[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, COLUMBIA UNIVERSITY AND THE UNIVERSITY OF CHICAGO]

A Study of the Mechanism and Intermediates in the Precipitation of Cations with Thioacetamide[1]

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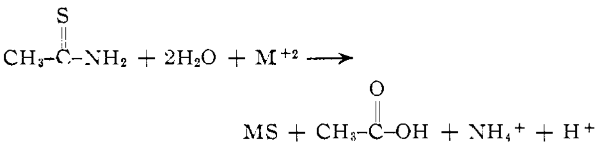
Possible mechanisms for the precipitation of cations with thioacetamide are considered. In some cases the cation is precipitated by the hydrogen sulfide liberated in the hydrolysis of thioacetamide. In other cases a metal-thioacetamide intermediate is formed. The evidence for the existence of such compounds is reviewed. In a study at room temperatures carbon containing intermediates were obtained in the reaction in acid solution between thioacetamide and cuprous or cupric chloride, cuprous or cupric bromide or mercuric chloride. No carbon containing intermediates were isolated for the other cations studied. The empirical formulas for the copper-thioacetamide compounds were $C_2H_5NSCuCl$ and $C_2H_5NSCuBr$. The stoichiometry of the precipitation reactions was determined, and copper was found to be present in the cuprous form. The X-ray powder diffraction patterns for these two compounds were satisfactorily indexed assuming hexagonal unit cells. The conditions of formation, solubility, stability and chemical properties of these compounds were investigated. The infrared spectra of these compounds, thioacetamide, *n*-substituted thioamides, tetrakisthioacetamide cuprous and argentous chloride and *s*-ethyl thioimidoacetate hydrochloride were determined. Structures in which the thioacetamide is in the thion form and in which the copper of the cuprous halide is apparently either coördinately bound to nitrogen or to nitrogen and sulfur are consistent with the observed properties of these two compounds.

Introduction

Thioacetamide is used as a reagent in precipitating cations as metallic sulfides in qualitative[3] and quantitative[4] analysis. The stoichiometric equation for these precipitations is



$$CH_3\text{-}\overset{S}{\overset{\|}{C}}\text{-}NH_2 + 2H_2O + M^{+2} \longrightarrow MS + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + NH_4^+ + H^+$$

where M^{+2} is a divalent metal ion not reduced by thioacetamide.

One means by which this reaction can occur is the hydrolysis of thioacetamide and subsequent precipitation of the metallic ion by the liberated hydrogen sulfide. The hydrolysis reaction is known to occur in acidic and basic solutions.[5-7] Swift and Butler have shown[5,8,9] that some precipitations occur by this mechanism at 90°.

Other possible mechanisms for the precipitation reaction involve either the formation of a metal-thioacetamide intermediate which subsequently decomposes to form the metallic sulfide, or the hydrolysis of thioacetamide to form thioacetic acid[7] which in turn could form a metal-thioacetic acid intermediate. These mechanisms will contribute significantly to the course of the precipitations only if the rates of formation of such intermediates are greater than or comparable to the rate of hydrolysis of thioacetamide (or thioacetic acid).

Swift and his co-workers[5,9] have shown that the rates of some precipitations at 90° are significantly more rapid than the hydrolysis rate and further that the reaction is first order in metal concentration. These results can be interpreted as indicating the presence of some kind of metal organic intermediate.

Several metal-thioacetamide compounds have been reported.[10-15] Most of these compounds were synthesized under conditions quite different from those employed when thioacetamide is used as a precipitant of metallic ions. Metal thioacetic acid compounds have also been reported.[16] In none of the reported syntheses were the conditions similar to the conditions employed in the precipitation of these metallic sulfides in qualitative or quantitative analysis.

The present studies were initiated when it was observed that relatively stable carbon containing precipitation intermediates were obtained by the reaction of thioacetamide with acidified solutions of Cu^{+2} and Hg^{+2} at room temperatures (see Experimental, section 1). This paper is concerned with the characterization of these intermediates and our attempts to determine their structure.

The Copper-thioacetamide Compounds. Preparation.—(See Experimental, 2a.) It was found that a yellowish-white precipitate could be isolated from a solution of thioacetamide with Cu^{+2} or Cu^+ ion in HCl or HBr. Black or brownish precipitates in which no carbon could be detected were obtained with solutions of thioacetamide, cupric ion and nitric or sulfuric acid. These latter precipitates were

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[3] M. D. Shvaikova, *Sudebn. Med.*, **1**, 103 (1934); *C. A.*, **31**, 3824 (1937); *Ber. ges. Physiol. u. exptl. Pharmakol.*, **84**, 352 (1935); H. H. Barber and E. Grzeskowiak, *Anal. Chem.*, **21**, 192 (1949); H. H. Barber and T. I. Taylor, "Semimicro Qualitative Analysis," Harper and Bros., New York, N. Y., 1953; H. Flaschka, *Chemist Analyst*, **44**, 2 (1955).

