

## THE STRUCTURES AND THERMAL DECOMPOSITION OF CUPRIC MONO, DI AND TRICHLORACETATES

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Magnetic moment measurements and ultra-violet diffuse reflectance spectroscopy have been used to investigate the structure of the chloroacetates of copper(II). These studies indicate that cupric monochloroacetate dihydrate is dimeric and cupric trichloroacetate tetrahydrate is monomeric. Cupric dichloroacetate tetrahydrate forms an intermediate case. The thermal decomposition of these compounds under nitrogen has been studied using thermogravimetry and differential thermal analysis, together with analysis of the products of the decomposition. The major organic product formed in the thermal decomposition of the mono- and dichloroacetates is the corresponding chlorinated acetic acid; the solid inorganic product is cuprous chloride. Thermal decomposition of the trichloroacetate yields cupric chloride and a mixture of trichloroacetic acid and trichloroacetyl chloride.

Much work has been published on the chloroacetates of copper(II); most of this, however, has been concerned with the structures of these materials and little attention has been paid to their thermal decomposition.

It is well established [1] that both the anhydrous and the tetrahydrated monochloroacetates have a dimeric structure, analogous to that of the hydrated unsubstituted acetate. A similar structure has been suggested for the anhydrous dichloroacetate, although it is not clear whether this is also true of the hydrated salt. Cupric trichloroacetate, however, has been shown to be monomeric in both the tri-hydrated and the anhydrous forms. The situation is complicated by the fact that the methods used in the preparation of these materials may affect the structure of the salt.

Two methods have been suggested for determining whether or not these materials are dimeric [1, 2]. The close proximity of the two copper atoms in the dimer leads to strong interaction, which approximates to the formation of a copper-copper bond. This causes a lowering of the magnetic moment, from a theoretical value of 1.73 B.M. for a simple cupric salt, to an actual value of about 1.40 B.M. for a dimer ( $1.00 \text{ Bohr Magnetron} = 9.27 \times 10^{-24} \text{ Am}^2$ ). The second method involves interpretation of the ultraviolet absorption spectrum.

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We have used both these methods in an attempt to establish the structure of our hydrated cupric monochlor-, dichlor- and trichloracetates. Also we have examined the decomposition of these chloracetates under nitrogen, using thermogravimetry (TG) and differential thermal analysis (DTA). The decomposition products in each case have been isolated and identified.

### Experimental

The cupric chloracetates studied were prepared by dissolving laboratory grade cupric carbonate in a 3.5 M aqueous solution of the appropriate acid until no more effervescence was observed. The resulting solution was filtered and crystallized at room temperature in a rotary evaporator. The crystals were dried at room temperature in a vacuum oven. Compounds were analyzed for carbon and hydrogen using a Perkin Elmer elemental analyser and for chlorine by combustion in an oxygen flask, followed by titration with standard mercuric nitrate solution. Copper was estimated by reaction of the chloracetate in aqueous solution with potassium iodide, followed by titration of the liberated iodine with standard sodium thio-sulphate solution.

Analytical results are recorded in Table 1, together with the established formulae for the compounds.

Table 1  
Analysis of the cupric chloracetates

Compound	Wt. % obtained by analysis				Theoretical wt. % for formula given			
	Copper	Carbon	Hydrogen	Chlorine	Copper	Carbon	Hydrogen	Chlorine
$\text{Cu}(\text{CH}_2\text{ClCOO})_2 \cdot 2\text{H}_2\text{O}$	22.20	16.93	2.64	24.69	22.16	16.75	2.79	24.78
$\text{Cu}(\text{CHCl}_2\text{COO})_2 \cdot 4\text{H}_2\text{O}$	16.89	12.14	2.49	36.02	16.22	12.26	2.55	36.27
$\text{Cu}(\text{CCl}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	13.65	10.96	1.69	46.77	13.79	10.42	1.74	46.25

Magnetic moments were determined at room temperature, using the well known Gouy-Rankine method, as modified by Evans [3]. Ultraviolet reflectance spectra of finely ground samples of the chloracetates were obtained using a Unicam SP 800 spectrophotometer, with a SP 890 reflectance unit.

