

Structural relationships between dicopper diacetylide ($\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$) and dicopper acetylide ($\text{Cu-C}\equiv\text{C-Cu}$)

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ABSTRACT.- Dicopper diacetylide $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$, prepared from butadiyne has been studied by FT-IR spectroscopy in comparison to dicopper acetylide $\text{Cu-C}\equiv\text{C-Cu}$. Upon ageing by exposure to air at room temperature, $\text{Cu-C}\equiv\text{C-Cu}$ has been transformed into $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$ as demonstrated by FT-IR spectroscopy and this compound is further transformed on standing in air. A special kind of solid state oxidative coupling reaction occurs so that polyynes chains are formed in these aged solids. It is shown that the FT-IR spectrum of copper acetylide prepared from ammonia solutions of Cu^+ and Cu^{2+} ions is comparable to that of air oxidized $\text{Cu-C}\equiv\text{C-Cu}$ (and $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$) prepared exclusively from Cu^+ ions in presence of a reducing agent demonstrating that Cu^{2+} ions display the same oxidizing effect as oxygen causing coupling reactions in solution and producing $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$.

$\text{Cu-C}\equiv\text{C-Cu}$ oxidized at 60-70°C with CuCl_2 produces a product which could be formulated as $\text{Cu}(\text{C}\equiv\text{C})_{20}\text{Cu}$; FT-IR absorption at 1950 cm^{-1} could suggest the presence of cumulenic carbon chain although acetylenic carbon chains cannot be excluded completely.

INTRODUCTION

In previous works^{1,2}, we have used dicopper acetylide as starting raw material for the preparation of carbyne, the fourth carbon allotrope by using Glaser¹ and Cadiot-Chodkiewicz² coupling reactions.

Another interesting compound which could be useful in the preparation of carbyne is dicopper diacetylide which can be obtained by reacting butadiyne (diacetylene) with $\text{Cu}(\text{NH}_3)_n^+$ solutions (Ilosvay's reagent³). Despite dicopper diacetylide is known since a long time³ and its inferior homologue dicopper acetylide³ even from longer time, our knowledge on them is somewhat limited especially on the former. This is probably due to the hazard connected in the isolation and handling of these two compounds because of their well known explosiveness.

In this paper we will present a study on the structure of dicopper diacetylide by FT-IR spectroscopy and we will show how dicopper acetylide on standing in air undergoes a transformation to the dicopper diacetylide.

EXPERIMENTAL

All solvents and reagents used have been supplied from Aldrich or Fluka.

The FT-IR spectra have been recorded on a Perkin Elmer 1710 spectrometer, using samples embedded in KBr pellets; electronic spectra were obtained on a Shimadzu 160A spectrophotometer.

Synthesis of dicopper diacetylide $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$.

Diacetylene (butadiyne) was prepared following published method⁴ consisting in an elimination reaction on 1,4-dichlorobutyne performed in KOH solution. Diacetylene gas generated according to Brandsma's procedure⁴ and diluted with N_2 , was delivered into a 6% aqueous ammonia solution containing dissolved 5.3 g of copper(I)iodide and 5.0 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ at room temperature. Dicopper diacetylide quantitatively is precipitated as a brown solid. It was collected by filtration. This compound was dark-brown but left in air on a filter paper it became black in 5 hours.

Warning! Freshly prepared dicopper diacetylide should be handled with the utmost care because it is extremely sensitive to shocks and easily explodes with a bright

glow. In fact, few mg of freshly prepared compound left on a Gooch funnel and partially dried in a stream of air (40°C), gave a material extremely sensitive to shocks, while when wet it did not present any handling hazard. A minimum amount of dried dicopper diacetylide was transferred into a small agate mortar, diluted with KBr powder ground cautiously with a pestle and then a pellet was prepared to record the FT-IR spectrum which is shown in Fig. 1A

Ageing of dicopper diacetylide Cu-C≡C-C≡C-Cu.

A sample of dicopper diacetylide was left in air (15-19°C, relative humidity 50%) on a filter paper. Upon ageing the material darkened and Fig. 1B shows the FT-IR spectrum of three-days aged sample while Fig. 1C reports the spectrum of a 1 month aged sample. After ageing the product seems no more shock sensitive, even when dry. However it remains explosive on heating in air (even after 1 month).

Synthesis of dicopper acetylide Cu-C≡C-Cu exclusively from Cu⁺ ions.

Dicopper acetylide (Cu-C≡C-Cu) was prepared as previously described¹⁻³, for instance by passing acetylene into a solution of 10.0 g of copper(I) iodide dissolved in 600 ml of 6% ammonia solution in presence of 13.5 g of NH₂OH HCl. FT-IR spectrum is shown in Fig. 1F. Warning! Freshly prepared dicopper acetylide should be handled with the utmost care because it is extremely sensitive to shocks and heating and explodes violently.

