance Reseaich, U. S. Army. From a portion of the Ph.D. Dissertation of W. E. Dean, West Virginia University, 1959.

[2] To be abbreviated hen(OH)$_2$. Ethylenediamine will be abbreviated en and hydroxyethylethylenediamine will be abbreviated hen(OH).

[3] J. L. Hall and W. E. Dean, THIS JOURNAL, **80**, 4183 (1958).

[4] J. L. Hall, F. R. Jones, C. E. Delchamps and C. W. McWilliams, *ibid.*, **79**, 3361 (1957).

[5] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *ibid.*, **79**, 3036 (1957).

[6] R. C. Courtney, R. L. Gustafson, S. Chabeiek, Jr., and A. E. Martell, *ibid.*, **81**, 519 (1959).

mixtures of both Cu(II)-hen(OH) and Cu(II)-hen(OH)$_2$ tend to form dimers in solution over a particular range of *p*H. Crystalline dimers of a similar type have been prepared by Hein and Beerstecher[7] from copper(II) salts and substituted ethanolamines.

The present report is concerned primarily with the range of *p*H over which the 1:1 and 1:2 complexes of copper(II) ion and hen(OH)$_2$ are formed and of the reactions of these complexes with strong base.

Experimental

Except for the amine. the reagents, standardizations, spectrophotometric methods and conductometric methods were all identical with those recently described.[3] The N,N'-bis-(2-hydroxyethyl)-ethylenediamine was a research sample obtained from the Union Carbide Chemicals Company. The molarity of solutions of the amine determined by titration with standard acid agreed very closely with the value from direct weighing.

Results

Spectrophotometric Studies.—The spectra of solutions formed by mixing copper(II) perchlorate, hen(OH)$_2$ and sodium hydroxide in various proportions show some distinct differences from the spectra of corresponding solutions involving hen(OH) which were studied previously[3] although the general pattern is somewhat similar. A solution 0.005 *M* in copper(II) perchlorate with copper(II) ion to hen(OH)$_2$ ratio of 1:2 shows a maximum of absorbance of 0.58 at 630 m*u*. At ratio 1:3 this maximum shifts to 0.65 at 615 mμ. Further increase of the amine concentration to ratio 1:20 causes the maximum to decrease in intensity and to increase in wave length. Greater increase in the amine concentration, to ratio 1:100, causes the long wave-length branch of the absorption curve to shift upwards as was noted previously for copper(II) ion and hen(OH)[3] and for copper(II) ion and en.[8] Addition of sodium hydroxide to the 1:2 solution to ratio 1:2:0.4, copper(II) ion: hen(OH)$_2$:NaOH, causes the maximum of absorption to increase slightly. More sodium hydroxide shifts the wave length of the maximum to about 640 m*u*. The characteristic isosbestic point observed for addition of sodium hydroxide to 1:2 solutions of copper(II) ion and ethylenediamine[9] and of copper(II) ion and hydroxyethylethylenediamine[3] was not observed, but solutions having more sodium hydroxide than in the 1:2:1 solution show an isosbestic point at 530 mμ, showing an equilibrium between the colored species in this solution and a single further product. The spectra for solutions of ratios 1:1:0, 1:1:1 and 1:2:0 are distinctly different showing that the action of the second amine molecule on the 1:1 complex is different from the action of sodium hydroxide. The spectra of solutions of ratios 1:1:2, 1:1:3 and 1:1:4 are nearly identical with each other but are different from the spectrum for ratio 1:1:1, indicating that the reaction between the 1:1 complex and strong base involves two but not more than two equivalents of hydroxide ion per mole of complex ion. The spectra for all solutions having a greater concentration of amine than of copper(II) ion approach that for the 1:1:2 solution as an excess of base is added, indicating that only one mole of amine per copper(II) ion is involved in the final product.

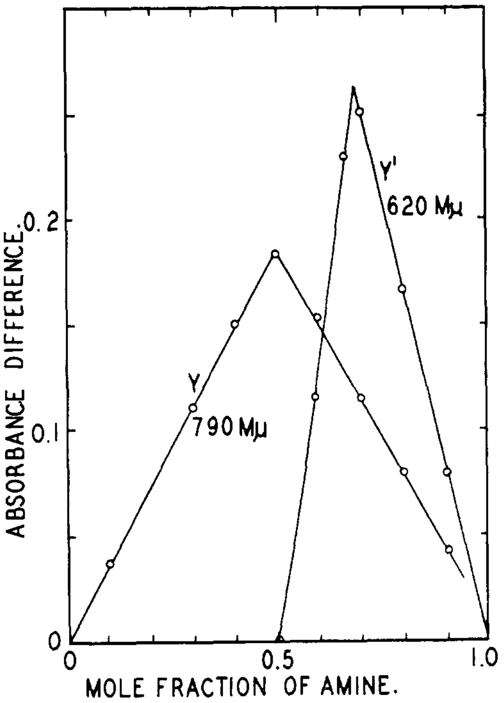

Fig. 1.—Results of the continuous variations study at 790 and 620 mμ for the system copper(II) perchlorate–dihydroxyethylenediamine.