Thermogravimetric studies were carried out using a Stanton Redcroft thermobalance, model TG #750. Samples (ca. 5 mg) were heated at a rate of rise of temperature of 5°/min under a flowing stream of nitrogen. Differential thermal analysis curves were obtained using a Standata 6-25 differential thermal analyser. Samples (ca. 50 mg) were heated under flowing nitrogen at a nominal heating rate of 10°/min. The method and apparatus used for product analyses have been described in detail in a previous paper [4].

## Results and discussion

### Structural studies

Experimental determination of the magnetic moments of cupric monochloracetate dihydrate, cupric dichloracetate tetrahydrate and cupric trichloracetate tetrahydrate gave values of 1.42, 1.62 and 1.70 B.M. respectively. The value for the

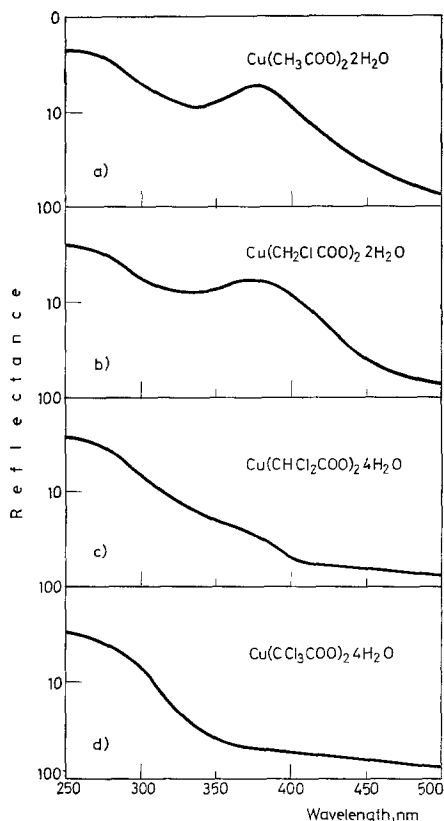


Fig. 1. Ultra-violet/visible reflectance spectra of the solid cupric chloracetates. (a) Cupric acetate dihydrate; (b) cupric monochloracetate dihydrate; (c) cupric dichloracetate tetrahydrate; (d) cupric trichloracetate tetrahydrate

trichloracetate shows quite clearly that this compound has one unpaired electron per copper atom. As this situation is found in simple cupric compounds, such as cupric sulphate, it must be concluded that the trichloracetate is monomeric. The magnetic moment of the monochloracetate is very close to the published figure of 1.41 B. M. [1] for dimeric cupric acetate dihydrate and this indicates a dimeric structure for the former. The nature of the mono- and trichloracetates is confirmed by their ultra-violet diffuse reflectance spectra (Fig. 1). Yamada et al. [2] have

stated that the presence of an absorption band at about 375 nm is characteristic of dimeric cupric compounds. It can be seen that this band is almost as well developed in the spectrum of the monochloracetate ( $\epsilon_{\max}$  at 372 nm, Fig. 1b) as it is in the spectrum of dimeric cupric acetate dihydrate ( $\epsilon_{\max}$  at 375 nm, Fig. 1a), while it is completely absent from the spectrum of the trichloracetate (Fig. 1d). Cupric dichloracetate tetrahydrate provides an interesting intermediate case, since its magnetic moment is too low for one unpaired electron per copper atom, yet is much higher than the moment for the dimeric monochloracetate. Further the 375 nm band in the U. V. spectrum is intermediate in intensity between that of the mono- and trichloracetate (Fig. 1c).

The intermediate nature of the dichloracetate is not too surprising when the electron-withdrawing properties of the substituted methyl groups are considered. As the electron-withdrawing ability of the groups increases in the order



it follows that the copper-copper interaction will be weakened progressively as the number of chlorine atoms in the acetate increases. Therefore a gradual, rather than an abrupt, change in properties is to be expected.