[4] H. Flaschka and H. Jakobljevich, *Anal. Chim. Acta*, **4**, 247, 351, 356, 482, 486, 602, 606 (1950); **5**, 60, 152 (1951); H. Flaschka and H. Abdine, *Chemist Analyst*, **44**, 8, 30 (1955).

[5] E. H. Swift and E. A. Butler, *Anal. Chem.*, **28**, 146 (1956).

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[7] D. Rosenthal and T. I. Taylor, THIS JOURNAL, **79**, 2684 (1957).

[8] E. A. Butler and E. H. Swift, *Anal. Chem.*, **29**, 419 (1957).

[9] D. F. Bowersox and E. H. Swift, *ibid.*, **30**, 1288 (1958); D. F. Bowersox, D. M. Smith and E. H. Swift, *Talanta*, **2**, 142 (1959).

[10] N. Kurnakow, *Ber. deut. chem. Ges.*, **27**^{4}, 43 (1894); *J. prakt. Chem.*, **51**, 246 (1895).

[11] P. C. Ray, *J. Chem. Soc.*, **111**, 101 (1917); **115**, 871 (1919); *Proc. Chem. Soc.*, **30**, 304 (1914).

[12] S. Ishikawa, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **7**, 301 (1928).

[13] E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 775 (1936).

[14] F. H. Brain and C. S. Gibson, *Brit. Assoc. Advance. Sci. Rept.*, 37 (1938).

[15] N. V. Vavilov, *J. Applied Chem. (U.S.S.R.)*, **11**, 356 (1938).

[16] N. Tarugi, *Gazz. Chim. Ital.*, **25** (I), 341 (1895); **27** (I), 317 (1897); **27** (II), 153 (1897); J. L. Danziger, THIS JOURNAL, **24**, 578 (1902).

presumably copper sulfide. Under certain conditions of precipitation (pH, temperature and ratio of reactants), the formation and subsequent decomposition of the intermediate was actually observed in the course of a sulfide precipitation.

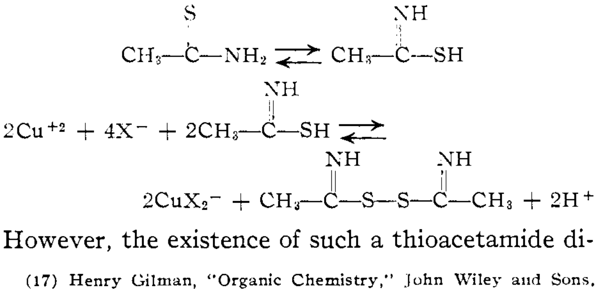
X-Ray and Crystallographic Evidence.—(See Experimental, 2b) X-ray examination of the thioacetamide-cuprous and cupric bromide and of the thioacetamide-cuprous and cupric chloride precipitates revealed the presence of narrow diffraction lines different from the diffraction lines of thioacetamide and the corresponding copper halide or sulfide. The d values and relative intensities obtained with the thioacetamide-cuprous and cupric chloride precipitates were identical within experimental error. The X-ray patterns for the precipitates obtained with cuprous and cupric bromide also were identical. However, the pattern for the chlorides was different from that of the bromides.

Each of these two different diffraction patterns was satisfactorily indexed by assuming a hexagonal unit cell. Thus, it appears there is a single crystalline entity in each case. The results of crystallographic studies with the polarizing microscope were consistent with the previous findings and permitted further characterization of the crystalline substances.

Paramagnetic Resonance Experiments.—(See Experimental, 2c.) Copper in the chloride and bromide-thioacetamide precipitates could be present in the cuprous form, cupric form or cuprous and cupric forms. Cupric copper is paramagnetic and yet neither the bromide nor chloride precipitates exhibited any paramagnetic resonance absorptions. These observations together with the results of the additional paramagnetic resonance experiments, the color of the pyridine solutions of the precipitates and the results of the stoichiometric studies indicate that the copper is present in the cuprous form.

Stoichiometry and Oxidation Product of the Precipitation Reactions.—(See Experimental, 2d.) The results of amperometric titrations suggest a ratio of one mole of thioacetamide per mole of cuprous ion, but with cupric ion two moles of thioacetamide are required. Therefore, one mole of thioacetamide must reduce one mole of cupric to cuprous ion.

