Copper(II) complexes with triphenylphosphine oxide. II. Decomposition of $Cu(OPPh_3)_4X_2 \cdot 2H_2O$

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The data obtained by the study of the decomposition of the complexes $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ (X = Cl, Br) are presented. The possible transformations of the complexes formed by decomposition were studied under different reaction conditions. Different dehydration procedures applied to $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ result in the splitting off of $OPPh_3$ to yield the $Cu(OPPh_3)_2X_2$ complexes. By thermal dehydration without vacuum $Cu(OPPh_3)_2Cl_2$ arises in addition to $Cu_4OCl_6(OPPh_3)_4$. Besides, the preparation of a new orange isomer $Cu(OPPh_3)_2Cl_2$ is also described.

В работе приводятся данные, полученные при изучении разложения комплексов $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ (X = Cl, Br). Изучались возможности взаимных превращений, образовавшихся комплексов, в зависимости от условий реакции. При различных способах дегидратации $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ происходит выделение $OPPh_3$ и образуются комплексы состава $Cu(OPPh_3)_2X_2$. При термической дегидратации без использования вакуума образуется одновременно с $Cu(OPPh_3)_2Cl_2$ и $Cu_4OCl_6(OPPh_3)_4$. В работе описаны и способы приготовления нового оранжевого изомера $Cu(OPPh_3)_2Cl_2$.

Copper(I) complexes and Ph_3PCl_2 are formed in the reaction of copper(I) chloride with triphenylphosphine in acetone—ethanol solutions. After separating the copper(I) complexes, the copper(II) complexes containing triphenylphosphine oxide formed by the solvolysis of Ph_3PCl_2 [1] appear in the reaction solutions. The $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ complex [2] was separated chromatographically on a column of Al_2O_3 from a mixture of copper(II) complexes. This complex was also prepared by a direct synthesis of $CuCl_2$ with triphenylphosphine oxide. In a similar way we prepared $Cu(OPPh_3)_4Br_2 \cdot 2H_2O$ [3], too.

A more detailed study of those complexes has shown that they exhibit some interesting properties. The dehydration of these substances gives rise to the formation of several complexes containing triphenylphosphine oxide the character of which depends on the conditions of dehydration.

The topic of this study is the decomposition of the $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ complexes and the possible transformations of the decomposition products. Moreover, the preparation of the orange modification of $Cu(OPPh_3)_2Cl_2$ by an experimental method based on the decomposition of the complexes with a more complicated coordination sphere is described in this paper.

Experimental

Chemicals, analytical methods, and equipments

Toluene, benzene, and diethyl ether used were anal. grade. They were purified and dried by usual methods. Copper was determined complexometrically using murexide as an indicator while halogenides were determined argentometrically with potentiometric indication of the titration end-point. Carbon and hydrogen were estimated by elemental microanalysis. The melting points were determined using a Kofler block and the infrared spectra were measured with a Perkin—Elmer 225 instrument using the Nujol mull technique. The thermal dehydration was performed in a metal block which ensured a uniform heat supply into the sample at 120—130°C while the thermal dehydration *in vacuo* was carried out in a ground glass apparatus excluding air humidity at 100°C and 2666 Pa.

Results and discussion

Decomposition of the $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ *complexes by thermal dehydration*

By thermal dehydration of the $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ complex the original blue colour changed through green to orange-red. The $OPPh_3$ species was removed from the product by maceration with toluene and the powdered orange-red product thus obtained was studied by means of infrared spectra in the region from 200 to 450 cm^{-1}.

As obvious from Fig. 1, the infrared spectrum of the product obtained is a combination of the spectra of $Cu(OPPh_3)_2Cl_2$ and $Cu_4OCl_6(OPPh_3)_4$.

The formation of the $Cu_4OCl_6(OPPh_3)_4$ complex is interesting with respect to the source of the oxygen atom which occurs in the centre of the tetrahedron formed by copper atoms [4]. The problem of the source of oxygen in an analogous complex containing 2-methylpyridine as a ligand has been already investigated, however, it cannot be concluded univocally

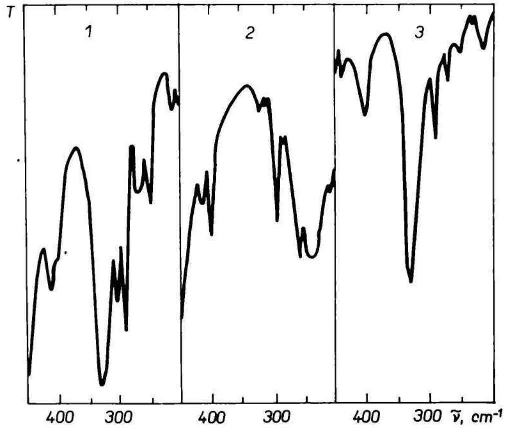


Fig. 1. The infrared spectra.
1. Spectrum of the product after thermal dehydration of $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$; *2.* spectrum of $Cu_4OCl_6(OPPh_3)_4$; *3.* spectrum of $Cu(OPPh_3)_2Cl_2$.

whether the source is water or air oxygen [4]. In order to investigate the effect of water released on the formation of the products of the thermal decomposition of $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ and to obtain solely $Cu(OPPh_3)_2Cl_2$, the thermal dehydration was performed under reduced pressure (2666 Pa) at 100°C with exclusion of air humidity. The 15 hrs' dehydration of $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ yields a mixture of the orange product with a white powder. White $OPPh_3$ was removed by a repeated maceration with toluene, thus obtaining pure orange $Cu(OPPh_3)_2Cl_2$.