#### *Thermal decomposition studies under nitrogen*

##### *Cupric monochloracetate, $\text{Cu}(\text{CH}_2\text{Cl} \cdot \text{COO})_2 \cdot 2\text{H}_2\text{O}$*

TG and DTA results for this material are shown in Figs 2a and 2b. As can be seen, the decomposition process occurs in three distinct stages; the corresponding temperatures from Fig. 2a are 40–120°, 160–300° and above 350°. The weight loss associated with the first stage is 12.0%, which corresponds well with the theoretical figure of 12.4% for the loss of two molecules of water of crystallization. In order to confirm that the anhydrous material is formed, a sample was evacuated in the thermobalance at 60°. A weight loss of 12.2% was recorded and the resultant anhydrous salt (which was deep green in colour) showed no further loss in weight on prolonged evacuation. On exposure to the atmosphere for about 24 hours, the anhydrous salt did not regain its water of crystallization, indicating that it was a stable material. Product analysis over this first stage of the decomposition process showed that the only volatile compound evolved was water.

The second stage, over the temperature range 160–300°, is accompanied by a further weight loss leading to an overall figure, at 300° of 65.5%. This is in excellent agreement with the figure of 65.6% expected for the formation of cuprous chloride. DTA shows that decomposition of the anhydrous monochloracetate is accompanied by complicated thermal effects, consisting of overlapping endothermic and exothermic reactions. When a sample was heated over this range in the gas flow equipment, a white solid was observed to condense out in the cold traps and in the glass lines. Analysis of this material (by infra-red and N. M. R. spectroscopy) showed it to be monochloroacetic acid, which was the major de-

composition product obtained; carbon monoxide and some carbon dioxide were also identified in the gaseous samples removed for analysis. Hydrogen was not found, although our method for its identification is somewhat insensitive. The copper-containing residue from the gas flow experiment was confirmed as cuprous

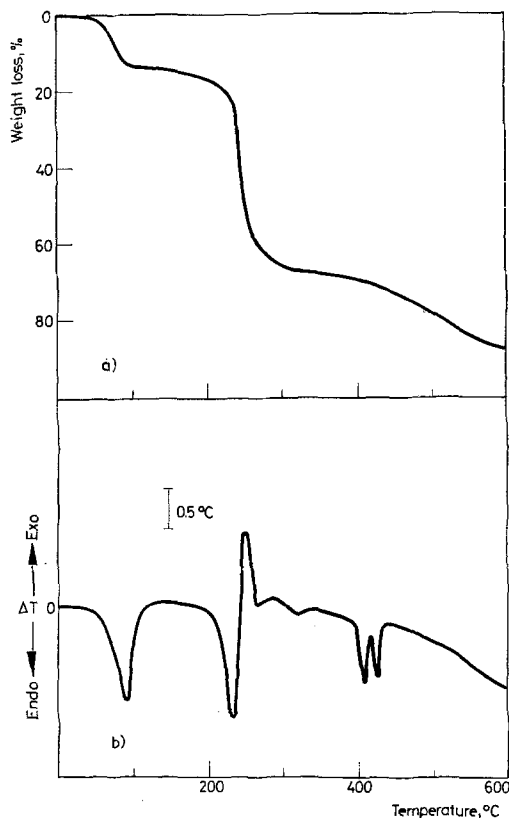


Fig. 2. Thermal decomposition under nitrogen of cupric monochloracetate dihydrate. (a) thermogravimetry; (b) differential thermal analysis

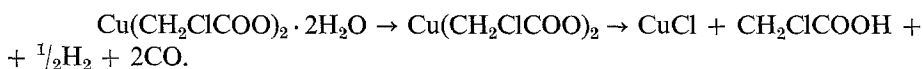
chloride by chemical analysis and by U. V. spectroscopy. It therefore appears that the decomposition of the monochloracetate closely resembles that of the simple acetate in that the corresponding acid is produced.

Further heating above 300° leads to a progressive weight loss which reaches a final value of 88% at about 600°. DTA shows that this process is accompanied by a very gradual endothermic effect, which is reflected in a slow drift of the DTA base line. In addition, two very sharp endotherms are superimposed with peak maxima at 410° and 420°. These peaks are reversible in that two exotherms are obtained on cooling and therefore they must be associated with phase transitions

in the cuprous chloride. The melting point of cuprous chloride has been reported [5] as being 422° so that the 420° endotherm can confidently be ascribed to this. A DTA run on a freshly prepared sample of cuprous chloride also showed these endotherms; therefore the peak at 410° must be associated with a phase transition in the solid chloride.