Ageing of dicopper acetylide Cu-C≡C-Cu.

A sample of dicopper acetylide was left in air on filter paper in the same conditions described above for dicopper diacetylide. Upon ageing the compound lost its bright reddish-metallic colour and became opaque-brown. Even dry it is no more easily shock-sensitive but it explodes when heated in air. FT-IR spectrum is shown in Fig. 1E.

Synthesis of dicopper acetylide Cu-C≡C-Cu in presence of Cu²⁺ ions.

Two solutions were prepared as follows: 2.9 g copper(II)dichloride in 100 ml of 6% ammonia solution; 4.0g of copper(I) iodide in 100 ml of 6% ammonia solution. A stream of acetylene was passed into the two solutions mixed together and the

maroon-brown precipitate formed was stirred at room temperature into its mother-solution in a closed flask for 20 hours. It was collected by filtration. About 9.0 g of wet product were recovered. FT-IR spectrum is shown in Fig. 1D.

Oxidation of dicopper acetylide by Cu^{2+} at 60°-70°C.

Copper(II)chloride 20.0 g were dissolved in 130 ml of dist. water. About 6 g of freshly prepared (as described above) dicopper acetylide hydrate $\text{Cu}_2\text{C}_2\text{nH}_2\text{O}$ were added to the solution under violent stirring. The mixture was stirred for 38 hours at 60°-70°C and then filtered. FT-IR spectrum is shown in Fig. 3.

If a sample of this product is hydrolyzed in HCl 12% solution under a layer of cyclohexane, the products evolved are extracted by the solvent and the UV-VIS spectrum shows the following maxima (in nm) : 209, 224 (the most intense), 238, 249, 267 and 279. This shows^{5,6} that together with acetylene also diacetylene and other products were evolved during the hydrolysis.

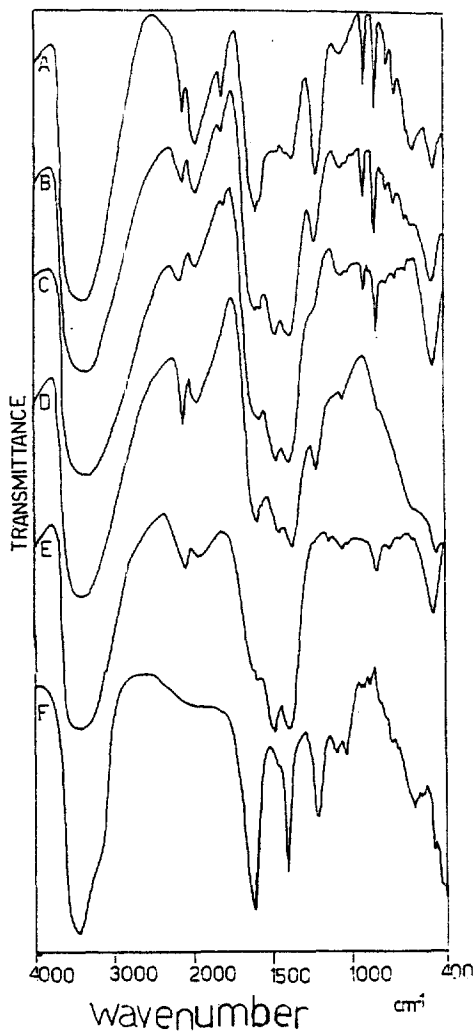
A sample of 1.14g of the oxidation product was dried under dynamic vacuum at 150°C. After this operation 0.587 g were recovered and ashed in a crucible at 750°C for 4 hours. Ashes recovered were 0.256 g; they consisted of CuO ; in fact they dissolved easily in nitric acid without emission of NO_x . Therefore $\text{Cu} = 34.8\%$ and the apparent composition is approx. $\text{Cu}(\text{C}\equiv\text{C})_{20}\text{Cu}$.

RESULTS AND DISCUSSION

Infrared spectroscopy on dicopper diacetylide $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$.