The oxidation product derived from thioacetamide was not isolated or identified. However, there are several reasons[17–19] for believing that the reaction proceeds as shown



$$\mathrm{CH_3{-}\overset{S}{\overset{\|}{C}}{-}NH_2 \rightleftharpoons CH_3{-}\overset{NH}{\overset{\|}{C}}{-}SH}$$

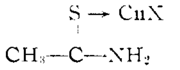
$$\mathrm{2Cu^{+2} + 4X^- + 2CH_3{-}\overset{NH}{\overset{\|}{C}}{-}SH \rightleftharpoons 2CuX_2^- + CH_3{-}\overset{NH}{\overset{\|}{C}}{-}S{-}S{-}\overset{NH}{\overset{\|}{C}}{-}CH_3 + 2H^+}$$

However, the existence of such a thioacetamide disulfide derivative has not been substantiated. As an alternative oxidation product the formation of a hydrazo compound could be postulated. There appears to be no good evidence that such a product would be formed under the prevailing conditions.[20]

The ultimate fate of the oxidation product was not determined. It is apparently not quantitatively precipitated, since elemental analysis of the cupric chloride-thioacetamide precipitate did not indicate the large excess of nitrogen, carbon or hydrogen that would otherwise be present. Analysis did reveal a stoichiometric excess of sulfur (24.2 S, 13.0 C, 2.74 H, 30.1 Cu and 18.9% Cl—see Experimental, 2e). Attempts to detect free sulfur in the precipitate failed.[21]

It is possible that under a different set of conditions a different oxidation product would be obtained. Butler and Swift conclude[8] in certain instances elemental sulfur is the oxidation product. In the present studies the oxidation of thioacetamide in acidified hydrogen peroxide and in iodine solution has been observed, but the nature of the oxidation product or products has not been investigated.

Elemental Analyses, Empirical Formulas and Possible Structures of the Precipitation Products.—(See Experimental, 2e.) The cuprous compounds were prepared and analyzed. Empirical formulas of $C_2H_5NSCuCl$ and $C_2H_5NSCuBr$ are in good agreement with the experimental data. Some of the more reasonable structures consistent with the results discussed thus far are (X = Cl or Br)



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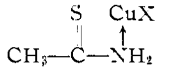
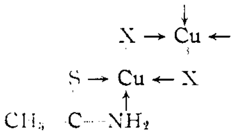
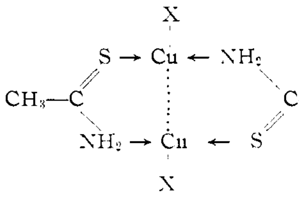


II

Monomeric Structures



III



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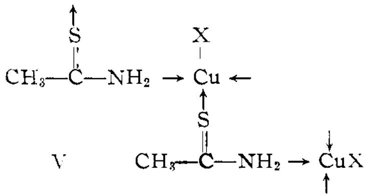
Dimeric Structures



V

Polymeric Structures

Evaluation of the Possible Structures.—(See Experimental, 2f and g.) Since no sulfhydryl vibration has been observed in the Raman spectrum,[22] crystalline thioacetamide probably has the

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[17] Henry Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, pp. 851, 861, 935.

[18] E. Turk and E. E. Reid, *Ind. Eng. Chem., Anal. Ed.*, **17**, 713 (1945).

[19] A. E. A. Werner, *Sci. Proc. Roy. Dublin Soc.*, **22**, 387 (1941).

[20] V. Grignard, "Traite de Chimie Organique," Vol. XIII, Masson and Co., Paris, 1941, p. 496; E. Fromm, *Ann. Chem. Liebigs*, **348**, 144 (1906); D. S. Hector, *J. prakt. Chem.*, **44**, 492 (1891); R. Sahasrabudhey and H. Krall, *J. Indian Chem. Soc.*, **19**, 25 (1942); K. B. Lal and H. Krall, *ibid.*, **16**, 31 (1939).

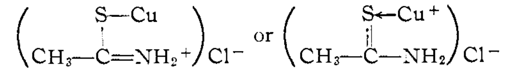
[21] H. Sommers, *Ind. Eng. Chem. Anal. Ed.*, **12**, 368 (1940).

[22] K. W. F. Kohlrausch and J. Wagner, *Z. physik. Chem.*, **B45**, 229 (1940).

[23] E. Spinner, *Spectrochem. Acta*, **15**, 95 (1959).

amide structure. The findings of Spinner[23] and Truter[24] seem to indicate that the carbon–sulfur bond in crystalline thioacetamide has negligible single bond character and the carbon–nitrogen bond has negligible double bond character so that thioacetamide may have no zwitterion character.[24a] The infrared spectrum of thioacetamide (KBr pellets) appears to be consistent with these findings. Absorptions were observed to which thioureide, primary amide, methyl-carbon and carbon–nitrogen assignments have been made. These same absorptions were observed in the spectra of the copper-thioacetamide compounds. This means that the cuprous copper and halogen must be bound in such a manner that the structure of thioacetamide is not profoundly altered. Structures in which thioacetamide is in the thiol form can be excluded because of this evidence.

