Solutions initially containing added NaOH required about the same time for the initial precipitation which was, however, more nearly complete. The product exhibited poorer crystallinity, as judged by powder X-ray diffraction patterns.

The solid forms irregular platelets of various colors and possessing metallic luster. It is extremely inert to cold acids, bases and complexing agents, but is oxidized slowly by boiling 4 M $HClO_4$ and by air when in fused Na_2CO_3. Boiling concentrated sulfuric acid slowly converts it to an inert solid which gives an X-ray pattern different from that of the original solid.

The solid from the refluxed solutions was dried at 100° and analyzed for chromium. The result led to the composition $Cr_2O_3 \cdot 1.7H_2O$. Further dehydration to approximately $Cr_2O_3 \cdot 1.2H_2O$ was effected by heating to 300° in a nitrogen atmosphere. Powder X-ray photographs of both the freshly filtered product and the material dried at 300° gave the same pattern, by which it was possible to establish that the bulk (crystalline portion) of the product is identical to the compound designated by Laubengayer and McCune as CrOOH,[10] and by Thamer, Douglass and Staritzky as $HCrO_2$.[11]

(10) A. W. Laubengayer and H. W. McCune, This Journal, **74**, 2362 (1952).

(11) B. J. Thamer, R. M. Douglass and E. Staritzky, ibid., **79**, 547 (1957).

The previous preparations employed hydrothermal methods at temperatures above 300°. Douglass recently has reported the structure to consist of distorted CrO_6 octohedra, each sharing six edges with six surrounding coplanar octahedra to form continuous sheets. The sheets are stacked so that oxygens of adjacent sheets are exactly superposed; hydrogens presumably lie midway between.[12]

In an attempt to determine the composition of refluxed solutions at equilibrium, a solution initially 0.05 M in $Cr(ClO_4)_3$ was refluxed for 30 months. After this time, the chromium remaining in solution was found to be 2×10^{-3} M. Refluxing of the solid product with 1.0 M $HClO_4$ for one year produced a solution that was but 4×10^{-3} M in chromium, as $Cr(H_2O)_6^{+3}$.[13] Thus, it seems that in acid solution at 100°, neither hexaquochromic ion nor its soluble polynuclear derivatives are stable with respect to formation of $HCrO_2$.

[Contribution from the Kedzie Chemical Laboratory, Michigan State University]

Hexacoördinate Copper(II) in Trisethylenediaminecopper(II) Sulfate

By Gilbert Gordon and Ralph K. Birdwhistell

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Evidence is offered for the existence of hexacoördinate copper(II) in its trisethylenediaminecopper(II) sulfate complexes. Studies of the infrared spectra of these and related compounds indicate that no free amine is present. Analytical data and visible absorption spectra are given. These data and optical rotation studies can be used in support of an octahedral structure. Clarification in procedures for the preparation of diaquomonoethylenediaminecopper(II) sulfate, bisethylenediaminecopper(II) sulfate and trisethylenediaminecopper(II) sulfate is given.

Introduction

Several recent papers[1-3] demonstrate that copper (II) can have coördination greater than four. The present paper offers evidence for the existence and the preparation of hexacoördinate copper (II) in the form of the trisethylenediaminecopper (II) sulfate.

Due to some inconsistences in the literature,[4-6] we attempted to clarify the preparation of bisaquoethylenediaminecopper(II) sulfate and bisethylenediaminecopper(II) sulfate (anhydrous).

Experimental

Reagents.—Eastman White Label ethylenediamine was purified using standard techniques (b.p. 117°, lit. b.p. ethylenediamine monohydrate 118°). Baker Analyzed Re-

agent copper sulfate pentahydrate was used without further purification.

The copper(II) content was determined by the method of Vogel.[7] The sulfate concentrations were determined using standard procedure.[8] Carbon, hydrogen and nitrogen were determined on all samples by Spang Microanalytical Lab., Ann Arbor, Michigan. The nitrogen was also checked by Kjeldahl determinations.

Infrared spectra were recorded on a Perkin–Elmer recording spectrophotometer, Model 21.

Visible spectra were run on a Beckman recording spectrophotometer, Model DK-2, with one cm. silica cells.

