[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS]

A Preparative Study of the Reaction between Copper(II) Chloride and Amine Hydrochlorides

BY ROGER D. WHEALY, D. H. BIER AND B. J. MCCORMICK

RECEIVED JUNE 22, 1959

Bis-methylammoniumtetrachlorocuprate(II), bis-dimethylammoniumtetrachlorocuprate(II), bis-ethylammoniumtetrachlorocuprate(II), bis-triethylammoniumtetrachlorocuprate(II), bis-*n*-butylammoniumtetrachlorocuprate(III), bis-isobutylammoniumtetrachlorocuprate(II) and 1,6-hexane-di-ammoniumtetrachlorocuprate(II) were prepared in relatively high purity. Some of the physical properties of these compounds were observed.

Introduction

The existence of trichlorocuprate(II) and tetrachlorocuprate(II) ions in solution has been proven by a number of physical methods. Moeller[1] studied the absorption spectra of copper(II) salt solutions with varying chloride concentrations and showed the presence of tetrachlorocuprate(II) ions. Rossi and Strocchi[2] determined the conductivity of copper(II) chloride solutions with varying amounts of hydrogen chloride and interpreted their results to indicate the presence of both trichloro and tetrachlorocuprate(II) ions. Asmus and Reich[3] made refractometric measurements of aqueous solutions of copper(II) chloride with varying amounts of NaCl, KCl, NH_4Cl or HCl. They concluded their results indicated the presence of both the trichloro- and tetrachlorocuprate(II) ions. Helmholtz and Kruh[4] prepared lithium tetrachlorocuprate(II) and studied the crystal structure of the solid and the absorption spectra of both the solid and aqueous solutions. The absorption spectrum of the solid was quite different from the absorption spectra of the solutions and they interpreted this as evidence of at least partial dissociation of the tetrachlorocuprate complex ion in solution. Dehn[5] reported the preparation of bis-quinoliniumtetrachlorocuprate(II) in aqueous solution by combining stoichiometric amounts of quinoline hydrochloride and cupric chloride and evaporating to a small volume. Remy and Laves[6] reported the preparation of bismethylammoniumtetrachlorocuprate(II), bis-dimethylammoniumtetrachlorocuprate(II), bis-ethylammoniumtetrachlorocuprate(II) and bis-butylammoniumtetrachlorocuprate(II) by a similar method. Our attempts to make this type of compound in aqueous solution always gave a poor yield of rather impure product so this study was initiated to develop a superior method of preparing these compounds.

Materials.—The amines and the amine hydrochlorides were all white-label Eastman chemicals and were used without further purification. Reagent grade cupric chloride dihydrate was converted to the anhydrous product by heating to 120°. All solvents were reagent grade.

Procedure.—Stoichiometric amounts of the dry amine hydrochloride and anhydrous cupric chloride were dissolved separately in a minimum amount of hot methanol. The dissolution of the amine hydrochlorides in methanol is an endothermic process. The rate of dissolution is increased and the volume of methanol reduced by using hot methanol. The solutions are cooled in an ice-bath and each portion is saturated with anhydrous hydrogen chloride. The solutions are then poured together with vigorous stirring. Precipitation occurs immediately in some cases but others require the addition of diethyl ether. The yield is largely governed by the amount of diethyl ether used to salt out the product. Yields of 70 to 90% can be obtained by the use of relatively large amounts of diethyl ether. The precipitate was separated by rapid filtration through a coarse sintered glass crucible. It was first washed by a solution of diethyl ether (80% by volume) and acetone and finally by pure diethyl ether. The precipitate then was dried in a vacuum desiccator. The introduction of water at any stage in the preparation tends to decompose the desired compound. The solid product seems in some cases to be especially susceptible to decomposition, so the filtration and washing should be done rapidly to avoid reaction with atmospheric moisture.

