The method is especially valuable for those metals which have volatile oxychlorides, such as Nb, Ta, Mo, W, Tc and Re, thereby requiring repeated sublimation of the chloride to free it from oxychloride even when the preparation is begun with "pure" metal.

It appears to be the method of choice for Tc since direct synthesis and other methods do not work.[15] In fact, interest in the method was greatly stimulated by the search for a means of synthesizing technetium chloride in pure form.

Technetium Tetrachloride.—Since previous work and these experiments prove that this reaction gives the highest known chloride of the metal in question (*cf.* $MoCl_5$, WCl_6, $ReCl_5$, etc.), it is of interest that technetium forms a tetrachloride rather than a penta- or trichloride as rhenium does. In this respect it resembles manganese more than rhenium. The fact that technetium tetrachloride can be isolated in a pure state bears out its expected greater stability over manganese tetrachloride. Thus, technetium, whose oxides differ from those of rhenium only in degree,[16] has a highest chloride which differs in kind from rhenium chlorides.[17] When compared to the behavior of the elements near Tc and Re in the periodic table, this reduced affinity of technetium for chlorine is not surprising on an empirical basis, as can be seen by considering the highest known anhydrous chlorides in this region

$NbCl_5$	$MoCl_5$	$TcCl_4$	$RuCl_3$
$TaCl_5$	WCl_6	$ReCl_5$	$OsCl_4$

The affinity for chlorine definitely falls off in going up as well as across the periodic table. The fluorides of these metals follow a similar pattern. To our knowledge, no satisfactory explanation has been given for the general phenomenon; stereochemical grounds alone are not sufficient.[18] We have none to offer, and regard the question as one of the interesting unsolved problems in inorganic chemistry.

Acknowledgments.—This work was financially supported in part by the U. S. Atomic Energy Commission and the du Pont Company, whose assistance is gratefully acknowledged. Appreciation is also expressed to the Oak Ridge National Laboratory for the loan of the technetium.

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[15] C. M. Nelson, G. E. Boyd and W. T. Smith, Jr., THIS JOURNAL, **76**, 348 (1954).

[16] W. T. Smith, Jr., J. W. Cobble and G. E. Boyd, *ibid.*, **75**, 5773, 5777, 5783 (1953).

[17] As pointed out by one referee, a higher chloride of Tc may later be found under conditions other than those of this experiment, maybe "as a constituent of the vapor phase or perhaps even as a solid at lower temperatures and higher chlorine pressures." Except for $MnCl_4$, the discussion refers to the highest chlorides stable at room temperature with no excess chlorine gas present. They are, in all the cases cited, the highest known chlorides under any condition thus far studied.

[18] Ref. 12, pp. 1301–1302.

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Complexes Formed between Copper(II) Ion and N,N,N',N'-Tetrakis-(2-hydroxypropyl)-ethylenediamine[1,2]

BY JAMES L. HALL, F. ROBERT JONES,[3] C. EUGENE DELCHAMPS AND CHARLES W. MCWILLIAMS[3]

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The compound N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, "Quadrol" (abbreviated "Q"), reacts with copper(II) ion in aqueous solution to form the complex ion CuQ^{+2}. This ion reacts further with Quadrol to form $Cu(Q-H^+)^{+1}$, and reacts with strong base to form successively, $Cu(Q-H^+)^{+1}$ and $Cu(Q-2H^+)^0$. The ions CuQ^{+2} and $Cu(Q-H^+)^{+1}$ have distinctly different absorption maxima in the vicinity of 700 mμ in the visible region but the two have nearly identical absorption maxima at about 280 mμ in the ultraviolet region. The ion CuQ^{+2} may be considered as a dibasic acid in solution and as such gives successive dissociation constants of 1.41×10^{-7} and 8.92×10^{-9}. The formation constant for formation of CuQ^{+2} from Cu^{+2} and Q is of the order of 10^9.