Fig. 1F shows that freshly prepared dicopper acetylide Cu_2C_2 does not display any $\nu_{\text{C}\equiv\text{C}}$ absorption band in agreement with previous observations³. The broad and weak band observable in the 2020 cm^{-1} region is due to water which is also responsible for the absorption at 3333 cm^{-1} . This is in agreement with the general rule⁷ that in symmetrical disubstituted acetylenes, the $\nu_{\text{C}\equiv\text{C}}$ vibration is forbidden in the infrared but is Raman active. However there are also many exceptions to this rule so that many symmetrical disubstituted acetylenes and diacetylenes show infrared medium and weak absorption bands in this region⁷⁻¹⁰, for instance the exceptions to this rule could be caused in the solid state from crystal field effects. Therefore the bands observed in freshly prepared dicopper diacetylide $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$ (see fig. 1A and 2A) can be assigned to the $\nu_{\text{C}\equiv\text{C}}$. For diacetylene these bands occur at 2175 and 2005 cm^{-1} (sym. and asym. $\nu_{\text{C}\equiv\text{C}}$)¹¹, while the bands of dicopper diacetylide $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$ (fig. 2A) detected at

FIGURE 1
FT-IR SPECTRA (KBr)
 (1A) Freshly prepared dicopper diacetylide $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$;
 (1B) $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$ after 3 days ageing in air;
 (1C) $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$ after 1 month ageing in air.
 (1D) Dicopper acetylide $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ prepared in presence of Cu^{2+} ions.
 (1E) $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ aged two weeks in air.
 (1F) $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ prepared exclusively from Cu(I) in presence of NH_2OH .



2117 and 1976 cm^{-1} can be tentatively assigned to sym. and asym. $\nu_{\text{C}\equiv\text{C}}$. The band at 1815 cm^{-1} could be due to acetylenic π -complex with copper³. Moreover, it is useful to note that $\text{CH}_3\text{C}\equiv\text{CCu}$ shows¹² the most intense IR band at 1980 cm^{-1} while copper-phenylacetylide¹² has $\nu_{\text{C}\equiv\text{C}} = 1933 \text{ cm}^{-1}$, the same absorption region where we observe the band of dicopper diacetylide.

It has already been discussed¹² the fact that in general copper acetylides have polymeric nature as demonstrated for instance by their insolubility in all common solvents; another feature demonstrating their polymeric nature is the shift in their infrared spectra of the $\nu_{\text{C}\equiv\text{C}}$ bands at lower wavenumber of 100 to 200 cm^{-1} on going from the free alkyne to its copper salt¹². Hence phenylacetylene absorbs at 2113 cm^{-1} but its copper salt absorbs at 1933 cm^{-1} . Thus the same reasoning applies for diacetylene originally absorbing at 2175 and in its copper salt at 60 cm^{-1} lower wavenumber, demonstrating its polymeric nature.

We may observe also some common feature between the IR spectrum of $\text{CuC}\equiv\text{CCu}$ and $\text{CuC}\equiv\text{C}-\text{C}\equiv\text{CCu}$ (compare fig. 1F with 1A). In both cases we observe intense bands at about 1610, 1400, 1220 cm^{-1} and weaker bands in the 1100-1000 cm^{-1} region. The bands at approx. 970, 915, 850, 760, 730 and 600 cm^{-1} are generally more well defined in the case of $\text{CuC}\equiv\text{C}-\text{C}\equiv\text{CCu}$ while are weaker and poorly defined in the inferior homologue. The band at about 470 cm^{-1} could tentatively be assigned to Cu-C vibration¹², those at 760 and 730 are believed in other acetylides as due to π -Cu-C $\equiv\text{C}$ ¹².

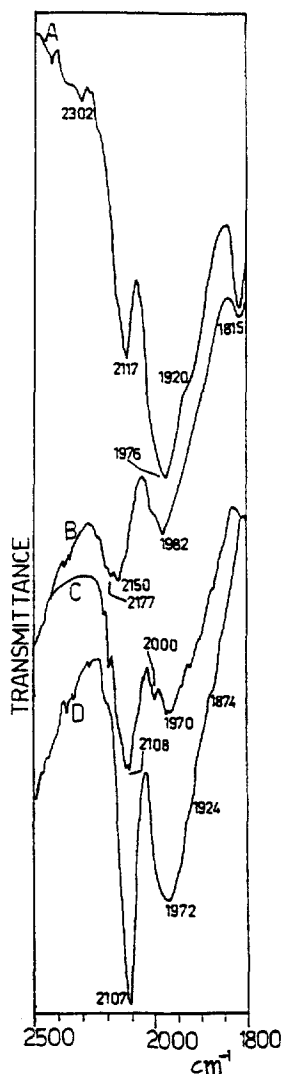


FIGURE 2

FT-IR SPECTRA (KBr)

- (2A) Freshly prepared $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$;
 (2B) $\text{Cu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Cu}$ after 1 month ageing in air.
 (2C) $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ aged two weeks in air.
 (2D) $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ prepared in presence of Cu^{2+} ions.