A study by the modified method of continuous variations[10] was made using solutions of constant total concentration of copper(II) ion plus amine of 0.01 *M*. One Y and one Y' curve from this study are shown in Fig. 1. The maximum of the Y' curve is at a mole fraction slightly greater than the value required for the 1:2 complex.

The spectrum for the 1:2 solution and of solutions containing a considerable excess of amine came to equilibrium only after several hours. The shift in the spectrum with time was in the same direction as the shift which was produced by adding a small amount of sodium hydroxide to the fresh solution.

These studies of spectra have led to certain tentative conclusions. At the *p*H of the 1:1 solution, 6.1, the colored species in solution consists almost entirely of an ion in which two coordination positions of the copper(II) ion are occupied by the two nitrogen atoms of a single amine molecule. Immediately after adding a solution of a copper(II) salt to a solution of the amine to form the 1:2 ratio, the principal colored species is the 1:2 complex in which four coördination positions of the copper(II) ion are occupied by the four nitrogen atoms of two amine molecules. Upon standing or upon addition of more amine or upon addition of sodium hydroxide, a mixture of several different colored species is produced. The pro-

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[7] Fr. Hein and W. Beerstecher, *Z. anorg. allgem. Chem.*, **282**, 93 (1955).

[8] J. Bjerrum and E. J. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

[9] H. B. Jonassen, R. E. Reeves and L. Segal, THIS JOURNAL, **77**, 2748 (1955).

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

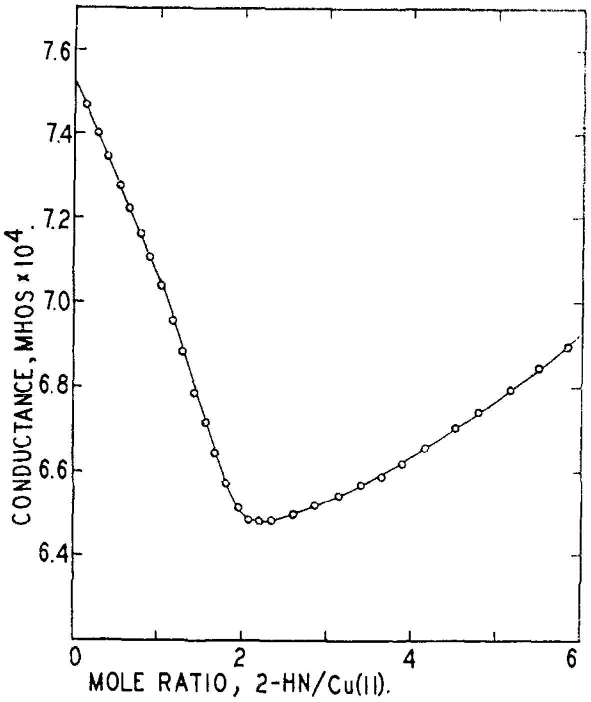

Fig. 2.—Conductometric titration of 0.003656 *M* copper(II) perchlorate with 0.0952 *M* dihydroxyethylethylenediamine.

portion of each species in the mixture depends upon the *p*H of the solution and upon the relative concentration of the amine. The species causing the greatest light absorption in the vicinity of 620 mμ evidently is similar to the one formed in the copper(II) ion and hen(OH) system[3] which was assumed to have two $-NHC_2H_4NH-$ and one $-NHC_2H_4O^{-}-$ chelate rings. The addition of amine to the 1:2 solution should encourage the formation of this product by raising the *p*H and by opposing the dissociation of the nitrogen coördination. The maximum concentration of this species evidently is in the 1:3 solution which has a *p*H of 9.2 as compared to a *p*H of 7.4 for the 1:2 solution. It is the presence of the small amount of this additional complex ion which causes the peak of the Y′ curve of Fig. 1 to be at a ratio greater than 1:2. With more amine,the higher *p*H probably results in dissociation of one of the two amine molecules from the copper(II) ion. As sodium hydroxide is added to the 1:2 solution, it appears that the maximum of the concentration of $Cu[hen(OH)_2hen(OH)(O^-)]^{+1}$ is reached at about ratio 1:2:0.4 for which the *p*H is 8.6. More base results in dissociation of one of the amine molecules from the copper(II) ion and there is finally formed the species in which one $hen(OH)_2$ molecule forms three chelate rings about the copper(II) ion.