Introduction

This paper reports a study of the complexes of copper(II) ion with the compound N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, "Quadrol" (abbreviated "Q"), with and without additional strong base added to the solutions. In the Quadrol molecule the nitrogen atoms and the hydroxyl radicals are in favorable position for the formation of stable five-membered chelate rings. The hydroxyl radicals of the Quadrol have nearly negligible acidic properties in solution in water but become appreciably acidic whenever the hydroxyl radical becomes a part of the chelate ring. These complexes have been investigated in aqueous solution by spectrophotometric methods and by potentiometric and conductometric titrations.

Experimental

The Quadrol was a gift of the Wyandotte Chemicals Corporation, and was designated as being at least 99.5% pure, the principal impurity being water. It was used without further purification. The concentration of the solutions as determined by titration with acid corresponded very closely to the concentration calculated from the weight of Quadrol used. The pure Quadrol and its dilute solutions are quite stable toward change on contact with the atmosphere. An 0.5 *M* solution, stored in contact with air, developed a slight yellow color after a few months.

Carbonate-free sodium hydroxide solutions and solutions of hydrochloric, nitric and perchloric acids were prepared from reagent-grade stock and were standardized by the usual methods. Sodium perchlorate was prepared by neutraliza-

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[1] The work upon which this paper is based was sponsored, in part, by the Office of Ordnance Research, U. S. Army.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, Sept. 17 to 21, 1956.

[3] Abstracted, in part, from M.S. theses presented at West Virginia University by Charles W. McWilliams, 1955, and F. Robert Jones, 1956.

tion of perchloric acid. Copper(II) perchlorate solutions were prepared from G. F. Smith Co. reagent or from basic copper carbonate as described previously.[4] The copper(II) perchlorate solutions were standardized by titration with disodium Versenate.[5]

The spectral data were obtained with a Beckman Model DU spectrophotometer, using 1 cm. matched silica cells. The solutions for spectrophotometric studies were made up to a constant ionic strength of 0.5 by addition of $NaClO_4$. Conductometric titrations were performed using a highly precise conductance bridge built around the Leeds and Northrup Co. No. 1553 ratio box.[5] A dip-type cell with a cell constant of approximately 0.1 was used. The potentiometric titrations were performed with a Beckman Model H-2 *p*H meter with appropriate calomel and glass electrodes. For all potentiometric and conductometric titrations the temperature was maintained constant at 25 ± 0.02°. The solutions for potentiometric titrations were made 0.5 *M* in KNO_3.

Results

Complexes Identified.—The complexes identified are believed to have the formulas CuQ^{+2}, $Cu(Q-H^+)^{+1}$ and $Cu(Q-2H^+)^0$. The first of these is believed to have the four coördination positions of the copper(II) ion occupied by the two nitrogen atoms and two oxygen atoms of the Quadrol, forming three five-membered chelate rings. The other two complexes have had removed one and two protons, respectively, from the two coördinated oxygen atoms of the first-formed complex.

Spectrophotometric Work.—Figure 1 shows the spectra in the visible region of solutions 0.005 *M* in copper(II) ion and containing varying amounts of Quadrol. The intermediate position of the 1:05 (Cu^{+2}:Q) curve midway between the 1:0 and 1:1 curves indicates that there is no complex of ratio less than 1:1. The intersection of the 1:1 and 1:2 curves near 850 mμ and the near coincidence of the 1:2, 1:3 and 1:4 curves strongly suggests that 1:1 and 1:2 complexes exist in these solutions. A series of solutions of various ratios of copper(II) ion to Quadrol was prepared at a constant total concentration of 0.005 *M*. Their spectra were determined and analyzed by the method of Vosburgh and Cooper.[6] The Y and Y′ curves at 850 and 675 mμ are shown in Fig. 2. Reaction of copper(II) ion with one and two moles of Quadrol is thus indicated.

