Synthesis of copper phthalocyaninetetrasulphotetra-carboxylic acid as an initial monomer for the production of phthalocyanine-containing polymers

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INTRODUCTION

Many phthalocyanine-containing polymers have been synthesised in recent decades. The aim of their development was to produce new materials with unique properties such as exceptional heat resistance [1], non-linear optical properties [2], semiconductor properties [3–5], etc. However, studies of the production of phthalocyanine-containing polymers that might be used as dyes are absent. Moreover, polymeric dyes as a special class of pigments have hitherto found no industrial use at all.

The present paper describes a simple method for synthesising a highly soluble derivative of copper phthalocyanine – copper phthalocyaninetetrasulphotetra-carboxylic acid – that is suitable for industrial use. The given monomer is proposed for use in the synthesis of phthalocyanine-containing polymers (oligomers), the end-purpose of which is to create organosoluble high molecular weight dyes for the colouring of plastics.

In previous work by the present authors [6], the production of a phthalocyanine-containing polymer by the polycondensation of copper phthalocyaninetetra-carboxylic acid and diethylene glycol was described. Features of the synthesis – the high temperature, the heterophase aspect, the proneness of the system to gelation, and consequently the poor controllability of the process and of the final properties of the product – force us to seek new means of producing phthalocyanine-containing polymers without complicating the technology.

The main problem encountered in this search is, as before, the low solubility of copper phthalocyaninetetra-carboxylic acid in any solvents (DMSO is the best solvent). This is holding back considerably the possibility of its chemical modification into commercially important products (films).

RESULTS AND DISCUSSION

Copper phthalocyaninetetrasulphotetra-carboxylic acid CuPhc(COOH)₄(SO₃H)₄ was produced by the chlorosulphonation of CuPhc(COOH)₄ (reaction I) by a procedure similar to the production of "direct turquoise light-fast dye" [7] and then by subsequent hydrolysis of the obtained tetrachlorosulphonic derivative (reaction II):

\[ \text{CuPhc(COOH)}_4 + 8\text{ClSO}_3\text{H} \rightarrow \]
\[ \text{CuPhc(COOH)}_4(\text{SO}_2\text{Cl})_4 + 8\text{HCl} \]  
\[ \text{(I)} \]

\[ \text{CuPhc(COOH)}_4(\text{SO}_2\text{Cl})_4 + 4\text{H}_2\text{O} \rightarrow \]
\[ \text{CuPhc(COOH)}_4(\text{SO}_3\text{H})_4 + 4\text{HCl} \]  
\[ \text{(II)} \]

The chemical structure of the product obtained was demonstrated by several independent methods – a chemical method, electron spectroscopy, and elemental analysis.

As CuPhc(COOH)₄(SO₃H)₄ has good water solubility (over 30 wt.% solubility), direct pH-metric titration is possible, in contrast to CuPhc(COOH)₄, which is not.
soluble in water:

\[ \sim\text{CONH}_2 + H_2O + H^+ = \sim\text{COOH} + \text{NH}_4^+ \]

Figure 1 shows two inflection points in different pH regions: the first in the 5.5 region, the second in the 9.5 region. From these data it is evident that there are two different types of acid group in the molecule: the first with NaOH gives a pH-neutral salt (-SO$_3$H group), the second with NaOH gives a pH-alkaline salt (weak organic carboxylic acid).

The amount of alkali consumed in the titration of sulpho groups is equal to that consumed for carboxyl groups. Here it is important to point out that the number of free carboxyl groups itself is equal to 4 on account of their complete regeneration from amide groups, which are formed during the synthesis of CuPhc(COOH)$_4$ by the following mechanism [8].