Optical rotation studies were carried out using a Schmidt polarimeter with a mercury lamp and Farrand interference filter (which removed all wave lengths except the mercury 435.835 mμ line). The light path was one dm.

Preparation of Bisaquoethylenediaminecopper(II) Sulfate (I).—$CuSO_4 \cdot 5H_2O$ and ethylenediamine were mixed in a mole ratio of 1:1 with enough water to make an approximately 1 M solution. A blue solution was formed. Addition of 5 volumes of 95% EtOH resulted in a light blue precipitate. This precipitate was washed with EtOH and Et_2O. The precipitate was placed in a desiccator and dried in vacuo for 24 hr.

(1) S. Kirschner, This Journal, **78**, 2372 (1956).

(2) H. B. Jonassen, R. E. Reeves and L. Segal, ibid., **77**, 2668 (1955).

(3) F. Basolo, Y. T. Chen and R. K. Murmann, ibid., **76**, 956 (1954).

(4) W. Wahl, Soc. Sci. Fennica Commentations Phys. Math., **4**, (14), 1 (1927); C. A., **22**, 3596 (1928).

(5) C. H. Johnson and S. A. Bryant, J. Chem. Soc., **6**, 1338 (1945).

(6) J. J. Fritz, R. Rao and S. Seki, J. Phys. Chem., **62**, 703 (1958).

(7) A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1953, p. 433.

(8) A. I. Vogel, ref. 7, pp. 400, 404, 499.

TABLE I

Compound	I		II		III		IV	
Formula	CuenSO$_4$·2H$_2$O		Cu(en)$_2$SO$_4$		Cu(en)$_3$SO$_4$		Cu(en)$_3$SO$_4$·H$_2$O	
Mol. wt.	255.75		279.81		339.91		357.93	
% compn.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
Cu	25.1	24.84	22.78	22.71	18.71	18.69	17.80	17.75
SO$_4$	37.6	37.56	34.3	34.33	28.45	28.26	27.0	26.84
C	..	9.4	17.3	17.2	21.5	21.2	20.5	20.1
H	..	4.7	5.77	5.8	7.08	7.1	7.35	7.3
N	9.8	10.94	20.2	19.7	24.8	24.7	23.6	23.5

Preparation of Bisethylenediaminecopper(II) Sulfate (II). —1:2 mole ratio of reactants were treated as above and then, with the addition of five volumes of 95% EtOH, a deep-purple precipitate was formed which was washed with EtOH and Et$_2$O. This precipitate was dried as above.

Preparation of Trisethylenediaminecopper(II) Sulfate (III).—1:6 mole ratio of the reactants were treated as above and a sparingly soluble precipitate was formed. The precipitate was sucked dry on a buchner funnel and then washed with Et$_2$O. It was placed next in a desiccator and dried in vacuo for 24 hr. Any attempt to wash the precipitate with EtOH or similar solvents resulted in conversion to compound II.

Preparation of Trisethylenediaminecopper(II) Sulfate Monohydrate (IV).—If the solution used in making compound III was evaporated slowly over a steam-bath, a deep blue crystalline solid separated. This solid was washed with Et$_2$O and allowed to air dry.

In spite of numerous attempts to prepare the dihydrate or the tetrahydrate (reported by Fritz[6]), we were unable to obtain anything but pure II or a mixture of II and III. Further, all attempts to prepare crystalline II by slow evaporation failed completely due to its extreme solubility.

Results and Discussion

Table I shows the four compounds formed, the probable formulas and both experimental and theoretical composition.

The solubility and related phenomena which were observed can be explained by use of equilibrium constants described in "Stability Constants."[9]

A comparison of the infrared spectra of samples of pure ethylenediamine and the tris complex was made. These samples were mulled in mineral oil or hexachlorobutadiene. The spectrum of the free base, ethylenediamine, shows two absorption peaks in the –NH$_2$ region, one at 3510 cm.$^{-1}$ and another at 1595 cm.$^{-1}$, both indicating uncoordinated secondary amine groups. Whereas in the spectrum for the complex, the –NH$_2$ band occurs at 3230 and 1620 cm.$^{-1}$. This shift can be interpreted to be due to the coördination of the amino groups.[1] The sharp peaks found further indicate that all of the groups are alike and therefore coördinated. The shift of the 3500 cm.$^{-1}$ peak to a lower frequency is indicative of an increase in electron localization of the –NH$_2$ group upon coördination, as was noted by Kirschner.[1]

The structure of III or IV could be either trigonalbipyramid (pentacoördinate)[10,11] or octahedral (hexacoördinate).[12] In either case, an assymetrical center could exist at the central atom.