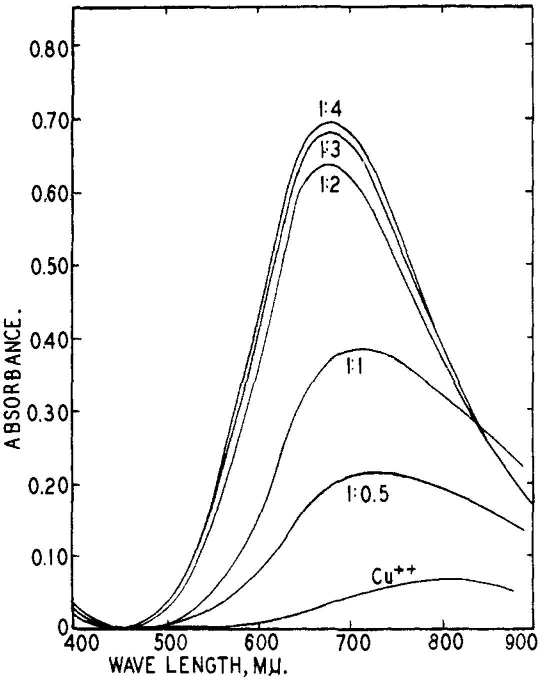

Fig. 1.—Absorption spectra of solutions 0.005 *M* in $Cu(ClO_4)_2$ with varying amounts of quadrol.

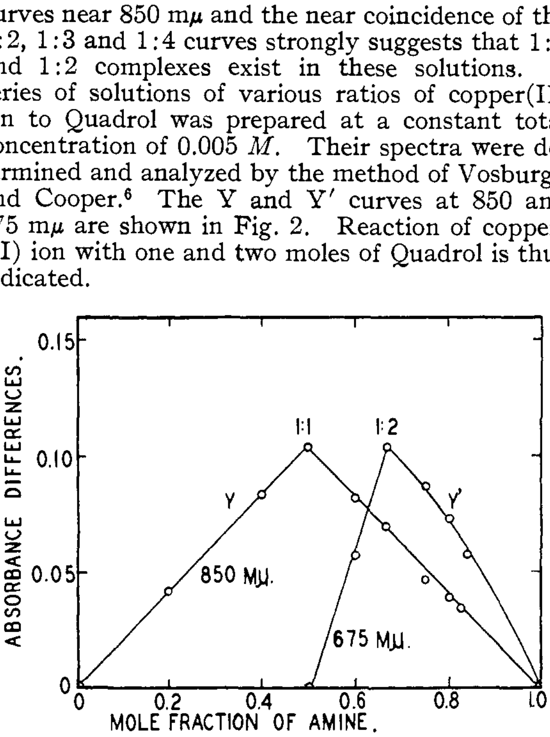

Fig. 2.—Derived absorbance curves for the copper(II) ion-quadrol system at 850 and 675 mμ.

In addition to the absorption maximum near 675 mμ, these copper(II) ion–Quadrol solutions show a second and much more intense absorption at about 280 mμ. Absorption curves for solutions 0.00025 *M* in copper(II) ion with varying amounts of Quadrol are shown in Fig. 3. In contrast to the results in the visible part of the spectrum, these curves show definite indication of only one complex with a Cu^{+2}:Q ratio of 1:1. Spectra were obtained for a series of solutions of constant total composition, copper(II) ion plus Quadrol, of 0.0005 *M*, and these data were analyzed by the method of continuous variations. At any wave

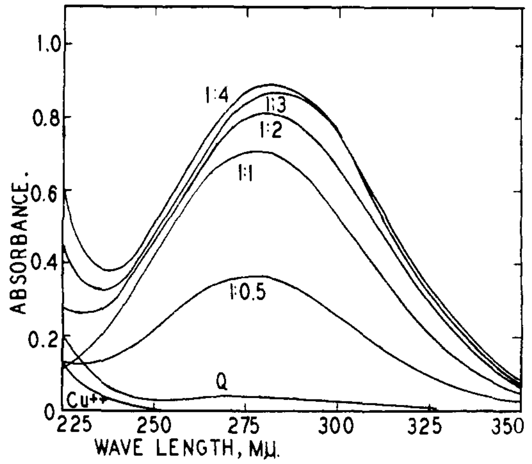

Fig. 3.—Absorption spectra of solutions 0.00025 *M* in $Cu(ClO_4)_2$ with varying amounts of Quadrol.

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[4] J. M. Bolling and J. L. Hall, This Journal, **75**, 3953 (1953).

