

A Compound between Polyvinylalcohol and Copper(II) Amines

BENGT NORDÉN

Division of Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund, Sweden

This paper describes the formation of a compound between polyvinylalcohol (PVA), which is normally very inert, and copper, if ammonia or an n-alkylamine is present. Though the composition or structure has not yet been revealed, the polarizing property of a stretched sheet of the mixture can justify a preliminary report as it might be of value, *e.g.* in manufacturing of polarizers.*

When mixing a PVA water solution with $\text{Cu}(\text{NH}_3)_4^{2+}$, the deep blue colour is immediately changed into green and the viscosity is strongly increased (with 5% PVA a substantial gel is obtained). If a PVA film is brought in contact with $\text{Cu}(\text{NH}_3)_4^{2+}$, $\text{Cu}(\text{butylamine})_4^{2+}$, or $\text{Cu}(\text{octylamine})_4^{2+}$, the analogous compound is formed, as judged from the absorption spectrum of the film. The reaction appeared irreversible as no copper could be soaked out of the product. The fact that the green colour cannot be obtained with an NaOH alkaline PVA solution (film) by adding a copper(II) salt or by using copper tartrate, makes us believe that the role of ammonia is not only to provide deprotonization in PVA but it also takes part in the compound. An interesting fact is that with triethanolamine the mixture is still deep blue even after evaporation of water to a solid film. Also with $\text{Cu}(\text{propylenediamine})_2^{2+}$ when dissolved in PVA the absorption spectrum is totally unaffected, and the linear dichroism of the stretched film has therefore in this case been assigned to an optical anisotropy of this ion. Such studies of linear dichroism of solutions of certain metal complexes in PVA will shortly be reported elsewhere.¹ It should be pointed out that in no other case has there been any indication of a complex formation between the solute and PVA

* We have recently observed an even more effective polarization with copper(II) acetate dissolved in stretched polyvinylalcohol, probably due to long polymeric Cu-species.

(except for precipitation or gel formation with certain anions, borate, sulphate *etc.*, in higher concentrations, *cf.* "salting out" effect,² "Netzmittellonen",³).

In a solution of 0.02 M $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ the absorbance at 600 nm (CuN_4) is fairly constant (small decrease and shift of maximum to longer wavelength) when increasing the PVA concentration from 0 to 0.1 M (the concentration referring to -OH groups of the polymer). A parallel approximately linear increase of the absorbance at 350–400 nm (*cf.* Fig. 1), how-

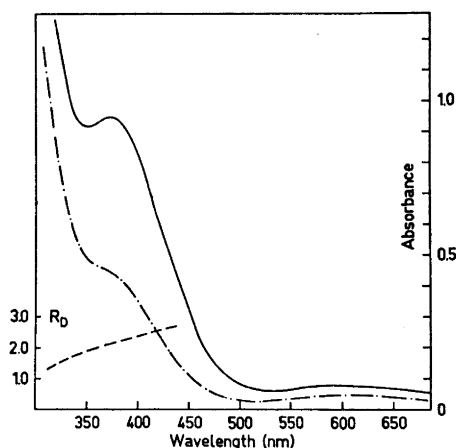


Fig. 1. Polarized absorptionspectra of PVA-film + $\text{Cu}(\text{NH}_3)_4^{2+}$ $A(//)$ —, $A(\perp)$ - - - and $R_D = A(//)/A(\perp)$ - · - (correction made for the absorption of PVA).

ever, indicates the successive formation of $\text{PVA-Cu}_x(\text{NH}_3)_y$. When having a PVA concentration of 0.05 M and Cu 0.01 M, precipitation occurs. However, with the same copper concentration but 0.06 M PVA, the green solution is obtained and if the PVA concentration is further raised the absorbance at 300–400 nm remains constant. Thus it seems reasonable to assume a rather high Cu content – Cu:O of at least 1:5.