For $Cu(OPPh_3)_2Cl_2$ (690.99) calculated: 9.20% Cu, 10.26% Cl, 62.57% C, 4.38% H; found: 9.18% Cu, 10.27% Cl, 61.79% C, 4.30% H. Melting point 173°C.

As to composition, the orange $Cu(OPPh_3)_2Cl_2$ prepared is identical with the yellow $Cu(OPPh_3)_2Cl_2$ which was obtained by the synthesis of $CuCl_2$ with $OPPh_3$ [6] as well as by chromatographic fractionation of the solution after the reaction between $CuCl_2$ and Ph_3P [2]. By thermal decomposition of $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ *in vacuo* we succeeded not only in preparing the orange isomer of $Cu(OPPh_3)_2Cl_2$ but also in obtaining information that the source of oxygen in $Cu_4OCl_6(OPPh_3)_4$ was water. By sucking off water from the reaction medium by means of vacuum during the dehydration of $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ the formation of $Cu_4OCl_6(OPPh_3)_4$ is prevented.

The original green colour of the complex $Cu(OPPh_3)_4Br_2 \cdot 2H_2O$ changes to red-brown during thermal dehydration under reduced pressure. We removed $OPPh_3$ released by decomposition from the product obtained by maceration with toluene and in this way we obtained pure $Cu(OPPh_3)_2Br_2$. This species was also prepared by a synthesis from $CuBr_2$ and $OPPh_3$ [6].

Decomposition of the $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ *complexes in non-polar solvents and over a dehydration agent*

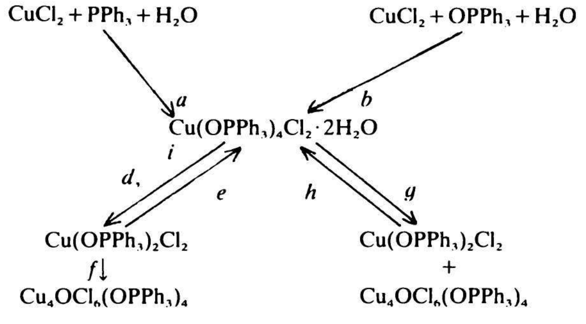
The qualitative estimation of solubility of the $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ complexes has shown that they do not dissolve in benzene and diethyl ether but undergo a decomposition. The orange microcrystalline substance is the final product of the decomposition of the chloro complex. The bromo complex also decomposes and its colour changes from green to red the red microcrystalline substance being the final product. The infrared spectrum of the orange product formed by decomposition of $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ is identical with the spectrum of $Cu(OPPh_3)_2Cl_2$. Similarly the spectrum of the red product formed by decomposition of $Cu(OPPh_3)_4Br_2 \cdot 2H_2O$ is identical with the spectrum of $Cu(OPPh_3)_2Br_2$.

For the dehydration by means of phosphoric oxide the samples were pulverized and allowed to stand over P_4O_{10} in a desiccator. In the course of 2 to 3 days the dehydration of the $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ complexes took place to yield $Cu(OPPh_3)_2X_2$ and $OPPh_3$.

If the mixture of products obtained after dehydration was put into a desiccator over water at 20°C and allowed to stand for 3 to 4 days, $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ was formed anew in all cases.

Transformations of the chloro- and bromotriphenylphosphine oxide complexes of copper(II)

The dependence of the transformations of the chlorotriphenylphosphine oxide complexes on reaction conditions can be described by the following scheme



where *a* — chromatographic fractionation of the product after oxidation-reduction process [2],
b — synthesis [3],
c — thermal dehydration *in vacuo*,
d — dehydration in a non-polar solvent,
e, *h* — reversibility of the process,
f — recrystallization from acetone, benzene or methyl isobutyl ketone,
g — thermal dehydration without vacuum,
— dehydration by means of a dehydration agent.

The thermal dehydration of the complexes $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ ($X = Cl$, Br) without or with vacuum over the dehydration agent as well as the dehydration in a non-polar solvent is not applicable to the preparation of anhydrous compounds of the composition $Cu(OPPh_3)_4X_2$. In all cases studied, except the thermal dehydration without vacuum, the loss of water was accompanied by a simultaneous splitting-off of $OPPh_3$ and $Cu(OPPh_3)_2X_2$ was the only reaction product.

The dehydration of the $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ complex resulted in the formation of the orange $Cu(OPPh_3)_2Cl_2$ complex in all cases. We studied the physicochemical properties of this complex and found that it showed the characteristics different from those of the yellow complex of identical composition [5] which had been for the first time prepared by *Goodgame* and *Cotton* [6].

The dehydration of the $Cu(OPPh_3)_4Br_2 \cdot 2H_2O$ complex led to the formation of $Cu(OPPh_3)_2Br_2$ in all cases. The formation of isomers was not observed.

The results of the study of decomposition products of the $Cu(OPPh_3)_4X_2 \cdot 2H_2O$ complexes may be used for the preparation of several Cu(II) complexes containing $OPPh_3$ as a ligand. It ensues from this study that by changing the reaction conditions it is possible to produce transformations of the complexes of different composition containing equal ligand, *i.e.* triphenylphosphine oxide. The study of these problems is of importance from the view-point of the search for the methods of preparation of the substances of an equal composition but a different structure which show the properties of distorted isomers [7].

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