Conductometric Titrations.—The reactions proposed as a result of the spectrophotometric studies were confirmed by the results of conductometric titrations. As is shown in Fig. 2, addition of the amine to a solution of copper(II) perchlorate produced a regular decrease in conductance to the ratio 1:1, $Cu(II):hen(OH)_2$, a further regular and greater decrease to the 1:2 ratio, followed by an increase of conductance. The decrease of conductance between ratios 1:1 and 1:2 is interpreted as being due to coördination of the second amine molecule. Had the second amine molecule acted to remove protons from the 1:1 complex and to form ammonium-type ions in solution, previous experience would indicate that an increase of conductance should be expected.

It was shown previously[3] that the addition of sodium hydroxide to copper(II) perchlorate alone or to $Cu[hen(OH)](ClO_4)_2$ produced quite similar conductance curves, showing reaction of two equivalents of hydroxide ion per mole of copper(II) ion for each. The addition of sodium hydroxide to $Cu[hen(OH)]_2(ClO_4)_2$ required a smaller amount of base. In the present work addition of sodium hydroxide to solutions of $Cu(ClO_4)_2$, $Cu[hen(OH)_2](ClO_4)_2$ and $Cu[hen(OH)_2]_2(ClO_4)_2$ produced very similar titration curves. This is evidence for the reaction of two equivalents of base with the $Cu[hen(OH)_2]_2^{+2}$ ion, and it is evident that the reaction goes very nearly to completion as the base is added.

Discussion

It has been shown[11] that ethylenediamine forms a 1:1 complex with copper(II) ion which is stable in water but reacts quantitatively upon addition of sodium hydroxide according to the equation.

$$2\ Cu(en)^{+2} + 2\ OH^- \longrightarrow Cu(en)_2^{+2} + Cu(OH)_2 \quad (1)$$

In this and the following equations coördinated water molecules are not included.

For the monoalkanol-substituted ethylenediamine it was shown that the complex ion $Cu[hen(OH)]^{+2}$ undergoes a reaction similar to (1) only to a slight extent and that the small amount of precipitate initially formed is dissolved upon addition of more sodium hydroxide. In the present study, no precipitate was formed upon addition of sodium hydroxide to a solution containing $Cu[hen(OH)_2]^{+2}$, although two equivalents of base reacted per mole of complex.

$$Cu[hen(OH)]^{+2} + 2\ OH^- \longrightarrow Cu[hen(O^-)](OH^-) + H_2O \quad (2)$$

$$Cu[hen(OH)_2]^{+2} + 2\ OH^- \longrightarrow Cu(hen(O^-)_2] + 2\ H_2O \quad (3)$$

Thus, although each of these three 1:1 complexes reacts with sodium hydroxide, a different type of product is obtained for each.

The 1:2 complex $Cu(en)_2^{+2}$ is not attacked appreciably by dilute sodium hydroxide[11] but does react somewhat with more concentrated sodium hydroxide, and for this reaction it has been suggested that the coördination of the nitrogen atoms is not disturbed but that the hydroxide ion is added to a fifth coördination position of the copper (II) ion.[9]

$$Cu(en)_2^{+2} + OH^- \longrightarrow Cu(en)_2(OH^-)^{+1} \quad (4)$$

The complex ion $Cu[hen(OH)]^{+2}$ has been shown[3] to react with sodium hydroxide in two steps, the first one being

$$Cu[hen(OH)]_2^{+2} + OH^- \longrightarrow Cu[hen(OH)hen(O^-)]^{+1} + H_2O \quad (5)$$

and the much greater equilibrium constant of

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(11) H. B. Jonassen and T. H. Dexter, This Journal, **71**, 1553 (1949).

reaction 5 as compared with (4) is accepted as evidence that this reaction is accomplished by removal of a proton (and formation of a chelate ring) as shown in equation 5 rather than by the simple addition of the hydroxide ion as in reaction 4. A similar argument may be applied to equations 2 and 3, and it will be shown later[12] that the equilibrium constant for reaction 3 is greater than for (2).

The complex ion $\mathrm{Cu(en)_2(OH^-)^{+1}}$ evidently undergoes no further reaction with strong base, even in 1 N solution.[9] The complex ion $\mathrm{Cu[hen(OH)hen(O^-)]^{+1}}$ decomposes above pH 10 to form the product shown in equation 2 with one mole of amine being set free. The complex ion $\mathrm{Cu[hen(OH)_2]_2^{+2}}$ reacts with sodium hydroxide but the type of complex shown by equations 4 and 5 is formed only to a limited extent. Instead, the decomposition of the 1:2 complex to form the product shown in equation 3 with the release of one mole of amine begins in the range of pH 8.5 to 9.0 which is at a lower concentration of base than is required for formation of the five-coördinate complex.