In both tetrakisthioacetamide-cuprous and argentous chloride, where the metallic ion is coördinately bonded to the sulfur from four thioacetamide molecules,[13] no thioureide absorption was observed. No thioureide absorption was observed in *s*-ethyl thioimidoacetate hydrochloride. These observations and the presence of a strong thioureide absorption in the copper-thioacetamide compounds would seem to rule out structures like



$$\left(\begin{array}{c}\mathrm{S{-}Cu}\\ | \\ \mathrm{CH_3{-}C{=}NH_2^+}\end{array}\right)\mathrm{Cl^-} \quad \text{or} \quad \left(\begin{array}{c}\mathrm{S{\leftarrow}Cu^+}\\ \| \\ \mathrm{CH_3{-}C{-}NH_2}\end{array}\right)\mathrm{Cl^-}$$

The insolubility of the copper-thioacetamide precipitates compared to the solubility of the tetrakis and *s*-ethyl compounds also suggests the fundamentally different nature of these compounds.

The observed properties of these precipitates are *consistent with* structures in which the halogen (chlorine or bromine) is bound to the cuprous copper and the copper is bound to nitrogen or nitrogen and sulfur. Thus, in the presence of hydrochloric (or hydrobromic) acid the dissociation of the cuprous chloride is suppressed and the cuprous chloride-thioacetamide compound is stable. In the presence of other acids, water or bases, the cuprous chloride dissociates, and the copper-thioacetamide compound decomposes. The greater stability of the cuprous chloride-thioacetamide compound in sodium chloride solution than in water can also be understood in terms of this picture.

The fact that hydrogen ions, as well as chloride or bromide ions, must be present in aqueous solution if the compound is to remain quite stable cannot be explained in terms of the copper–chlorine bond but could be explained in terms of other structural configurations in the molecule. The extent of this stability is also significant. Although thioacetamide hydrolyzes in four molar hydrochloric acid with a half life of about three hours at room temperature, the copper-thioacetamide compound shows no visible signs of decomposition even after three months. This could be explained if copper was coördinately bound to the nitrogen so that proton addition, a prerequisite to hydrolysis of thioacetamide,[7] could not occur. Also, such coördinate bonding would place a less positive charge upon carbon than would proton addition. This would decrease the likelihood of addition of water to carbon and the likelihood of possible subsequent displacement of nitrogen and resultant decomposition of the compound. Coördination to nitrogen and sulfur would inhibit proton addition to either atom. Of course, the insolubility of the copper-thioacetamide compound may also help to explain its stability.

Whereas thioacetamide is quite stable in distilled water, the copper-thioacetamide compound rapidly decomposes. This can be explained in terms of the postulated structures. For, in the absence of added hydrogen, ionization of one of the amide hydrogens followed by decomposition could occur more easily. (More ready addition of hydroxyl ion to carbon could also bring about decomposition). This would also explain the decomposition of the precipitates in organic liquids which are sufficiently strong bases and the stability of the precipitates in some of these solvents when saturated with hydrogen chloride. Comparison of the infrared absorption spectra of thioacetamide and of the thioacetamide compounds indicates shifts and intensity changes for the carbon–nitrogen and nitrogen–hydrogen vibrations. These shifts could be due to bonding of copper to the nitrogen atom.

Cuprous copper is known to have a pronounced affinity for sulfur.[25] In tetrakisthioacetamide-cuprous and argentous chloride the metal is bound to the sulfur.[13] Aurous bromide is similarly bonded to thioacetamide.[14] In view of this preferential bonding to sulfur in these compounds the possibility exists that copper bonds to sulfur in the copper-thioacetamide compounds. In this case the absence of the thioureide absorption in the tetrakis compounds and its presence in the copper compounds might be explained in terms of the greater effect upon the thioureide absorption of the coördination to sulfur of a copper ion, than of a copper atom which is bound to chlorine and perhaps also to nitrogen as in structures such as III, IV and V.

Bonding to nitrogen rather than to sulfur has been proposed in at least one case.[12] Ishikawa has postulated the formation of a mercury–nitrogen bond for a variety of thioamides. These mercury compounds possess solubility and stability properties similar to those of the copper-thioacetamide compounds.

Based on the available evidence coördination of cuprous chloride to nitrogen seems reasonable. The copper may also be coördinated to sulfur. The possibility that cuprous chloride is bonded only to sulfur cannot be entirely rejected, but the other configurations appear to explain the observed properties more readily.

Several different copper-thioacetamide compounds have been prepared in alcoholic solution.[10,11] Those described by Kurnakow were soluble in alcohol. The properties of the compound prepared by Ray were not extensively described. Although the postulated structure is different, the color and results of elemental analysis are not very different

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(24) M. R. Truter, *J. Chem. Soc.*, 997 (1960).

(24a) N. R. Kunchur and M. R. Truter, *ibid.*, 2551 (1958).

(25) N. V. Sidgwick, ref. 21, pp. 142–143.