In Fig. 1 is depicted the absorption spectra with linearly polarized light, of a PVA film dyed with $\text{Cu}(\text{NH}_3)_4^{2+}$ and stretched to three times its original length: $A(//)$ is the absorbance, the electric vector of light being parallel to the direction of stretch, $A(\perp)$ the corresponding absorbance

with perpendicular polarization. Experimental and methodical details about this type of linear dichroism studies can be found elsewhere.¹⁻⁴ From the fact that the dichroic ratio $R_D = A(\parallel)/A(\perp)$ increases when passing from 300 to 400 nm, it can be concluded that the transition responsible for the shoulder at about 400 nm has a considerably higher degree of parallel polarization than the transition indicated at higher energy (at least in the visualized range). The extraordinary high R_D (4-5) which has been obtained in a few cases with high stretch ratio (major problem: fragility of film) implies a very high degree of orientation (f is at least 0.5-0.8).^{2,3}

From the high degree of orientation and from our experience of the dependence of the orientation effect on the molecular shape, it can be concluded that the chromophore must be situated on a long molecule, i.e. probably on the PVA molecule itself. The requirement of optical anisotropy in the complex (we assume that the transition is connected with the copper atom) makes us rule out the cubic configurations $\text{Cu}(\text{O}-)_6$ (regularly octahedral) and $\text{Cu}(\text{O}-)_4$ (tetrahedral). There remains *trans*- $\text{Cu}(\text{O}-)_2(\text{NH}_3)_2$ (planar), *trans*- $\text{Cu}(\text{O}-)_2(\text{NH}_3)_4$ and *trans*- $\text{Cu}(\text{O}-)_4(\text{NH}_3)_2$. The last mentioned arrangement might be obtained with four polymer chains parallel to the N-Cu-N axes but is not very probable. In the other alternatives, the O-Cu-O axes should be parallel to the direction of orientation, i.e. parallel to the polymer chain. However, it seems difficult to force a copper atom on the line between two adjacent enol oxygens (assuming the Cu-O distance to be 1.9 Å).^{6,7} As a final alternative there remains the possibility that the discussed band is a product of coupling between a series of transitions along the polymer chain. In that case the individual transitions can be allowed to form non-zero angles to the chain axis but still a chelatic bonding is required unless the transitions are not charge transfers between the copper atoms or between the oxygen atoms along the chain.

If a sheet of PVA is soaked in 20 ml 1 M CuSO_4 and 3 ml 25 % NH_3 for 10 min it will become dark green but will keep its size. However, if CuCl_2 is used instead (the same pH, 9.0) the sheet will expand 1.3 times, and have a gluey appearance. Its colour will be blue, changing to dark green after washing with water, but will thereafter give the same spectrum as the product

obtained from CuSO_4 (Fig. 1). The reasons for these peculiarities have not yet been elucidated but it seems probable that the counter ion may influence the formation of intra- and intermolecular hydrogen bonds.

It should finally be noted that the spectrum of our compound resembles the spectra which have been reported for certain "complexes between cuprammonium and glycosides" (see Ref. 9 and references therein). These have been supposed to be 1:1 complexes but their composition seems still to be unknown.

1. Nordén, B. *To be published.*
2. Nordén, B., Håkansson, R. and Sundbom, M. *Acta Chem. Scand. In press.*
3. Larsson, R. and Nordén, B. *Acta Chem. Scand.* **24** (1970) 2681.
4. Nordén, B. *Acta Chem. Scand. In press.*
5. Maeda, H., Kawai, T. and Sekii, S. *J. Polymer Sci.* **35** (1959) 288.
6. Beevers, C. A. and Lipson, H. *Proc. Roy. Soc. (London)* **A 146** (1934) 570.
7. Frasson, E., Bardi, R. and Bezzi, S. *Acta Cryst.* **12** (1959) 201.
8. Saito, S. *Kolloid-Z.* **154** (1957) 19.
9. Reeves, R. E. *J. Am. Chem. Soc.* **73** (1951) 957.

Received November 2, 1971.

Unsaturated γ -Thiolactones

XVI. Alkylation of the Thallium Salt of the 5-Methyl-2-hydroxythiophene System

BJÖRN CEDERLUND and ANNA-BRITTA HÖRNFELDT

Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

In previous work, the 5-methyl-2-hydroxythiophene system was alkylated with methyl iodide and dimethyl sulphate¹ by means of the ion pair extraction method developed by Brändström *et al.*² Using this