Analytical Procedure and Results

Samples of each of the compounds were dissolved in a few milliliters of a mixture of concentrated nitric and sulfuric acid. The organic material is oxidized rapidly and the solutions are heated until fumes of sulfur trioxide are given off. This removes all of the carbon dioxide, nitric acid and hydrochloric acid. They were then diluted and the copper determined by electrodeposition on platinum electrodes. Separate samples of each compound were dissolved in water and the chloride was titrated with standard silver nitrate solution. The end-point was determined potentiometrically using a silver indicating electrode and a mercury–mercurous sulfate reference electrode. The results of the analysis are shown in Table I.

Physical Properties of the Compounds.—The compounds are all golden yellow in color and most of them form thin plates which are similar in appearance to small particles of gold leaf. These compounds are all very soluble in water, but the complex ion is apparently always decomposed when they are dissolved in water. They are quite soluble in methanol, ethanol and acetone, somewhat less soluble in isopropyl alcohol and only slightly soluble in diethyl ether. Their solubility seems to be directly proportional to the dielectric constant of the solvent. Absorption spectral studies indicate that the tetrachlorocuprate ion is partially decomposed in the dissolution process. The solvent molecule acts as a Lewis base and displaces one or more chloride ions from the complex ion. This seems to be an equilibrium process and the tetrachlorocuprate ion can be reproduced by saturating the solvent with anhydrous hydrogen chloride. The compounds are practically insoluble in benzene, chloroform and carbon tetrachloride. They may be recrystallized from an 80% (by volume) diethyl ether–acetone solution which is saturated with anhydrous hydrogen chloride. They all seem to decompose at temperatures below their melting points and most of them cannot be dried at 105° because of decomposition. The ab-

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[1] T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944).

[2] G. Rossi and P. M. Strocchi, *Gazz. chim. Ital.*, **78**, 725 (1949).

[3] E. Asmus and J. G. Reich, *Angew. Chem.*, **61**, 208 (1949).

[4] L. Helmholtz and F. Kruh, THIS JOURNAL, **74**, 1176 (1952).

[5] William M. Dehn, *ibid.*, **48**, 111 (1926).

[6] H. Remy and G. Laves, *Ber.*, **66B**, 401 (1933).

TABLE I

Compound	Copper, % Theoretical	Copper, % Found	Chloride, % Theoretical	Chloride, % Found
Bis-methylammoniumtetrachlorocuprate(II)	23.58	23.50 ± 0.06	52.63	52.50 ± 0.10
Bis-dimethylammoniumtetrachlorocuprate(II)	21.35	21.18 ± .06	47.65	47.28 ± .10
Bis-trimethylammoniumtetrachlorocuprate(II)	19.51	19.53 ± .08	43.56	43.50 ± .12
Bis-tetramethylammoniumtetrachlorocuprate(II)	17.97	17.97 ± .06	40.09	39.90 ± .12
Bis-ethylammoniumtetrachlorocuprate(II)	21.35	21.26 ± .07	47.65	47.66 ± .09
Bis-triethylammoniumtetrachlorocuprate(II)	15.53	15.51 ± .08	34.66	35.68 ± .10
Bis-*n*-butylammoniumtetrachlorocuprate(II)	17.97	17.84 ± .07	40.09	40.15 ± .12
Bis-isobutylammoniumtetrachlorocuprate(II)	17.97	17.94 ± .08	40.09	40.00 ± .12
1,6-Hexane-di-ammoniumtetrachlorocuprate(II)	19.95	20.13 ± .08	43.81	44.22 ± .10

sorption spectra of these compounds give some rather unusual results. The spectra are quite different in methanol, acetone and isopropyl alcohol, indicating the compounds are reacting with the solvent.

COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polarographic and Solubility Studies on Mercuric Oxycyanide[1]

BY LEONARD NEWMAN AND DAVID N. HUME

RECEIVED JANUARY 19, 1959

Studies on the solubility of mercuric oxide in aqueous mercuric cyanide solutions indicate the product to be HgOHCN. The equilibrium constant, K_m, of the reaction $Hg(CN)_2 + Hg(OH)_2 = 2HgOHCN$ was found to be 260 at 23° and an ionic strength of 2.0 by this method. Polarographic reduction of mercuric oxycyanide solution gave a value of 280 for K_m. The dissociation constant of mercuric hydroxide, measured polarographically, was found to be 4.0×10^{-22}. The formation constant of mercuric hydroxycyanide is 7.3×10^{28}.

