

sap is firmly adsorbed on an anion exchanger, but rather little on a cation exchanger. Anthocyanins from fruits or berries behave in the opposite way.

In practice, paper electrophoresis can be used to detect the addition of red beet sap to fruit juices, as only the beet pigments migrate towards the anode in weakly acid solution. An addition of 10 % of red beet sap is easily detected.

Electrophoresis on cellulose columns has been used with some success in attempts to isolate the beet pigments. A very simple apparatus built after the same principle as that described by Porath⁷ was used. The buffer solutions were volatile, consisting of 0.1 M formic acid and 0.1 M pyridine in varying proportions. The separation was generally carried out at a pH about 3.5, because the pigments then can be separated from most proteins and amino acids, which move in the opposite direction. The "main red zone" was eluted from the electrophoresis column and further purified by adsorption on a talc column⁶. Lyophilisation (evaporation from a frozen solution) was generally used for concentration of the solutions, since the pigments are easily changed even during vacuum distillation at low temperature. The dark red solid fractions obtained by this method are at present being further investigated.

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Added in proof: In a recent communication (*Naturwiss.* 43 (1956) 159). O. T. Schmidt and W. Schönleben have arrived at similar results, and, in addition, shown that the beet pigments do not contain nitrogen.

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The Cuprous Salts of some N,N-Disubstituted Dithiocarbamic Acids and their Degree of Polymerisation

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Among the cuprous salts of the N,N-disubstituted dithiocarbamic acids, only the diethyl compound is mentioned in the literature. It was first prepared by Cambi and Coriselli¹. They treated the sodium salt of diethyldithiocarbamic acid in inert atmosphere with cuprous oxide, stirring for about twelve hours; the salt was recrystallized from chloroform + petroleum ether. Fredga² prepared cuprous diethyldithiocarbamate by shaking thiuramdisulphide with copper bronze in chloroform solution, at room temperature. The compound isolated by him consisted of yellow, glistening needles, with a molecular weight of about 1 000 (determined in boiling chloroform). At about the same time, Tamminen and Hjelt³ obtained a mixture of the cupri- and cuprous compounds, by boiling tetraethylthiuramdisulphide in benzene solution with metallic copper.

It was the author's intention to synthesize more of such compounds, and examine their polymerity. An X-ray examination of the cuprous diethyldithiocarbamate was begun in The Inorganic Department of this Institute by Hesse⁴; about the same time a molecular weight determination in boiling carbon disulphide was made, and later, an ultracentrifugation according to Archibald's method. It appeared that the true molecule consists of four formula units. The determination of the structure of the complex now completed, evidently shows that the molecule is tetrameric and that the four copper atoms are situated in the corners of a tetrahedron.

When the cuprous dithiocarbamates were prepared, the thiuramdisulphide was shaken with an excess of copper bronze in carbon disulphide until the colour of the solution became yellow or yellow-brown. After the copper bronze had settled, the solution was filtered and the cuprous complexes were isolated by means of their different solubilities. Several

Table 1.

| No. | CuI-dithiocarbamates | M.p., °C | Crystalline solvent | Mol. wt. | Postulated polymerity | Part. spec. volume in toluene at 25°C | Crystalline form colour |
|-----|---|----------|---|--|-----------------------|---------------------------------------|--------------------------------------|
| 1 | (CH ₃) ₂ NCS ₂ Cu | 270° d | | 831, 865 * | ? | 0.600 | yellow needles |
| 2 | (C ₂ H ₅) ₂ NCS ₂ Cu | 190° d | | 970 * | tetrameric | | yellow needles |
| 3 | (n-C ₃ H ₇) ₂ NCS ₂ Cu | 200° d | ‡ CHCl ₃ , ‡ CS ₂ ‡ C ₆ H ₆ | 684, 725, 705, 733 * 869, 834, 880, 839 † | trimeric | 0.686 | yellow needles or hexagonal crystals |
| 4 | (n-C ₄ H ₉) ₂ NCS ₂ Cu | 113—114° | | 783, 793 † | trimeric | 0.724 | hexagonal crystals |
| 5 | (n-C ₅ H ₁₁) ₂ NCS ₂ Cu | 106—107° | | 1070 †, 857 † | trimeric | 0.765 | yellow crystals |
| 6 | (iso-C ₅ H ₁₁) ₂ NCS ₂ Cu | 300° d | | polymeric ? | high | | yellow leaves |
| 7 | (iso-C ₆ H ₁₃) ₂ NCS ₂ Cu | 165° d | | | | | yellow powder |
| 8 | (sec-C ₆ H ₁₁) ₂ NCS ₂ Cu | 146—147° | | 861 †, 970 † | trimeric | 0.775 | yellow crystals |
| 9 | C ₆ H ₅ CH ₂ NCS ₂ Cu | 190° d | | 950 † | tetrameric | 0.632 | hexagonal crystals |
| 10 | (C ₆ H ₅ CH ₂) ₂ NCS ₂ Cu | 284—286° | | | | | yellow crystals |
| 11 | CH ₃ CH ₂ NCS ₂ Cu | 245° d | ‡ CHCl ₃ | | ? | | yellow needles |
| 12 | C ₆ H ₅ CH ₂ NCS ₂ Cu | 290° d | ‡ CHCl ₃ | | ? | | yellow needles |
| 13 | NCS ₂ Cu | | | | ? | | yellow needles or hexagonal crystals |