Optical activity alone would not preclude other degrees of covalency in the complex. Large crystals of the Cu(en)$_3$SO$_4$·H$_2$O complex were grown from an 80% solution of ethylenediamine. Observation of these crystals under a microscope indicated that two different crystalline forms might be present. These were separated. Due to the intense color of the bisethylenediaminecopper(II) sulfate, the rapid dissociation of the trisethylenediamine complex and the insolubility of the tris complex in anhydrous ethylenediamine, the measurements were made as follows. A single crystal of compound IV was added to pure ethylenediamine in the polarimeter cell with subsequent small additions of water until dissolution occurred. The very wide absorption peaks at 546 mμ for the bis and 647 mμ for the tris forced the use of the 435.835 mμ line of Hg. Repeatedly, the authors were able to detect 2 to 3 degrees of rotation (± depending upon the crystal used). Racemization was complete in about five minutes and again zero rotation was observed. The solvent gave zero rotation when treated as above.

Absorption studies of the tris complex were made in 80 wt. % ethylenediamine. This concentration was necessary to maintain a measurable amount of undissociated tris complex in solution. Optical density measurements for all three complexes were made over the range of 320 to 900 mμ. The absorption maxima that occur in the visible region for the various complexes are given in Table II.

TABLE II

	λ$_{o.d.}$ max.	λ$_{lit.}$
I	652	652[2,13,14]
II	546	546[2,13,14]
III	647	Unreported
IV	635	635[2,14]

In earlier papers, J. Bjerrum[10] maintained that insufficient evidence was available to postulate hexacoördination. He has now shown[12] that the spectra of the ammonia complexes of copper(II) ions in aqueous solution can be explained by assuming a planar configuration with two more-distant neighbors perpendicular to the plane. The shift of the absorption maxima to the blue when going from II to III is in agreement with the shift noticed by Bjerrum for the hexammine complex and is further evidence to support the postulate of hexacoördinate copper(II) ion.

(9) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants," Chemical Society, London, 1957, part I, p. 5.

(10) J. Bjerrum and E. J. Nielson, Acta Chem. Scand., 2, 297 (1948).

(11) J. C. Bailar, "Chemistry of Coördination Compounds," Reinhold Publ. Corp., London, 1956, p. 387.

(12) J. Bjerrum, et al., Acta Chim. Scand., 8, 1275 (1954).

(13) H. B. Jonassen, ibid., 8, 2748 (1954).

(14) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, 63, 437 (1941).

It would appear to the authors that trisethylene-diaminecopper(II) sulfate is hexacoördinated in both solid state and in aqueous solutions which are

sufficiently concentrated in ethylenediamine to stabilize the tris complex.

EAST LANSING, MICHIGAN

Coördinating Tendencies of Alkyl Substituted Thioureas in Solvents of Varying Dielectric Constant[1]

BY T. J. LANE, C.S.C., J. W. THOMPSON AND J. A. RYAN

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Polarographic studies of copper(I) and cadmium(II) complexes of thiourea and its methyl-, 1,3-dimethyl-, trimethyl-ethyl- and 1,3-diethyl- homologs were carried out in solvent mixtures of different dielectric constant. Values for the formation constants of copper(I) complexes in aqueous, 50% dioxane–water and 70% dioxane–water mixtures were considered on a relative basis. Formation constants for cadmium complexes in aqueous, 50% ethanol–water and 50% dioxane–water mixtures were determined by the DeFord–Hume method. The order of decreasing stability for the substituted thiourea complexes was: ethyl > diethyl > methyl > dimethyl > trimethyl. The nature of the solvent system affected only the complexes of unsubstituted thiourea.