[5] J. L. Hall, J. A. Gibson, Jr., P. R. Wilkinson and H. O. Phillips, *Anal. Chem.*, **26**, 1484 (1954).

[6] W. C. Vosburgh and G. R. Cooper, This Journal, **63**, 437 (1941).

length in the vicinity of the maximum of absorption a Y curve was obtained with a simple sharp maximum showing the 1:1 complex and giving no indication of any other complex.

The small increase in absorbance at the maximum, beyond the 1:2 ratio in the visible region and beyond the 1:1 ratio in the ultraviolet region was attributed to reaction of the complex with base formed by the additional Quadrol in solution. To further study this question, spectra were determined for solutions having a copper(II) ion concentration of 0.005 *M* and to which Quadrol and sodium hydroxide had been added to obtain final solutions with Cu^{+2}:A:OH^- ratios of 1:1:0, 1:2:0, 1:1:1, 1:2:1, 1:1:2 and 1:2:2. These are shown in Fig. 4. The near identity of the spectra of the 1:2:0 and 1:1:1 solutions indicates that these both contain the complex $Cu(Q-H^+)^{+1}$. The near identity of the spectra of the 1:1:2 and 1:2:2 solutions suggests that these both contain the complex $Cu(Q-2H^+)^0$.

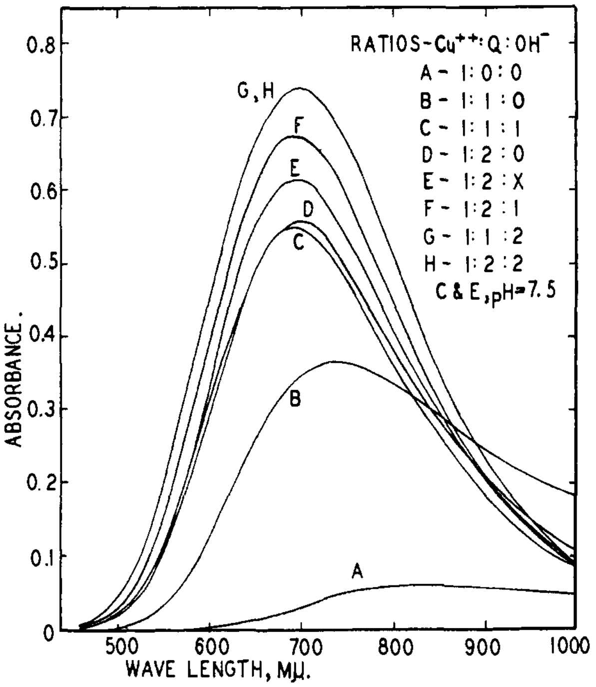

Fig. 4.—Absorption spectra of solutions made by mixing copper(II) perchlorate, Quadrol and sodium hydroxide in various ratios.

Potentiometric Titrations.—Figure 5 shows the results of addition of 1.0097 *M* sodium hydroxide solution to solutions initially 0.5 *M* in KNO_3, 0.01 *M* in Quadrol, 0.03 *M* in HNO_3, and with solution A containing no copper(II) ion, solution B being 0.005 *M* in $Cu(ClO_4)_2$, and solution C being 0.01 *M* in $Cu(ClO_4)_2$. At corresponding values of *p*H, curve B is nearly midway between curves A and C, indicating that the complex formed in these solutions contains only one mole of Quadrol per mole of copper(II) ion. After neutralization of the excess acid in addition to that required to form the amine salt, curve C, for the solution containing Cu^{+2} and Q in the ratio 1:1, shows definite end points corresponding to 2, 3 and 4 moles of hydroxyl ion.