TABLE I

CATION-THIOACETAMIDE PRECIPITATIONS AT ROOM TEMPERATURE

Cation	Color ppt. formed in HCl	Results of test for carbon[a]	Appearance after 21 months
Ag^+	White (AgCl) turns black	Negative[b]	...
As^{+3}	Yellow	Negative	Yellow
As^{+5}	Yellowish white	Negative	...
Bi^{+3}	Gray-black	Negative	White
Cd^{+2}	Orange	?	Orange
Cu^{+2}	Yellowish white	Positive	...
Hg^{+2}	White	Positive	Black
Pb^{+2}	Traces of black	Negative[c]	Some white (S?) Some black
Sb^{+3}	Orange	Not tested	Black
Sn^{+2}	Brown	Not tested	Yellowish brown

[a] Tested for carbon after one day by sealed capillary method, F. L. Schneider, "Qualitative Organic Microanalysis," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 77. [b] H_2SO_4 precipitate tested. [c] H_2O precipitate tested.

TABLE II

CONDITIONS OF PREPARATION AND STABILITY OF COPPER HALIDE-THIOACETAMIDE PRECIPITATES

Copper halide	Final Concentrations in Precipitating Solution: Copper halide	Thioacetamide	Hydrohalic acid[a]	No sign of decomposition in
$CuCl_2$	0.0072 *M* (0.0018–0.011)[b]	0.0068 *M* (0.0068–0.012)	0.33 *M* (0.078–0.065)	Yellow needle-like ppt. in 92 hr.
CuCl	0.0015 *M*[a] (0.00018–0.0018)	0.0068 *M*	0.38 *M* (0.18–0.46)	Yellowish white ppt. after 95 hr. in 0.3 *M* HCl
$CuBr_2$	0.0036 *M* (0.0018–0.0054)	0.0068 *M*	0.11 *M* (0.11–0.44)	Yellow needle-like ppt. in 99 hr.
CuBr	0.0036 *M*[a] (0.002–0.01)	0.0068 *M*	0.4 *M* (0.24–0.56)	Yellowish white ppt. after 17 hr. in 0.4 *M* HBr

[a] Copper halide dissolved in hydrohalic acid solution. The thioacetamide solution was mixed with this solution. [b] Concentrations in parentheses indicate the range of concentrations examined.

from those of the cuprous chloride-thioacetamide compound. This alcoholic precipitate was prepared and found to have a diffraction pattern identical with that of the aqueous precipitate. Therefore, these two precipitates are actually the same compound.

Other Precipitates.—The results of the preliminary study of the unindexed cupric bromide-thioacetamide and mercuric chloride-thioacetamide precipitates (see Experimental, 2b and 3) were inconclusive in establishing any detailed structures for these precipitates.

Experimental Details and Calculations

1. **Tests for Stable Carbon Containing Intermediates.**—Test solutions containing 10 mg. cation/ml. were prepared in accordance with the directions of Noyes and Swift[26]; 5 ml. of test solution was added to 10 ml. of a solution 1.0 *M* in HCl and 0.03 *M* in thioacetamide. The solutions were examined on mixing, one hour, a few weeks, a few months and 21 months after mixing. Significant observations may be found in Table I.

2. **Copper-Thioacetamide Compounds. a. Preparation.**—A series of solutions was prepared containing various concentrations of copper halide, acid and thioacetamide. The stability and nature of the precipitate in each precipitating solution were observed. The concentrations at which the precipitation should preferably be performed was determined on the basis of these observations (see Table II).

Upon first addition of thioacetamide in the preparation of the cuprous bromide precipitate described in Table II, a yellow precipitate was formed which subsequently disappeared. The nature of this initial precipitate was not further investigated.

b. X-Ray and Crystallographic Data. X-Ray Powder Data.—Thirty diffraction lines obtained for the cuprous and cupric chloride precipitates and forty-two lines for the bromide precipitates were satisfactorily indexed assuming hexagonal unit cells (see Table III). The average absolute difference between the experimental and calculated *d* values was 0.002 Å. No difference larger than 0.011 Å. was obtained. The Miller indices arranged in order of decreasing relative intensity of the copper $K\alpha_1$ diffraction lines are: For the chloride precipitates—002, 300, 112 or 200, 212, 310 or 222, 320, 330, 220, 203, 420, 421, 512 or 424, 401, 203, 221, 402, 227, 110, 312, 601, 201, 210, 322, 422, 425, 600, 602 or 430, 432. For the bromide precipitates—110, 220, 211, 101, 300, 112, 412, 310, 403, 302, 212, 322, 402, 410, 100, 501, 222, 102, 210, 430, 600 or 413, 332, 500, 401, 400, 110, 422, 511, 114, 223, 213, 103, 202, 002, 200, 314, 431, 421, 300. Three weak diffraction lines of the chloride precipitate which appeared at 2θ equal to 25.91, 38.81 and 47.08° ($CuK\beta$?) could not be satisfactorily indexed. Since only a small number of powder diffraction lines were obtained for the chloride and bromide compounds, no unequivocal space group assignment is possible.