The overall weight loss of 88% can be explained by assuming that above 350° some decomposition of the cuprous chloride occurs. Above 420°, the molten chloride will tend to vaporize, leading to a progressive loss in weight, with some copper being left as the residue.

Thermal decomposition of cupric monochloracetate dihydrate may thus be represented as follows.



#### *Cupric dichloracetate, Cu(CHCl<sub>2</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O*

As is the case with the monochloracetate, the dichloracetate decomposes in three stages as shown by the TG trace (Fig. 3a). The weight loss over the temperature range 40–100° is 13.5% which corresponds fairly well with that expected (13.8%) for the loss of three molecules of water of crystallization. In the temperature range 100–140° a further 4.5% weight loss occurs which corresponds to the loss of an additional one molecule of water of crystallization. Product analysis in both temperature ranges confirmed that water was the only product formed. Evacuation of a sample at 140° showed a weight loss of 18.5%, confirming the formation of the anhydrous salt. This material (which is pale green in colour) is not as stable as the anhydrous monochloracetate, since some water was regained on standing in air overnight.

Further heating above 150° leads to a third weight loss continuing up to 350° of 76.5% which is slightly greater than that expected for the formation of cuprous chloride (74.7%). DTA (Fig. 3b) once again demonstrates the complex nature of this process; the formation of cuprous chloride is shown by the two endotherms with peak maxima at 410° and 420°. Analysis of the gaseous products, over the temperature range 150–200° showed that the major product was dichloroacetic acid, together with some carbon monoxide and carbon dioxide. Further heating above 200° led to a colourless liquid condensing out in the glassware below the furnace; analysis of this showed it to contain dichloroacetic acid together with some anhydride and acid chloride, whereas a gaseous sample indicated that some HCl had been formed. It is not surprising that products other than the acid should be formed at a later stage of the decomposition process since the acid, formed as the primary product, will have to pass through a hot bed of decomposed material.

Further heating above 400° leads to a gradual weight loss as the cuprous chloride vaporizes, leaving a small amount of copper (5%) as the final product at 600°.

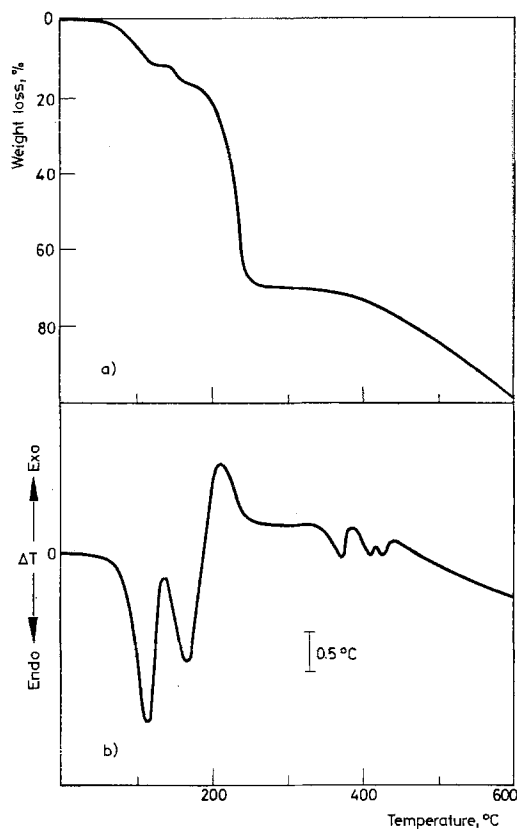
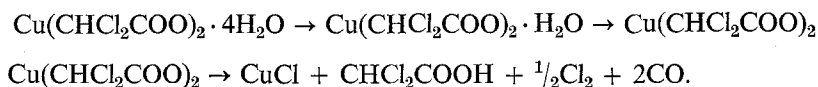


Fig. 3. Thermal decomposition under nitrogen of cupric dichloroacetate tetrahydrate. (a) thermogravimetry; (b) differential thermal analysis

The decomposition mechanism may therefore be represented as:



(We were unable to confirm the presence of chlorine, or phosgene, which could have been formed by reaction between chlorine and carbon monoxide.)