Ageing of dicopper diacetylide CuC≡C-C≡C-Cu.

Upon ageing in air, the IR spectrum of dicopper acetylide shows the development of the bands at about 1380 and 1460 cm^{-1} (see fig. 1B and 1C vs 1A), while the band at about 1220 cm^{-1} weakens and after 1 month ageing appears just as a shoulder. Fig. 2B shows that after 1 month ageing the original dicopper diacetylide band at 1976 is now at 1982 cm^{-1} while the band at 2117 now appears at 33-60 cm^{-1} higher wavenumber (doublet at 2150 and 2177 cm^{-1}), demonstrating that some degradation of the original polymeric structure occurred with formation of new products.

In particular, we explain the development of the band at 2177 cm^{-1} as due to copper-terminated carbyne formation which we have already shown to absorb in this region^{1,2} and we will show how this interpretation is correct in the following paper⁶. Which kind of mechanism is acting during ageing of these acetylides is still not fully understood, but it is reasonable to think that a solid state coupling reaction of the organic substrate occurs under the action of oxygen present in air leading to the formation of carbonaceous matter⁶ like carbyne and polyynes⁶ (coupling products of diacetylene).

Ageing of dicopper acetylide Cu-C≡C-Cu: proofs of dicopper diacetylide Cu-C≡C-C≡C-Cu formation and solid state coupling reaction.

Fig. 1E shows the FT-IR spectrum of dicopper acetylide Cu-C≡C-Cu aged two weeks in air at room temperature. It appears very similar to the spectrum of three days aged or one month-aged dicopper diacetylide Cu-C≡C-C≡C-Cu (compare with fig. 1B and 1C). Judging from the IR spectra, we can conclude that very similar final products are obtained both starting either from Cu-C≡C-Cu or Cu-C≡C-C≡C-Cu by the action of air. This fact implies that dicopper acetylide is initially converted to its superior homologue dicopper diacetylide and then further solid state coupling reactions lead to the formation of longer chains.

Looking at fig. 2C, which is the detail of two-week aged Cu-C≡C-Cu, it is evident that band position is closer to fig. 2A due to unaged Cu-C≡C-C≡C-Cu than to fig. 2B due to aged Cu-C≡C-C≡C-Cu, hence confirming our interpretation that dicopper acetylide is initially converted into dicopper diacetylide upon ageing.

We have already applied and discussed the Glaser oxidative coupling reaction to dicopper acetylide in order to prepare copper-terminated carbyne^{1,2}, some kind of

solid state oxidative coupling reaction occurs on solid dicopper acetylide exposed to air converting it into dicopper diacetylide. Dicopper diacetylide is even more prone to spontaneous oxidative coupling reaction: after one month ageing in air, when hydrolyzed in 16.5% hydrochloric acid it yields 23.5% by weight of insoluble carbonaceous matter whose FT-IR spectrum is comparable to carbyne prepared by Glaser reaction^{1,2}.

Direct preparation of dicopper diacetylide from acetylene.

It has been reported that dicopper acetylide $\text{Cu-C}\equiv\text{C-Cu}$ can be oxidized with CuCl_2 solution at 80°C and then by air to produce $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$ ³. However this information dates back many decades ago when spectroscopic techniques were not available. In the present work, the re-examination of this problem was conducted with two different approaches. The first approach was to deliver acetylene gas into an ammonia solution of Cu^+ and Cu^{2+} ions at room temperature (while in all other cases $\text{Cu-C}\equiv\text{C-Cu}$ and its homologue have been prepared exclusively from Cu^+ ions in the presence of a reducing agent as hydroxylamine to eliminate all Cu^{2+} ions). In this case the acetylide obtained is darker than that prepared in the absence of Cu^{2+} ions; the FT-IR spectrum of this product is shown in fig. 1D: it is completely analogous to the spectrum of aged dicopper acetylide (fig. 1E) and aged dicopper diacetylide (fig. 1B and 1C). Moreover fig. 2D demonstrates that the $\nu_{\text{C}\equiv\text{C}}$ bands of this acetylide are almost coincident with those of the two-week aged dicopper acetylide (fig. 2D vs fig. 2C).

It is clear that the presence of Cu^{2+} ions in the solution where $\text{Cu-C}\equiv\text{C-Cu}$ is forming causes an immediate oxidation of it to the diacetylide:



Additionally we could consider that Cu^{2+} ions could take the place of Cu^+ ions in the solid "crystal" structure of the acetylide during this synthesis. Probably during solid state oxidation in air also oxidation of Cu^+ ions to Cu^{2+} ions occurs in the acetylide structure.