TABLE III

PROPERTIES OF COPPER HALIDE-THIOACETAMIDE PRECIPITATES

	$CuBr_2$–CuBr	$CuCl_2$–CuCl
Color	Light yellowish white	Light yellowish white
Habit	Long needle-like crystals, difficult to observe in cross section; appeared to be hexagonal in one case with $CuBr_2$	
Size	Cupric—as large as 2 mm. long by 0.01 mm. in diameter; cuprous—smaller in size (estimated visually)	
Extinction	Parallel extinction	Parallel extinction
Refractive index (white light)	ω—greater than 1.80 ϵ—1.745 ± 0.005	Less than 1.4 1.680 ± 0.005
Density, g./ml.	2.464	2.155
Unit cell-hexagonal		
a = b	11.505 Å.	11.414 Å.
c	7.677	19.66
Number of empirical formula units (C_2H_5NSCuX) per unit cell[a]	5.97 (6)	16.5[b] (18, 16 or 17)

[a] Volume of unit cell = $a^2c \sin 60°$, weight in unit cell = V(in Å.^{3}) x D (g./cc.)/1.660_4. [b] Considering the observed crystallographic properties, a unit cell containing 18 or 16 empirical units seems most reasonable. The apparent error is larger than expected.

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[26] A. A. Noyes and E. H. Swift, "Qualitative Chemical Analysis of Inorganic Substances," Macmillan Co., New York, N. Y., 1942, pp. 398–399.

The yellow precipitate obtained from a solution 0.064 *M* in cupric bromide, 1.8 *M* in hydrobromic acid and 0.024 *M* in thioacetamide gave an X-ray diffraction pattern some of whose lines were identical with those of the indexed copper bromide-thioacetamide compound (Table II). The other lines were not those of thioacetamide, cuprous or cupric bromide or sulfide. It was not found possible to index the lines assuming a cubic or hexagonal unit cell. These facts, coupled with the considerable variation in relative intensity of lines obtained from two different precipitates, make it seem likely that the precipitate was a mixture. No detailed study was made of this precipitate.

Crystallographic Properties of the Precipitates.—Some of the optical and physical properties are summarized in Table III.

c. **Paramagnetic Resonance Experiments.**—The instrument used[27] easily will detect 10^{-9} mole of hydrazil in a capillary. No resonance absorption could be detected in the cupric chloride, cupric bromide or cuprous chloride-thioacetamide precipitates when they were examined as solids. Cupric bromide or chloride gave a very easily detected absorption. The absence of detectable absorption does not prove the absence of paramagnetism. In some cases even where high concentrations of paramagnetic material are present, the absorption is so broad it can not be detected. However, cupric compounds frequently have rather sharp absorptions.[28]

The cuprous chloride-thioacetamide compound was dissolved in pyridine. When the solution was sealed in a capillary and examined, no paramagnetic resonance absorption was observed. Even after standing for one week, no resonance absorption was observed and the solution remained yellow in color. (Cuprous chloride dissolved in pyridine is yellow. Thioacetamide dissolved in pyridine is colorless.) When the solution was left exposed to air for one week, a blue precipitate was formed and the solution was green. (Cuprous chloride and bromide in pyridine do the same thing.) Paramagnetic resonance absorptions, identical with what was obtained with cupric chloride in pyridine, were found in this green solution. (Cupric bromide gives a green solution with pyridine. Cupric chloride gives a blue solution and blue crystals.) These results can be understood if we assume that the compound contains cuprous copper which is oxidized to the cupric form by oxygen in the air (see also 2f).

d. **Stoichiometry of the Precipitation Reactions. Amperometric Titrations.**—Varying amounts of a 0.02 *M* thioacetamide solution were added to 15 ml. portions of a solution 0.01 *M* in cupric chloride and 0.7 *M* in HCl. The final solutions were 0.4 *M* in HCl. These solutions were shaken and allowed to stand for about 10 hours to ensure completeness of the reaction. The polarographic recorder current readings of a dropping mercury electrode were measured at −0.8 volts *vs.* s.c.e. for each of the solutions. Molar ratios of thioacetamide to cupric chloride of 2.06, 2.14 and 2.00 were found for three different titrations. The mean value, 2.07, was not significantly different from 2.00. The rather poor precision and apparently poor accuracy of these results are due to the inherent difficulties associated with these titrations.

Varying amounts of a 0.0293 *M* thioacetamide solution were added to 0.154 millimole of cuprous chloride in 30 ml. of a 0.9 *M* HCl solution. After 16 hours, readings were taken at −0.95 volts *vs.* s.c.e. The titration end point corresponds to a stoichiometric ratio of 0.83 mole of thioacetamide to one mole of cuprous chloride. No precautions were taken to exclude oxygen in this titration. The sources of error make it seem likely that the molar ratio is not significantly different from 1.00.

e. **Elemental Analyses and Empirical Formulas.**—The cuprous compounds were prepared, dried and analyzed.[29]

Empirical formulas of $C_2H_5NSCuCl$ and $C_2H_5NSCuBr$ are consistent with the experimental data.

