Inorganica Chimica Acta, 55 (1981) L27–L28

A Reinvestigation of the Solid State Thermal Reactivity of Bis-methylsulphoniummethioninatocopper (II) Perchlorate Dihydrate

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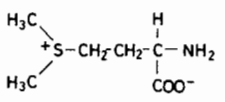
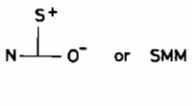
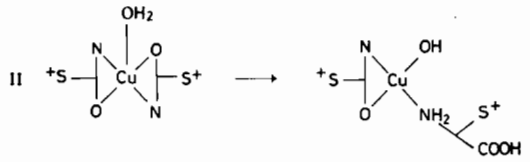
Received November 10, 1980

The amino acid LS methyl Methionine (L methylsulphonium methionine L-S.M.M.) (I) has been isolated from various plants [1]. McAuliffe [2] precipitated a copper complex of the racemic modification of this amino acid as the perchlorate. On heating the complex in the solid state he observed an unusual solid state reaction which on the basis of infra red evidence he concluded to be a proton transfer (II).

I 



II 

The process was considered to be analogous to certain enzymatic reactions [3, 4] and has been cited as such [5].

The reaction envisaged by McAuliffe was considered to be unlikely for a number of reasons; in analogous complexes of Pd(II) and Pt(II) solid state ring closures not openings are observed [6], the reaction occurs at a temperature greater than the dehydration temperature of many copper(III) complexes and finally S methyl methionine is well known to contain labile groups [7]. The solid state reactivity of this interesting complex has hence been reinvestigated.

The perchlorate salt of the copper complex of DL S-methyl methionine was prepared by the method of McAuliffe* *et al.* Thermogravimetric analysis was performed using a Stanton Redcroft TG750 (Fig. 1). Three obvious stages in the decomposition were observed, 45 to 75 °C(1.5%), 92 to 110 °C (4.5%) and 122 to 165 °C (9.2%). By examining the infra red spectra the first two stages were readily assigned to dehydration of the complex, bands at 3540 and 1660 cm^{-1} disappear after this step. This leads to the conclusion that the complex is a dihydrate (found 6.0%, calculated 5.8%), the stages corresponding to the loss of 0.5 mol (found 1.5%, calculated 1.44%) and 1.5 mol (found 4.5%, calculated 4.32%) of water per mol of complex. McAuliffe suggested the complex to be a monohydrate, no modification of the carboxylate stretches was observed at this stage in the decomposition.

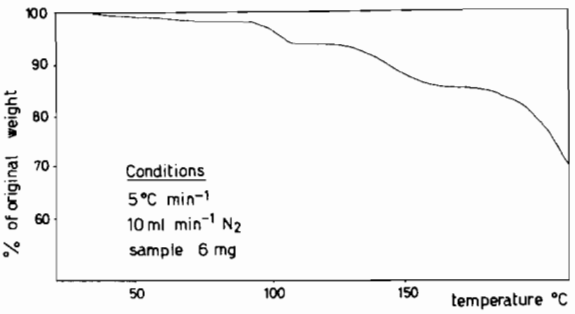


Fig. 1. Thermogravimetric analysis of bis DL-methylsulphoniummethioninatocopper(II) perchlorate dihydrate.

After heating above 122 °C the complex showed exactly the behaviour reported by McAuliffe [2], notably a greatly modified infrared spectrum in the region 1660 to 1800 cm^{-1}, a major band appearing at 1770 cm^{-1}: this has previously been attributed to protonation of the carboxylate group [2]. Isothermal studies gave similar results. On heating at 112 °C the complex lost 5.8% weight; in contrast on heating at 145 °C total weight loss was ~ 15.2%. A small quantity of the complex was heated in a sealed vial at 145 °C for 5 min, the evolved gas was readily identified by its characteristic smell and infra red spectrum as dimethyl sulphide. The third stage of the thermogram may thus be explained as the loss of one mol of dimethyl sulphide per mol of complex (9.2% observed, 9.9% calculated).

The decomposition of sulphonium compounds of methionine in solution has been studied by various workers [7]; the elimination of dimethyl sulphide (or another thioether) often leads to the initial production of α amino γ-butyrolactone (IV). The solid complex was analysed for this compound by ascending paper chromatography [7]. The results are summarized in Table I. Small quantities of homoserine were often detected in the chromatography of samples which had been heated. We attribute this

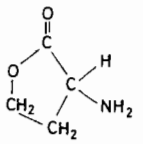
*A modification of McAuliffe's preparation has been developed; it produced a complex which was identical by I.R. and reflectance spectroscopy, micro and thermogravimetric analysis and powder diffraction; details will be reported at a later date.

TABLE I. Chromatographic Results.

Compound	Comments	Rf values[a]	Rf values[b]
DL-SMM Cl		0.13	0.16 0.63
$Cu(DL\text{-}SMM)_2(ClO_4)_2$		0.14	0.17
DL-SMM Cl	heat for 5 min at 135 °C	0.13, 0.23, 0.39, 0.49[c]	0.16, 0.30, 0.66
$Cu(DL\text{-}SMM)_2(ClO_4)_2$	heat for 5 min at 135 °C	0.13, 0.39,	0.17, 0.67
DL-Homoserine		0.24	0.32
α amino γ butyrolactone		0.39	0.66
DL-Methionine		0.51	

[a]n-butanol–acetic acid–water (60:15:25 v/v). [b]n-butanol–pyridine–water (1:1:1 v/v). [c]A weak spot occasionally observed assigned to methionine.

to hydrolysis of the lactone during chromatography; the lactone gave a characteristic yellow spot on development with ninhydrin. The new band observed in the infra red spectrum (1770 cm^{-1}) after heating above 120 °C is now readily assigned to the (C=O) stretch of the lactone.



III

The solid reaction product is amorphous in contrast to the starting material which is microcrystalline. On heating the ligand DL S methyl methionine at 140 °C a similar reaction occurs, dimethyl sulphide and α amino γ butyrolactone being the major products, an occasional trace of methionine was detected.

The elimination of dimethyl sulphide from the coordinated ligand is an unusual reaction, the first mol of dimethyl sulphide is lost reasonably cleanly. The product of this reaction is presumably a mixed complex of DL S methyl methionine and α amino γ butyrolactone with copper(II). The reaction is analogous to that catalysed by certain bacterial enzymes [7]. The results of this work and that of McAuliffe are consistent with this interpretation. At low percentage conversions the previous workers may have been misled by their analytical results, however our thermogravimetric results show that the onset of the reaction leading to the new IR bands occurs with a mass loss and after dehydration has occurred. This interesting reaction has also been shown to occur for the corresponding zinc complex. The details of the kinetics of this solid state reaction are at present being studied and compared with the reaction of the free ligand.

References

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