#### *Cupric trichloroacetate*, $\text{Cu}(\text{CCl}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$

Decomposition of the trichloroacetate does not follow a similar pattern to that described for the other chloroacetates. Loss of water commences at about 65° and a plateau on the TG curve (Fig. 4a) is reached at a weight loss of 11.5%. This corresponds to the loss of three molecules of water of crystallization (theoretical figure 11.7%). A similar effect was obtained on evacuation of a sample of the

trichloroacetate at 65°, when a weight loss of 11.3% was obtained; increasing the temperature slowly to 140° led to a further violent evolution of volatile matter, accompanied by decomposition of the monohydrate.

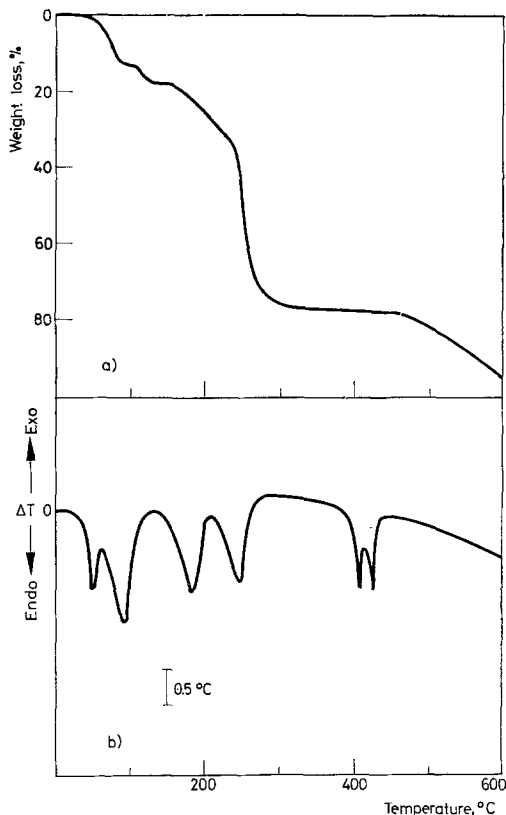


Fig. 4. Thermal decomposition under nitrogen of cupric trichloroacetate tetrahydrate. (a) thermogravimetry; (b) differential thermal analysis

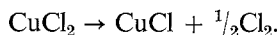
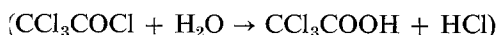
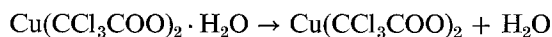
Heating the sample under nitrogen on the TG balance, above 140° showed a further two stage weight loss. The first stage, although not clearly resolved, involves a further weight loss of approximately 4.5%; this is then followed by rapid decomposition such that a final value of 70% is obtained. This final value corresponds to that expected for the formation of cupric chloride (theoretical 70.8%). DTA (Fig. 4b) shows that loss of the final molecule of water of crystallization leads to complete decomposition of the salt, the endotherm associated with dehydration being inseparable from the exothermic decomposition. As would be expected, the presence of water vapour among the gaseous decomposition products leads to some interesting effects and the following compounds were identified: trichloroacetic acid, trichloroacetyl chloride, hydrogen chloride, carbon mon-



oxide and carbon dioxide. It is difficult to decide which is the primary product but, if it is assumed that most of the water is evolved before decomposition commences, then it is reasonable to suppose that the acid chloride is the primary product. Some of this would then be hydrolysed by the water vapour present to form the acid together with some hydrogen chloride.

Above 300°, a further gradual loss in weight is observed which finally reaches a value of 98% at 600°. It is well known that cupric chloride disproportionates to cuprous chloride and chlorine in this temperature range and it is possible that the small exothermic-endothemic effect at 375° reflects this reaction. Ill-defined endotherms at 410° and 425° can be attributed to small amounts of cuprous chloride formed from the cupric salt.