Anal. (Percentage found is followed in parentheses by percentage calculated.) $C_2H_5NSCuCl$: C, 13.88 (13.79); H, 3.23 (2.89); N, 8.25 (8.04); S, 18.37 (18.41); Cu, 36.61 (36.49); Cl, 20.25 (20.36). $C_2H_5NSCuBr$: C, 11.47 (10.99); H, 2.81 (2.31); N, 6.19 (6.41); S, 14.25 (14.66); Cu, 29.06 (29.08); Br, 36.15 (36.55).

f. **Chemical and Physical Properties. Solubility and Stability of the Precipitates in Various Solvents and Solutions.**—A small amount of the copper-thioacetamide precipitate was placed in several different liquids. The liquid was examined to determine whether there were any visible indications of solubility or decomposition. The cuprous chloride precipitate was insoluble and stable at room temperature in nitrobenzene, dimethylaniline, chloroform, carbon disulfide, benzene, ethyl alcohol, acetone, formic acid, glacial acetic acid and in 4 *M* and concentrated HCl. In concentrated HCl, the solution appeared slightly yellow in color, indicating possible slight solubility or decomposition but the bulk of the precipitate appeared unchanged even after three months.

In 6 *M* HCl solution at 85° decomposition occurs and black particles can be seen after five minutes. There is a pronounced black color after fifteen minutes. In water the precipitate begins to turn black after a few minutes even at room temperature. In 1.8 *M* sulfuric or nitric acid or in saturated potassium chloride decomposition occurs slowly. After ten minutes the supernatant liquid is slightly brownish-yellow and the precipitate is gray in color. In contrast to this 1.8 *M* hydrochloric acid produces no noticeable decomposition.

The precipitate decomposes very rapidly with the formation of a black precipitate in bases such as ammonia, *n*-butylamine, *tert*-butylamine, piperidine and morpholine; more slowly in di-*n*-propylamine, formamide and dimethylformamide.

The copper-thioacetamide precipitate is soluble in pyridine and many of its derivatives, *e.g.*, 2-methyl, 3-methyl, 2,6-dimethyl and 2,4,6-trimethyl pyridine and quinoline (see Experimental, 2c).

Dimethylformamide saturated with hydrogen chloride dissolves the precipitate and forms a yellow solution. (Cuprous chloride is insoluble in dimethylformamide but dissolves to give a yellow solution when saturated with hydrogen chloride.)

Chemical Reactions.—The cuprous chloride precipitate can be heated to 120° without decomposition or change of state. At 190° there is some slight decomposition. At more elevated temperatures the precipitate turns black and decomposition occurs. Upon heating with a Bunsen flame, the precipitate decomposes and a black residue of copper oxide remains.

When treated with potassium iodide in slightly acidified solution, the precipitate seemed to turn more definitely yellow in color, but no iodine was detectable. Iodine, if formed, *e.g.*, if cupric copper were present, could be subsequently reduced by thioacetamide. An iodine solution was decolorized by the precipitate. This could be due to the presence of cuprous copper or thioacetamide. Thioacetamide was observed to decolor iodine solutions.

A silver nitrate solution 1.8 *M* in nitric acid gave a gray colored solution as soon as the cupric chloride-thioacetamide precipitate was added. Silver chloride was probably precipitated.

Hydrogen sulfide bubbled through a 1.8 *M* hydrochloric acid solution containing the cupric chloride precipitate immediately gave a brown precipitate—probably copper sulfide.

g. **Infrared Data.**—For purposes of correlation and comparison the infrared spectra of thioacetamide, thioacetamide·CuCl (and CuBr), tetrakisthioacetamide·CuCl (and ·AgCl), *n*-thioacetylpiperidine, *n,n*-diphenylthioacetamide, ethyl thioimidoacetate hydrochloride and *n,n*-dimethyl thioacetamide, thioacetanilide, thiobenzanilide and *n,n*-dimethylacetamide in KBr pellets were obtained. Probable assignments for some of these compounds are given in Table IV.

All the thioamides had an absorption assigned to thioureide in the 1500–1470 cm.$^{-1}$ region except for the anomalous absence of an absorption in *n,n*-dimethylthioacetamide. The infrared spectrum of this compound has other peculiarities, *e.g.*, the absence of a medium to strong absorption at 960–1000 cm.$^{-1}$ so characteristic of the other thioamides.

3. **Mercuric Chloride—Thioacetamide Precipitate.**—The precipitation was performed in a solution 0.02 *M* in mercuric chloride, 0.3 *M* in HCl and 0.014 *M* in thioacetamide. The filtrate was decanted after 6 hours and replaced with 0.3 *M* HCl. After 24 hours the solution was filtered.