The carbamide, heated above the melting temperature (135°C), is isomerised into ammonium cyanate, after which it breaks down into ammonia and isocynic acid, which, interacting with carbamide, forms biuret or is isomerised into cyanuric acid:

\[
\begin{align*}
\text{NH}_2\text{CONH}_2 &\rightleftharpoons \text{NHCO} + \text{NH}_3 \\
\text{NH}_2\text{CONH}_2 + \text{NHCO} &\rightarrow \text{NH}_2\text{CONHCONH}_2 \\
3\text{NHCO} &\rightarrow (\text{NHCO})_3
\end{align*}
\]

The ammonia formed goes on the amination of trimellitic anhydride. Isocynuric acid is a very reactive compound (two double bonds) and can react with proton-donor compounds with the addition of a proton and the formation of an amide derivative:

\[
\text{RCOOH} + \text{NHCO} \rightarrow \text{RCOOCONH}_2 \rightarrow \text{RCONH}_2 + \text{CO}_2
\]

Data of reverse pH-metry indicate that there are no free carboxyl groups in the copper phthalocyaninetimescarboxylic acid molecule – they are all in amide form. Consequently, certain endeavors are necessary for the hydrolysis of amide groups to carboxyl groups. As mentioned above, in the final product the number of free carboxyl groups is 4, and consequently the procedure for recovering CuPhc(COOH)$_4$ from CuPhc(CONH)$_4$ can be recognised as good.

Thus, from data of pH-metric titration is can clearly be concluded that the formula of the compound obtained is CuPhc(COOH)$_4$(SO$_3$H)$_4$.

The UV spectra of CuPhc(COOH)$_4$(SO$_3$H)$_4$ in DMSO are completely identical to those for CuPhc(COOH)$_4$ in the same solvent.

EXPERIMENTAL

Synthesis of CuPhc(COOH)$_4$

Quantities of 0.1 mol of CuSO$_4$, 0.18 mol of urea, 0.4 mol of trimellitic anhydride, 0.02 mol of ammonium molybdate, and 0.04 mol of ammonium chloride were ground together thoroughly and sintered at 180°C for 4 h in a 2 L round-bottomed flask with a reflux condenser and a thermometer.

Isolation and purification of CuPhc(COOH)$_4$

The obtained reaction mass was removed, thoroughly ground, and placed in a 2 L round-bottomed flask with a reflux condenser, distilled water was poured over it, it was alkalised with KOH, and then boiled for 15 min. The hot suspension was filtered on a Büchner funnel with a vacuum pump. The operation was carried out 3 times to get rid of biuret entirely, and for high-quality preparation.
of the mass for subsequent stages of purification. The mass was then dried at 100°C in a drying oven. It was then dissolved in 500 mL of 96% sulphuric acid. The solution was heated to 60°C during stirring for 30 min. It was then cooled to room temperature without turning off the stirrer, diluted to 85% with distilled water, and again heated to boiling temperature over a period of 20 min, after which it was diluted to 50%, and, after precipitation, the suspension was cooled and filtered on a Schott funnel, with rinsing several times with distilled water. The precipitate was dried and then ground and boiled in distilled water. The hot solution was refiltered. The given operation was repeated several times until a neutral pH of the filtrate was achieved. The precipitate was dried.

Synthesis of CuPhc(COOH)₄(SO₃H)₄

A quantity of 0.1 mol of CuPhc(COOH)₄ was dissolved in 2 mol of chlorosulphonic acid and heated in a round-bottomed flask to 135°C for 2 h. It was cooled to 0°C, and the unreacted acid was hydrolysed with 100 mL of cold water, added in drops over a period of 1 h.

The CuPhc(COOH)₄(SO₂Cl)₄ precipitate was filtered on a Schott funnel, rinsing with distilled water until the filtrate began to colour appreciably.

The suspension was then dissolved in 50 mL of water and heated to 80°C in a 150 mL round-bottomed flask to hydrolyse the tetrachlorosulphonic derivative to sulphonic acid. The HCl vapours removed from the reaction zone were passed through a 10% aqueous solution of NaOH in a Drechsell vessel, using a low vacuum of the water-jet pump. The temperature was then raised to 100°C and the water was evaporated off. After this, the product was removed and dried in a vacuum drying oven for 1 h at 100°C.

Elemental analysis:

- Found, %: C 38.21; H 1.47; N 9.83; Cu 4.46; O 31.25; S 14.78.
- Calculated, %: C 40.32; H 1.5; N 10.45; Cu 5.93; O 29.84; S 11.96.

From the elemental analysis data it can be seen that the sulphur content was slightly too high. This seems to be due to the residual content of non-washed-out sulphuric acid.

The product yield was 70%.

REFERENCES