CHEMISTRY LETTERS, pp. 735-738, 1977. Published by the Chemical Society of Japan

THE FORMATION OF A STABLE COPPER(II) COMPLEX WITH L-ASCORBIC ACID

Yasuo YAMAMOTO, Keiko ISHIZU, and Yoko SHIMIZU
Department of Chemistry, Faculty of Literature and Science,
Shimane University, Nishikawatsucho, Matsue 690

The formation of stable L-ascorbato(2,2'-bipyridine)copper(II) complex in solution was confirmed and studied chiefly by means of its absorption and CD spectra.

There are a number of reports on the metal catalyzed oxidation of ascorbic acid and the electron transfer reaction involved in them.[1-4] It is generally thought that ascorbic acid is quite easily oxidized, especially in the presence of copper(II) or iron(III). It has been found, however, that the copper(II) complex with its anion is formed in solution, when 2,2'-bipyridine is chelated at the opposite site to it. The strong π acidity of 2,2'-bipyridine seems to stabilise the chelation of the ascorbate anion. The complex in solution is surprisingly stable unless oxygen is introduced.

When an aqueous solution of 2,2'-bipyridinediaquacopper(II) $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$ is poured into a solution of ascorbic acid which is more than five times as concentrated as that of $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$, the solution turns green. This green color remains as long as the $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$ concentration, its ratio to ascorbic acid, and the pH of the solution are kept at considerably lower level. In the case of 1/150 M $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$ and 1/15 M ascorbic acid, after the solution was entirely deoxygenated by bubbling nitrogen, green color did not change and the d-d band of copper(II) was retained even after a month. Along with the increase of either the $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$ concentration or its ratio to ascorbic acid, the green color fades to brown, and a precipitate containing copper(I) follows the color change. When the pH was higher than 2.5, the green complex seemed to become unstable.

As is seen from Fig. 1, the peak which appeared at around 425 nm has a great deal to do with the green color in the solution. Hayakawa et al. have reported that they observed the similar peak at 420 nm during the initial few seconds of the electron transfer reaction between ascorbic acid and copper(II) in an acetate buffer.[2)] The peak in their case was so transient that a rapid scanning spectrophotometer had to be employed for the observation. They have concluded that the peak is attributed to an intermediate complex of copper(II) with the ascorbate anion. In our case, however, the peak did not disappear and it enabled us to use the ordinary spectrophotometer for measurement.

The CD spectrum of this green solution is also shown in Fig. 1. Since the Δε is not so large, one might suspect that this CD may be due to an induced effect rather than a vicinal effect, or that the ascorbate anion may be monodentate even if it is coordinated. Therefore, the CD of a similar solution, in which nickel(II) was substituted for copper(II), was examined. Although no CD was observed when the pH was low(2.5), it began to appear with the increase of pH(over 7.0), its θ value reaching a magnitude similar to that of copper(II) complex. This change showed itself in the resutant greenish yellow of the solution, which indicates the coordination of ascorbic acid to nickel(II). In addition, when bis(2,2'-bipyridine)nickel(II) $[\mathrm{Ni\ bip_2}]^{2+}$ was employed in place of $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$, no CD spectrum could be obtained. Even when the pH of the solution was increased, an appreciable change was not observed. On the basis of these facts, the contribution of an induced effect on the CD of the copper(II) complex can be excluded. Moreover, since neither ascorbic acid nor its radical nor $[\mathrm{Cu\ bip(OH_2)_2}]^{2+}$ has an absorption at around 410 nm and 425 nm, the CD and the absorption spectra in this region strongly support the coordination of the ascorbate anion to copper(II). It can be said, therefore, that the CD is attributed to the vicinal effect of coordinated ascorbic acid.

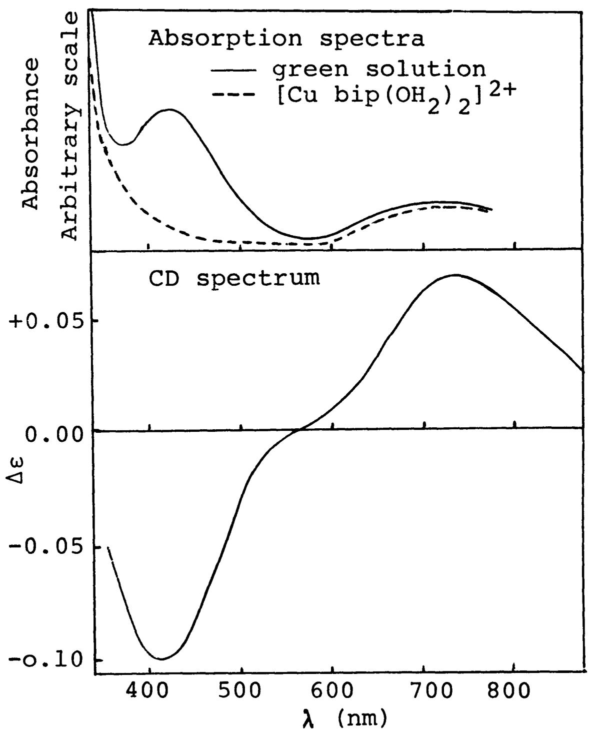

Fig. 1

In the case of the reaction of [Cu bip_2]$^{2+}$ with ascorbic acid, a rapid reduction was observed, and the solution turned brown in a minute. The electron transfer reaction from ascorbic acid to copper(II) has been reported[3)] to be of second order with regard to the copper(II) concentration. This means that the intermediate should be the ascorbate bridged binuclear complex. Because an ascorbate anion can be coordinated to [Cu bip_2]$^{2+}$ only as a monodentate ligand, it tends to bridge two copper(II) ions; the monodentate ascorbate can not be so stable (fig. 2).