1. Uncorrected.

2. Determined in boiling CS₂.

3. Determined by ultracentrifugation according to Archibald's method.

4. Determined in boiling C₆H₆.

solvents were examined as a reaction medium for the above mentioned reaction. However, carbon disulphide proved to be the most suitable. As the cuprous compounds are easily oxidized in solution, and also have a tendency to absorb various impurities on the surface of the newly-formed crystals, repeated re-

crystallisation is required for their purification.

The compounds hitherto prepared are listed in Tables 1 and 2, together with some data. As seen from these tables, some of the compounds are postulated tetrameric

Table 2.

| Substance No. | Cu (calc.) | Cu (found) | H (calc.) | H (found) | C (calc.) | C (found) |
|---------------|------------|------------|-----------------|--------------|----------------|----------------|
| 3 | * 21.21 | 21.25 | 4.88 ** 5.66 | 4.44 5.49 | 30.06 34.32 | 30.00 34.13 |
| 4 | 23.72 | 23.37 | | | | |
| 5 | 21.47 | 21.10 | | | | |
| 10 | — | — | 4.20 | 3.99 | 53.62 | 53.46 |
| 12 | 28.40 | 28.33 | 4.5 | 4.0 | 32.20 | 32.50 |

* Calculated for $(nC_3H_7)_2NCS_2Cu \frac{1}{2} CHCl_3$.

** " " " $(nC_3H_7)_2NCS_2Cu \frac{1}{2} CS_2$.

and some are postulated trimeric. The latter may possibly be built up of copper triangles. Preliminary data from a recently commenced X-ray examination⁴ of one of the postulated trimeric compounds, $(nC_3H_7)_2NCS_2Cu$, seem to support the postulate of its trimerity. It should also be observed here, that several of these trimeric cuprous compounds crystallized with solvents (see Table 1). These solvents could be removed by careful heating *in vacuo* without the crystals being deformed, as far as could be seen. Obviously, these trimeric compounds are so packed that a crystal structure with "hollow spaces" could be well imagined. These "hollow spaces" can thus, partly or entirely, be filled out by the organic carbon chains, provided that these chains are large enough (*e. g.* $(nC_4H_9)_2NCS_2Cu$). They can also be filled by solvents (*e. g.* $(nC_3H_7)_2NCS_2Cu \cdot 1/2 CHCl_3$).

It is remarkable that a change from a tetrameric to a trimeric structure takes place in the series of cuprous *n*-dialkyl-dithiocarbamates if the carbon chain is increased by one carbon atom. It should be observed that the only trimeric copper compounds which, up to this time, have been published, are some esters of phosphoric acid⁵ (*e. g.* $CuClP(OPr-iso)_3$). The cuprous di-*isopropyl*-dithiocarbamate may possibly be high polymeric.

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Determination of Small Amounts of Deuterium Oxide in Water by Infra-red Spectroscopy

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In studies of isotope effects it was of interest to know the absolute deuterium concentration of various deuterium substituted organic compounds. For that reason the compounds were burned to water and the deuterium content of the water was determined by means of infra-red spectroscopy. A method, similar to that of Thornton and Condon¹, but more accurate, has been worked out.