It therefore appears that the decomposition may be represented as follows.



### Conclusion

Our structural studies of the cupric chloracetates, when taken in conjunction with data reported elsewhere, suggest that cupric monochloracetate dihydrate is dimeric in the solid state while cupric trichloracetate tetrahydrate is monomeric. Cupric dichloracetate tetrahydrate is shown to be intermediate in structure between the mono- and trichloracetates.

Thermal studies of these compounds show that the final solid decomposition product is cuprous chloride in the case of the mono- and dichloracetates while the major organic product is the corresponding substituted acetic acid. Cupric trichloracetate is shown not to follow this decomposition pattern, the solid product being cupric chloride, which undergoes a separate decomposition at higher temperatures to cuprous chloride. The primary organic product appears to be trichloroacetyl chloride, which in the presence of evolved water is hydrolysed to the corresponding acid.

Data obtained from both TG and DTA are consistent in suggesting that for the di- and trichloracetate tetrahydrates, one molecule of water is appreciably more strongly bound than the other three.

### References

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RÉSUMÉ — La mesure du moment magnétique et la spectroscopie de réflexion diffuse dans l'U. V. sont utilisées pour étudier la structure des chloroacétates de cuivre (II). Les résultats indiquent que le monochloroacétate de cuivre (II) dihydraté est dimère et que le trichloroacétate de cuivre (II) tétrahydraté est monomère. Le dichloroacétate de cuivre (II) tétrahydraté représente un cas intermédiaire. La décomposition de ces composés dans l'azote a été suivie par thermogravimétrie et analyse thermique différentielle, en analysant simultanément les produits de décomposition. Le principal produit organique formé lors de la décomposition thermique des mono et dichloroacétates est l'acide chloroacétique correspondant; le produit solide inorganique est le chlorure de cuivre (I). La décomposition thermique du trichloroacétate fournit le chlorure de cuivre (II) et un mélange d'acide trichloroacétique et de chlorure trichloroacétylique.

ZUSAMMENFASSUNG — Messungen des magnetischen Momentes sowie diffuse UV-Remissionspektroskopie wurden zur Untersuchung der Struktur der Kupfer(II)-chloracetate eingesetzt. Die Ergebnisse deuten darauf hin, daß Kupfermonochloracetat-Dihydrat dimer und Kupfertrichloracetat-Tetrahydrat monomer ist. Das Kupferdichloracetat-Tetrahydrat bildet hierbei eine Zwischenstufe. Die thermische Zersetzung dieser Verbindungen wurde in Stickstoffatmosphäre unter Anwendung der Thermogravimetrie und Differentialthermoanalyse untersucht, bei gleichzeitiger Analyse der Zersetzungsprodukte. Das bei der thermischen Zersetzung des Mono- und Dichloracetats gebildete organische Hauptprodukt ist die entsprechende chlorierte Essigsäure; der feste anorganische Rückstand das Kupfer(I)-chlorid. Die thermische Zersetzung des Trichloracetats ergibt Kupfer(II)-chlorid sowie eine Mischung von Trichloressigsäure und Trichloroacetylchlorid.

Резюме — Измерения магнитных моментов и ультрафиолетовая диффузная отражательная спектроскопия были использованы для исследования структуры хлороацетатов меди (II). Проведенные изучения показали, что дигидрат монохлороацетата меди (II) находится в виде димера, а тетрагидрат трихлороацетата меди (II) — в виде мономера. Тетрагидрат дихлороацетата меди(II) находится в промежуточной форме. Было изучено термическое разложение этих соединений в атмосфере азота, используя термогравиметрию и дифференциальный термический анализ, совместно с анализом их продуктов разложения. Главным органическим продуктом, образующимся при термическом разложении моно- и дихлороацетатов, является соответствующая хлоруксусная кислота, в то время как твердым неорганическим продуктом является хлорид меди (I). Термическое разложение трихлороацетата меди (II) дает хлорид меди (II) и смесь трихлоруксусной кислоты и ее хлорангида.