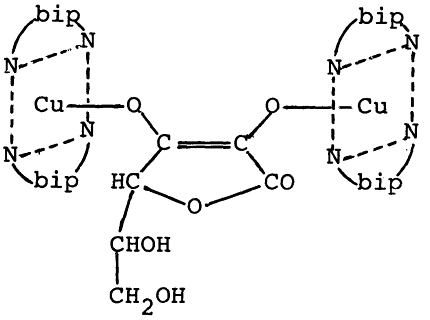

Fig. 2

Table 1. The observed θ values.

[Cu bip$(OH_2)_2$]$^{2+}$ = 1/140 M

[AH_2]	pH	θ° (410 nm)	θ° (720 nm)
1/14 M	2.34	3.79	2.38
3/14 M	2.17	6.34	3.98
5/14 M	2.02	7.59	4.76
6.5/14 M	—— 6)	24.50	——

From these facts, it has become clear that the ascorbate anion is coordinated, as a bidentate ligand, with its two oxygen atoms of the enol groups rather than those of the other groups. Its asymmetric carbon atoms are thus forced out of the chelate ring; this configuration is consistent with the observed small Δε value. It was observed that at much higher concentration of ascorbic acid two [Cu AH bip]$^+$ (AH is ascorbate anion) were bridged by the third ascorbate anion probably in a way similar to Fig. 2, and the electron transfer began to occur. The reason why [Cu AH bip]$^+$ requires such higher concentration than [Cu bip_2]$^{2+}$ does for its reduction is presumably because its π accepting character is weaker than the other. When the concentration of [Cu bip$(OH_2)_2$]$^{2+}$ was 1/140 M and that of ascorbic acid was lower than 5/14 M, the solution maintained a constant pH (table 1). But when the concentration of ascorbic acid was higher than 1/2 M, the pH decreased gradually during the measurement, suggesting the reduction of copper(II). The pH drift was faster with the higher concentration of ascorbic acid.

During the measurement of the CD spectra, the observed θ value increased with the increasing concentration of ascorbic acid (Table 1), indicating the equilibrium:

$$[\mathrm{Cu\ bip(OH_2)_2}]^{2+} + \mathrm{AH}^- \rightleftharpoons [\mathrm{Cu\ AH\ bip}]^+ + 2\ \mathrm{H_2O}$$

The constant of this equilibrium was estimated using the data in Table 1. Its logarithm seems to fall between 2.4 and 2.6, which is significantly larger than the 1.57 previously reported.[2,4] The reason can be that, in the present complex, a cooperative effect may occur between the π systems of 2,2'-bipyridine and ascorbate anion which are the strong π acceptor and the π donor respectively, and reinforce the chelation of ascorbate anion.[5] Thus both of the copper(II)-oxygen linkages are so firm that they prevent the formation of the ascorbate bridged binuclear complex. The situation is quite similar to that of the ternary copper(II) complex with 2,2'-bipyridine and pyrocathecol.[5] From the facts that the electron of the chelated ascorbate is not transferred to copper(II) ion and that the intermediate of the electron transfer reaction is ascorbate bridged binuclear complex, it is suggested that the electron is transferred not through the σ bond but the pπ-dπ interaction between oxygen atom of ascorbic acid and metal ion.

The isolation of the complex is not yet completed. There seems to be a considerable difficulty in the crystallization. We are still performing the study on the isolation of the complex.

REFERENCES AND NOTE

1) A. Weissberger, J. E. Luvalle, and D.S. Thomas, J. Am. Chem. Soc., 65, 1934(1943). A. Weissberger and J.E. Luvalle, J. Am. Chem. Soc., 66, 700(1944). M.M.T. Kahn and A.E. Martell, J. Am. Chem. Soc., 90, 3386(1968); 91, 6011(1968); 91, 4688(1969). Y. Kurimura, R. Ochiai, and N. Matsuura, Bull. Chem. Soc. Jpn., 41, 2234(1969).

2) K. Hayakawa, Y. Hayashi, and S. Nakamura, Presented at the 26th Conference on Coordination Chemistry of the Chemical Society of Japan. Sapporo, August, 1976.

3) K. Hayakawa, S. Minami, and S. Nakamura, Bull. Chem Soc. Jpn., 46, 2788(1973).

4) M. M. T. Kahn and A. E. Martell, J. Am. Chem. Soc., 89, 4176(1967).

5) R. G. Riesser and H. Sigel, Inorg. Chem., 9, 1238(1970).

6) Note to Table 1: In the CD measurements, a dilute sodium hydroxide solution was added until the highest θ was obtained at 410 nm, the Δε in Fig. 1 is based on this θ, and the Δε's at the other wavelengths in the figure were obtained by the rule-of-three. The pH could not be measured because of its rapid drift.

(Received March 19, 1977)