Introduction

Mercuric cyanide solutions have long been known to dissolve significant amounts of mercuric oxide,[2] and from these solutions solid mercuric oxycyanide, usually written $HgO \cdot Hg(CN)_2$, can be obtained. Friend[3] gives numerous references on the preparation and reactions of the solid, which has been used extensively in pharmacy. Little or nothing appears to have been done about determining the properties of the compound in solution other than some early cryoscopic studies[4] and the present investigation deals with this problem.

Materials and Methods

All the chemicals were of reagent grade and deionized distilled water was employed throughout. The mercuric oxide was Mallinckrodt "mercuric oxide, yellow." Solubility studies were carried out by shaking mercuric oxide in excess with mercuric cyanide solutions for five days in a constant temperature room. Total dissolved mercury was determined by pipetting an aliquot into 50 ml. of a mixture containing 0.2 *M* sodium cyanide, 1.8 *M* sodium nitrate and 0.008% gelatin. The *p*H of this mixture was 11.5. The sample then was made up to 100 ml. with 2.0 *M* sodium nitrate for measurement of the diffusion current of mercury. Under these conditions, the diffusion current is linear with mercury concentration and independent of small changes in cyanide ion concentration. Polarographic measurements were carried out using the apparatus and technique described in a previous communication.[5]

Solubility Studies.—Excess mercuric oxide was shaken at 23° for five days with 2 *M* sodium nitrate solutions containing various known concentrations of mercuric cyanide. The *p*H before and after shaking was approximately 6.5. Filtered samples were taken for polarographic analysis. The time allowed was found to be more than sufficient to attain equilibrium. The results are summarized in Table I.

TABLE I

SOLUBILITY OF HgO IN $Hg(CN)_2$ SOLUTIONS, 2.0 *M* IN $NaNO_3$[a]

a	*t*	*a* − *x*	*x*
0	0.39	..	..
1.00	2.35	0.04	0.96
2.00	4.22	.17	1.83
5.00	9.57	.82	4.18
10.0	18.2	2.18	7.82
50.0	77.2	23.2	26.8

[a] All concentrations in millimoles per liter. *a* = initial concentration of $Hg(CN)_2$, *t* = total concentration of Hg(II) in equilibrium mixture, *a* − *x* = concentration of free $Hg(CN)_2$ at equilibrium, *x* = formal concentration of $HgO \cdot Hg(CN)_2$ at equilibrium.

The simplest equation which can be written for the reaction is

$$HgO(s) + Hg(CN)_2 \longrightarrow HgO \cdot Hg(CN)_2 \quad (1)$$

assuming that the reactants combine in a ratio of 1:1. This assumption is in accord with the composition of the solid product which can be obtained by evaporation and it was found that the data do not fit other assumptions such as 1:2 or 2:1 combining ratios. If *a* is the initial concentration of mercuric cyanide and *x* is the formal concentration of the product, $(a - x)$ becomes the equilibrium concentration of mercuric cyanide. The total analytical concentration of mercury in solution, *t*, if corrected for the solubility of mercuric oxide in the absence of mercuric cyanide may be designated t', which is then seen to be $t' = (a - x) + 2x = (a + x)$. Thus *x* is readily determinable from the known values of *a*, the solubility of mercuric oxide and the corresponding measured values of *t*. If dissolved mercuric oxy-

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[1] Taken in part from the Ph.D. Thesis of Leonard Newman, Massachusetts Institute of Technology, June, 1956. This work was supported in part by the Atomic Energy Commission under Contract AT(30-1)905.

[2] J. F. W. Johnston, *Phil. Trans.*, 113 (1839).

[3] J. Newton Friend, "A Textbook of Inorganic Chemistry," Vol. III, Part 2, Griffin and Co., London, 1926.

[4] K. Holdermann, *Arch. Pharm.*, **244**, 133 (1906).

[5] L. Newman, J. deO. Cabral and D. N. Hume, THIS JOURNAL, **80**, 1814 (1958).