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TABLE IV

PROMINENT INFRARED ABSORPTIONS FROM 3100 TO 650 CM.$^{-1}$ FOR THIOACETAMIDE AND METAL HALIDE-THIOACETAMIDE DERIVATIVES

T[k,l]	T·CuCl	T·CuBr	T_4·CuCl	T_4·AgCl	Probable assignments
3050s-br	3020s-br	3080s-br	3010s-br	3070s	NH_2str,[a,b] CH_3str[a,c,d]
2900w		2895w-sh			CH_3str[a,c,e]
1640s	1653s	1628s	1610s	1623s	—NH_2 amide II[f]
1478s	1477s	1475s			—C(=S)—N[g]
1453w-sh	1458m-s	1460w-sh	1433s	1441s	CH_3—C def[c]
1390m	1403m-s	1400m	1408m-s	1374m-s	C—N?[f,h]
1357s	1368m-s	1367m-s	1368m-s	1362m-s	CH_3—C def?[c,i]
1300s	1311s	1300s	1269s	1272s	C—N?[f,h,j]
1040m	1036w	1030w		970s	
974s	772w	966s	970s	704s-br	
708s-br	737s	699s-br	671s-br	674s-br	
	688s		662w	662m	

[a] K. W. K. Kohlrausch and J. Wagner, *Z. physik. Chem.*, 45B, 229 (1940). [b] H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand, New York, N. Y., 1949, p. 47. [c] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 13. [d] Ref. b, p. 48. [e] Ref. b, p. 49. [f] Ref. c, p. 205. [g] Ref. c, p. 350. [h] Ref. c, p. 249. [i] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 77, 171, 526 (1956). [j] R. Mecke and R. Mecke, *Ber. deut. chem. Ges.*, 89, 343 (1956). [k] s, strong; m, medium; w, weak; sh, shoulder; br, broad. [l] See E. Spinner, *Spectrochim. Acta*, 15, 95 (1959).

The X-ray diffraction pattern of the white precipitate was different from that of the reactants. The most intense diffraction lines had *d* values of 9.03, 6.34, 5.24, 3.614 and 2.583 Å. The fourteen diffraction lines observed could not be indexed as a cubic, tetragonal or hexagonal unit cell. This precipitate may be a mixture.

Elemental analysis gave results most closely corresponding to an empirical formula containing one mole of thioacetamide per mole of mercuric chloride (C, 5.44; H, 0.92; N, 3.12; Hg, 61.07; Cl, 18.65; S, 8.90%). The differences between the observed and calculated percentages, corresponding to the empirical formula $C_2H_5NSHgCl_2$, were outside the limits of experimental error. This is consistent with the conclusion that the precipitate is a mixture.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN]

The Structure of Copper(II) Tartrate Trihydrate[1a]

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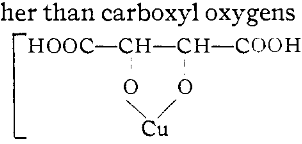
Several proposed structures of copper(II) tartrate trihydrate in the solid state are discussed in the light of infrared studies of the compound. Only one of the proposed structures is fully consistent with the results of these studies.

Introduction

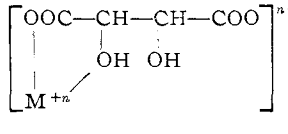
The composition and structure of copper(II) tartrate and tartrate complexes of copper have been subjects of much interest and speculation for many years.[1b–15] There is little doubt that the tartrate anion in copper(II) tartrate-3-hydrate is coördinated to the copper cation, but there has been a difference of opinion[1b,2,7,9] as to exactly how the anion is bonded to the copper and as to the location of the water molecules.

There are five principal proposals which describe the bonding of the tartrate ion in metal tartrate complexes. Various methods have been used in the study of these materials in order to verify each of the proposed structures. They include conductometric, spectrophotometric, potentiometric, *p*H and polarographic methods,[9] as well as polarimetric[15] and crystallization[1b,13] procedures. One proposed structure[1,2] for tartrate to copper bonding in copper-tartrate complexes involves coördination through the hydroxyl oxygens rather than carboxyl oxygens



$$\left[\begin{array}{c}\mathrm{HOOC{-}CH{-}CH{-}COOH}\\ \mathrm{O\quad O}\\ \mathrm{Cu}\end{array}\right] \qquad \mathrm{I}$$

A second proposal[12,14,15] implies that one carboxylate oxygen and one hydroxyl oxygen of the tartrate anion coördinate to a metal ion



$$\left[\begin{array}{l}\mathrm{OOC{-}CH{-}CH{-}COO}\\ \quad\ \mathrm{OH\ \ OH}\\ \mathrm{M}^{+n}\end{array}\right]^{n-2} \qquad \mathrm{II}$$

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