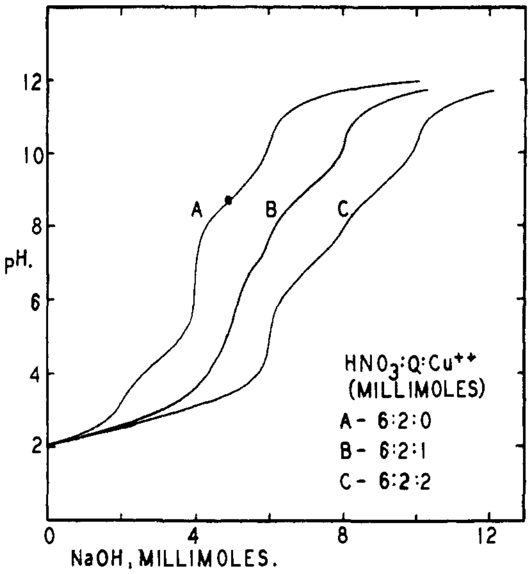

Fig. 5.—Titration of acid-Quadrol and acid-Quadrol-copper(II) ion mixtures with sodium hydroxide.

Conductometric Titrations.—The addition of Quadrol to copper(II) perchlorate solution was studied conductometrically. Quadrol solution, 0.1005 *M*, was added to a solution 0.00493 *M* in copper(II) perchlorate. The conductance decreased throughout. The plot of conductance as a function of the mole ratio of Quadrol added showed three straight-line segments, with decreasing slope, and with distinct breaks corresponding to 1 and 2 moles of Quadrol per mole of copper(II) ion. The decrease of conductance to the first break is due to the decreased mobility of the copper(II) ion as its size is increased by addition of the ligand. The further decrease to the second break is due to a reduction in the charge of the complex ion from +2 to +1.

A conductometric titration was performed by adding 0.4653 *M* sodium hydroxide to a solution made 0.00493 *M* in both copper(II) perchlorate and Quadrol. The results are shown in Fig. 6.

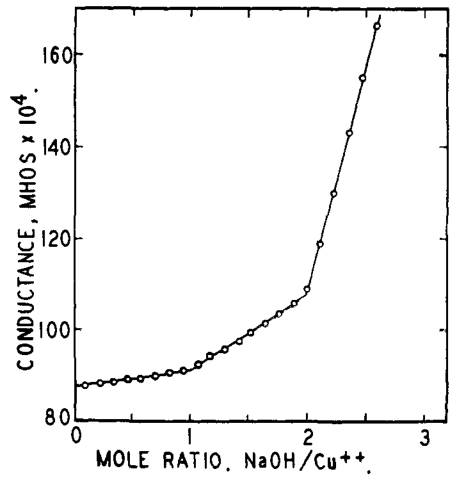

Fig. 6.—Conductometric titration of a solution 0.00493 *M* in CuQ^{+2} with 0.4653 *M* NaOH.

The first two straight-line segments of the curve represent the neutralization of the two hydrogen atoms of the two coördinated hydroxyl radicals of the CuQ^{+2} complex. Beyond the second break the regular increase in conductance is due to the increase in sodium hydroxide concentration. A similar titration with the initial solution having Cu^{+2} and Q in the ratio 1:2 produced only one end-point at 2 moles of NaOH per Cu^{+2} ion.

The titration of mixtures of Quadrol and sodium hydroxide with copper(II) perchlorate produced very interesting results. A solution 0.00493 *M* in Quadrol and 0.00985 *M* in sodium hydroxide (1:2 ratio) was titrated with 0.0985 *M* copper(II) perchlorate. The results of this titration are plotted in Fig. 7. The first segment, with the end-point at the end of the rounded section, corresponds to the formation of the compound $Cu(Q\text{-}2H^+)$.[6] The second segment, of increasing conductance, is accompanied by the formation of a precipitate and the length of the segment indicates the reaction of one mole of copper(II) ion for each two moles of $Cu(Q\text{-}2H^+)^0$ in the solution. The precipitate was judged to be $Cu(OH)_2$, and this was confirmed. A portion of the precipitate was separated by filtration, washed, dried and analyzed for copper. The dried precipitate was copper(II) oxide. Other titrations were performed by addition of copper(II) perchlorate to solutions for which the Quadrol–NaOH ratio was 1:3 and greater. For these solutions an additional amount of $Cu(OH)_2$ was formed corresponding to the excess of hydroxyl ion over the 1:2 ratio in the initial solution.