In a previous paper,[2] polarographic studies of thiourea complexes with cadmium(II) and lead-(II) ions in aqueous media were reported, and the method[3] of DeFord and Hume was applied in the calculation of consecutive formation constants for the respective species existing in solution. As an extension of this work the relative stabilities of various alkyl substituted thiourea complexes with cadmium(II) ion and with copper(I) ion have been determined and a correlation between the nature of the alkyl group on the thiourea ligand and the stability of the resulting complex has been established. Since solvent effects are of interest in coördination processes, an attempt has been made to determine the effects of four solvent systems of varying dielectric constant on the coördinating tendencies of the various ligands.

Experimental

Materials, Apparatus and Solutions.—1-Methyl-2-thiourea, 1-ethyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,3-diethyl-2-thiourea and 1,1,3-trimethyl-2-thiourea were prepared by the method of Moore and Crossley.[4] Thiourea (Eastman Kodak) was recrystallized from 95% ethanol and dried *in vacuo* over sulfuric acid. Reagent grade cadmium nitrate was used without further purification. Other materials and apparatus used are described in a previous paper.[2]

Stability constants for cadmium complexes of the thioureas were measured in three different solvent systems: aqueous, 50% v./v. dioxane–water and 50% v./v. ethanol–water. Each system was 0.1 M in potassium nitrate, 10⁻³ M in cadmium nitrate and 0.004% (% by weight) in Triton X-100.

Three separate solvent systems: aqueous, 50% v./v. dioxane–water and 70% v./v. dioxane–water also were used in the studies of the copper(I) complexes. The aqueous and 50% dioxane systems were 0.1 M in potassium nitrate, 10⁻³ M in crystalline copper(I) complex[5] and 0.004% Triton. The 70% dioxane system was 1.67 M in acetic acid, 0.1 M in sodium acetate, 10⁻³ M in copper(I) complex and 0.004% in Triton. The acetate buffer was used in 70% dioxane solutions since use of potassium nitrate as supporting electrolyte in this solvent system yielded distorted polarographic curves.

The following procedure was used in polarographic analysis of the complexes in each solvent system. Each of the above solvent systems was made 1.0 M with respect to each ligand under study. A 30-ml. aliquot of the 1.0 M ligand solution was transferred to the polarographic cell, deaerated, brought to temperature, and the current voltage curve was recorded. A measured amount of diluent, containing all components of the appropriate solvent system except the ligand itself, was then added to the solution, bringing about a decrease in ligand concentration while the concentrations of metal ion, supporting electrolyte and maximum suppressor remained constant. The diluted solution was deaerated and the current–voltage curve recorded. By repeated application of this method of dilution and subsequent current–voltage measurement, a series of half-wave values and diffusion currents for each metal complex in solutions containing successively smaller known amounts of ligand was obtained. Three separate series of polarographic determinations were made for each ligand with cadmium ion in the solution and for each ligand with copper ion in the solution. Each series differed only with respect to the solvent system employed.

All polarographic measurements were made with a Sargent cell (S-29438). The dioxane used as a solvent component was purified according to the method of Vogel.[6]

Treatment of Data.—The method of DeFord and Hume[3] was used to determine consecutive formation constants when its application was possible. Since the values of the half-wave potential and of the diffusion current for simple cadmium ion in 50% dioxane had to be known for calculation of formation constants, a graphical procedure was employed in their determination. The diffusion currents of the cadmium complexes were plotted against concentration of excess ligand and the curve was extrapolated to zero concentration of ligand. This value for the diffusion current of the simple ion was used in the DeFord–Hume equation for $F_0(X)$, with an arbitrarily assumed value for the half-wave potential of the simple ion. The function $F_0(X)$ was plotted against concentration of ligand and extrapolated to zero concentration of ligand. At ligand concentration equal to zero, $F_0(X)$ must equal unity. The arbitrary value for the half-wave potential was corrected by the amount necessary to fulfill this condition, and the resulting value, −0.564 volt, was used as the half-wave potential of simple cadmium ion. The procedure is sufficiently accurate to give comparative values for formation constants in 50% dioxane, although comparison of these constants with those observed in other solvent systems may not be warranted.

Results

Polarographic data for the copper(I) thiourea complex in 70% dioxane and for 1,3-dimethyl-2-

(1) Presented before the Physical and Inorganic Division of the 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957.

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(4) M. Horning, "Organic Syntheses," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 617.

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(6) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1956, p. 177.