The 1:1 complexes of copper(II) ion and each of the amines en, hen(OH) and hen(OH)$_2$ may all be formed at pH 5.5 to 6. As more amine is added to solutions of these 1:1 complexes the second amine molecule is added to each below pH 7.5. The second amine molecule is not displaced from $\mathrm{Cu(en)_2^{+2}}$ by 1 N sodium hydroxide. The ion $\mathrm{Cu[hen(OH)]_2^{+2}}$ is so decomposed by 1 N sodium hydroxide, and $\mathrm{Cu[hen(OH)_2]_2^{+2}}$ is decomposed by a much lower concentration of sodium hydroxide. For the tetraalkanol-substituted ethylenediamine there is no evidence for formation of a 1:2 complex. The reactions of equations 1, 2 and 3 all take place at about pH 7.0. The 1:1 complex of the tetraalkanol-substituted amine reacts with sodium hydroxide at a slightly lower pH.

The reactions which have been established between sodium hydroxide and the copper(II) ion complexes of ethylenediamine and of the three alkanol-substituted ethylendiamines form a groundwork for the interpretation of pH titration curves for a number of systems involving various metallic ions and a number of alkanol-substituted amines. Several such studies are included in an accompanying report.[12]

[12] J. L. Hall, W. E. Dean and E. A. Pacofsky, THIS JOURNAL, **82**, 3303 (1960).

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

Metal Chelates of Alkanol-substituted Amines[1]

BY JAMES L. HALL, WARREN E. DEAN AND EDWARD A. PACOFSKY

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The chelate compounds formed between each of the metallic ions copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II) and each of seven different alkanol-substituted ethylenediamine molecules have been investigated by the potentiometric method of Bjerrum. The mono- and di-substituted amines form both 1:1 and 1:2 complexes with metallic ions.[2] In general the 1:1 complexes of these amines react with strong base either to form 1:2 complexes and the metallic hydroxides or to form uncharged chelate compounds by loss of protons from the 1:1 complexes. In several instances the 1:2 complexes are decomposed in alkaline solution to yield the same final product as for the 1:1 complexes. In general the chelates having the highest stability as shown by log K_1 have the lowest acidity as shown by pK_{A_1} and pK_{A_2}. The tetraalkanol-substituted amines form only 1:1 complexes with the metallic ions. In general 2-hydroxypropyl substitution leads to greater stability of the chelate compounds than does 2-hydroxyethyl substitution. For each amine, the order of stability of the complexes with the various metallic ions follows the usual order except that the cadmium(II) ion complexes of the tetraalkanol-substituted amines are more stable than would be anticipated.

Introduction

There is considerable evidence for the participation in chelation of the hydroxyl groups of certain alkanol-substituted amines. Such chelation may be expected if the nitrogen and oxygen atoms can be included in the same five-membered ring. Coördination of both nitrogen and oxygen atoms evidently is involved in the complex ions formed in solution and in the solid compounds formed between transition metal salts and the ethanolamines[3-6] and substituted ethanolamines.[7] A previous study in this Laboratory[8] has shown that the 1:1 copper(II) ion complex of a tetraalkanol-substituted ethylenediamine (4-hpn, included in Table I) acts in solution as a dibasic acid of appreciable strength. There is evidence to support the assumption that this acidic property is due to enhancement of the acidity of hydrogen atoms of the hydroxyl groups upon coördination of the oxygen atoms. Similar conclusions have been reached for the copper(II) ion complexes of hn[9] and 2-hn.[10] Martell, Chaberek, Courtney, Westerback and Hyytiainen[11] have considered the ques-

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[1] Supported by the Office of Ordnance Research, U. S. Army. From a portion of the Ph.D. Dissertation of W. E. Dean, West Virginia University, 1959.

[2] Ratios represent the relative proportions of the metallic ion and amine in that order.

[3] W. Hieber and E. Levy, *Ann.*, **500**, 14 (1933); *Z. anorg. allgem. Chem.*, **219**, 225 (1934).

[4] H. Brintzinger and B. Hesse, *ibid.*, **248**, 345, 351 (1941).

[5] P. S. James, Master's Thesis, West Virginia University, 1957.

[6] W. E. Dean, Master's Thesis, West Virginia University, 1956.

[7] Fr. Hein and W. Beerstecher, *Z. anorg. allgem. chem.*, **282**, 93 (1955).

[8] J. L. Hall, F. R. Jones, C. E. Delchamps and C. W. McWilliams, THIS JOURNAL, **79**, 3361 (1957).

[9] J. L. Hall and W. E. Dean, *ibid.*, **80**, 4183 (1958).

[10] J. L. Hall and W. E. Dean, *ibid.*, **82**, 3300 (1960).

[11] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *ibid.*, **79**, 3036 (1957). See this article for several references to previous work.