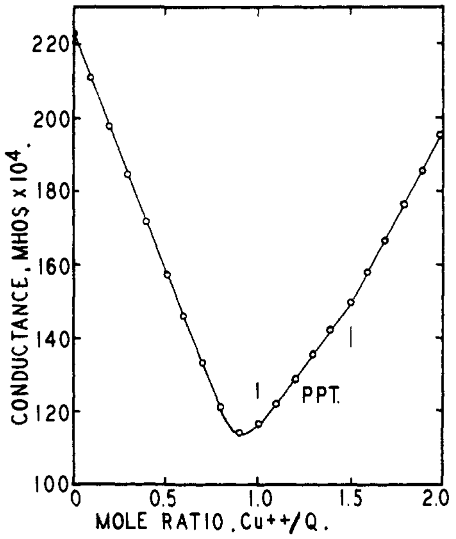

Fig. 7.—Conductometric titration of a solution 0.00493 *M* in Quadrol and 0.00985 *M* in NaOH with 0.0985 *M* $Cu(ClO_4)_2$.

Discussion

The initial results of the spectrophotometric studies were misleading in that complexes of copper(II) ion and Quadrol were indicated in 1:1 and 1:2 ratios. The spectra of the solutions containing added sodium hydroxide and the titration curves show that the second molecule of Quadrol serves as a base to neutralize a hydrogen atom from one of the two coördinated hydroxyl radicals of the first Quadrol molecule. The successive acid ionization constants of the two acidic hydrogen atoms of the complex and the dissociation constants of the QH_2^{+2} ion are such that the second hydrogen atom of the complex is only partially neutralized in solutions containing a considerable excess of Quadrol. If sodium hydroxide is added to any solution containing copper(II) ion and an equivalent or greater amount of Quadrol, an end-point is always obtained at the ratio of two equivalents of hydroxyl ion per mole of copper(II) ion. The reactions which take place in the various solutions may be written as follows where OH^- represents hydroxyl ion from sodium hydroxide.

$$CuQ^{+2} + Q \longrightarrow Cu(Q\text{-}H^+)^{+1} + QH^+$$

$$Cu(Q\text{-}H^+)^{+1} + OH^- \longrightarrow Cu(Q\text{-}2H^+)^0 + H_2O$$

$$CuQ^{+2} + 2OH^- \longrightarrow Cu(Q\text{-}2H^+)^0 + 2H_2O$$

$$QH^+ + OH^- \longrightarrow Q + H_2O$$

It is interesting that the spectra in the visible region give evidence for the successive reaction of one and two moles of Quadrol with copper(II) ion while the spectra in the ultraviolet region give evidence for the combination of only one mole. It seems that the visible spectrum is more directly concerned with the copper–oxygen links in the chelate ring and the loss of the proton shifts the absorption due to these links to lower wave lengths.

Some useful information may be obtained from the potentiometric titration data shown in Fig. 5. If we consider the complex CuQ^{+2} as a dibasic acid, the two successive ionization constants may be calculated from the mid-points of the last two steps of the titration curve. These values are 1.41×10^{-7} and 8.92×10^{-9} for the first and second acid dissociation constants, respectively. The acid dissociation constants of the QH_2^{+2} ion were calculated from the mid-points of the steps of curve A giving values of 4.67×10^{-5} and 1.45×10^{-9} for K_1 and K_2, respectively. These values have been verified by a series of determinations over a range of *p*H values using the method of Bjerrum.[7]

The very distinct rise of *p*H after addition of two equivalents of hydroxyl ion to the Cu^{+2} and QH_2^{+2} mixture indicates that the formation of CuQ^{+2} ion is essentially complete before neutralization of the hydrogen atoms of the bound hydroxyl radicals is begun. One should then be able to calculate a stability constant for the formation of CuQ^{+2} from Cu^{+2} and Q by the method of Bjerrum.[7] Values of [Q] and $\bar{n}$ were calculated for the interval *p*H 2.3 to 5 and the corresponding values of *K* were determined. The value of *K* is approximately 2.9×10^9 if $\bar{n}$ is between 0.2 and 0.5. The values of *K* decrease outside this range.

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