The other approach used was to prepare $\text{Cu-C}\equiv\text{C-Cu}$ exclusively from Cu^+ in the presence of NH_2OH and then to stir this acetylide into a solution of CuCl_2 (see experimental section) and heating for a long period. The reaction product is different from solid state oxidation product of $\text{Cu-C}\equiv\text{C-Cu}$ and $\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$ as checked by the FT-IR spectrum reported in fig. 3, which shows considerable differences in comparison to the spectra of fig. 1. One of the main feature is the

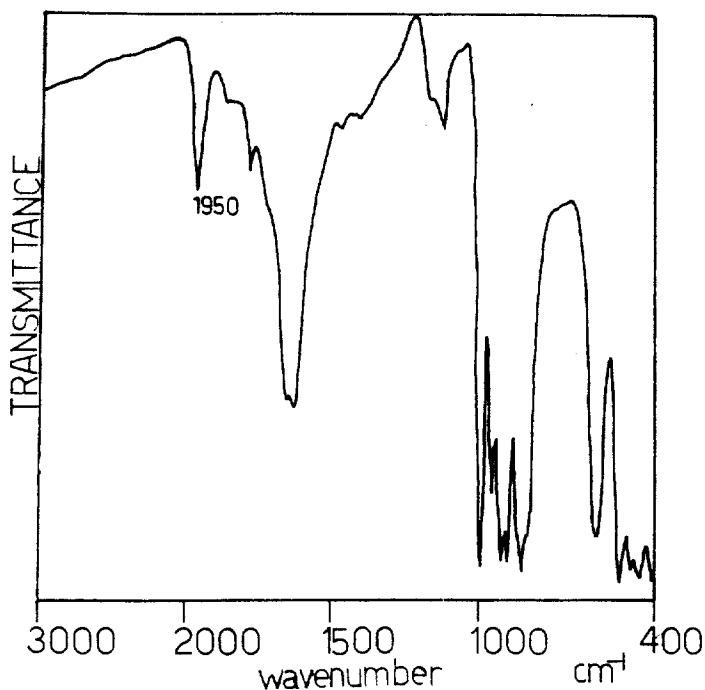


FIGURE 3

FT-IR SPECTRUM (KBr)

Cu-C≡C-Cu oxidized with Cu²⁺ ions at 60°-70°C for 38 hours.

unique band at 1950 cm⁻¹ which could be assigned both to polymeric acetylides¹² or to allenic structures^{7,11} formed by oxidation of terminal Cu(I), e.g.:



Anyway, the acid hydrolysis of this compound demonstrates that extensive coupling reactions occurred since diacetylene and its superior homologues were detected in hydrolysis products. The presence of allenic species was not evident but it is already known that they are present for instance in Mg₂C₃ and upon hydrolysis they are rearranged to the more stable methylacetylene¹³, hence a similar phenomenon could happen also in our case. Ashing of this acetylide derivative has also demonstrated that some depletion/extraction of copper ions occurs in solution so that a considerably lower copper content than the expected one was found suggesting long copper-terminated chains formation (see experimental section).

CONCLUSIONS

We have shown by FT-IR spectroscopy that dicopper diacetylide ($\text{Cu-C}\equiv\text{C-C}\equiv\text{C-Cu}$) can be obtained by reacting butadiyne (diacetylene) with ammonia Cu^+ solution as well as by passing acetylene into a $\text{Cu}^+/\text{Cu}^{2+}$ ammonia solution. Additionally on standing in air also dicopper acetylide ($\text{Cu-C}\equiv\text{C-Cu}$) is initially converted by oxygen to dicopper diacetylide. Dicopper diacetylide is not stable in air but undergoes additional solid state coupling reaction leading to copper-terminated polyynes as recognized by FT-IR spectroscopy, and as suggested by the evolution of a mixture of polyynes by acid hydrolysis of this oxidation product (detected by electronic spectroscopy) and by the formation of an insoluble carbonaceous matter whose spectrum corresponds to carbyne produced by Glaser coupling reaction^{1,2}.

By oxidizing dicopper acetylide with CuCl_2 at 70°C , the product it is not dicopper diacetylide as reported in a very old communication³ but it is a product with a peculiar FT-IR spectrum which could be formulated as $\text{Cu}-(\text{C}\equiv\text{C})_{20}-\text{Cu}$. The band at 1950 cm^{-1} could suggest the presence of an important fraction of cumulenic carbon (β -carbyne), while generally the most common carbyne or carbyne-rich carbonaceous matter prepared up to now consisted of acetylenic carbon chain or α -carbyne. Thermodynamic calculations show that α -carbyne should be more stable and hence more easily obtained than β -carbyne¹⁴.

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