

## Effect of Solvent and Strong Base on Electrochemical and Chemical Behaviour of Copper Tetraaza Macrocyclic Complex

JÁN LABUDA, VLADIMÍR PLASKOŇ

*Department of Analytical Chemistry, Slovak Technical University, 812 37 Bratislava, Czechoslovakia*

and VITALY V. PAVLISHCHUK

*Institute of Physical Chemistry, Ukrainian Academy of Sciences, 252 028 Kiev, U.S.S.R.*

(Received July 27, 1987)

### Abstract

Reactions of copper(II) complex with tetrabenzo-[b, f, j, n][1, 3, 9, 13]tetraazacyclohexadecine (TAAB) as a Lewis acid have been studied. Coordination of solvent molecules and stabilization of the copper(II) oxidation state according to solvent donor properties has been confirmed. The product of hydroxyl ion nucleophilic addition has been isolated and characterized. Differences in electrochemical as well as chemical reduction and reoxidation of the complex in acidic and basic medium have been investigated and the reaction mechanism is discussed.

### Introduction

The axial ligand is, together with the nature of the donor atoms as well as with  $\sigma$ -donor and  $\pi$ -acceptor behaviour of the equatorial cyclic ligand, a factor determining the reactivity of macrocyclic complexes of transition metals. The additional ligand plays an extraordinarily important role in the activity of natural macrocyclic complexes. The formation of copper pentacoordinated states has been studied by interactions of solvents as well as monodentate ligands (most often anions of inorganic acids) with  $\text{CuN}_4$  [1–8] and  $\text{CuN}_2\text{S}_2$  [9] complexes. It has been found that the equilibrium constant of axial ligand addition is influenced in a decisive way by the structure of the macrocyclic ligand, thus by electronic factors and deformation of the coordination unit. The most stable adducts form complexes with the greatest deformation from square-planar surrounding the copper atom. Herewith the Cu(I) complexes form the most stable adducts with  $\pi$ -acids and the Cu(II) complexes with  $\sigma$ -donors [1].

Sixteen atoms in the cycle of the ligand TAAB (tetrabenzo[b, f, j, n][1, 5, 9, 13]tetraazacyclohexadecine) form a more flexible set than there is in a fourteen-member macrocycle which fully encircles the copper atom [10]. The TAAB ligand possesses at

the same time a high delocalized electron structure. Both these factors cause easy Cu(II) to Cu(I) reducibility with respect to other tetraaza macrocyclic complexes, generally stabilizing the oxidation degree of Cu(II). The mentioned factors also explain the indifference of  $\text{Cu(TAAB)}^+$  to  $\pi$ -acid ligands [1] and substantiate the assumption for  $\text{Cu(TAAB)}^{2+}$  interaction with electron-donor particles.

In neutral as well as weak alkaline solution  $\text{Cu(TAAB)}^{2+}$  is changed into the form which is reduced by ascorbic acid [11, 12] as well as by hydroxylamine [13] substantially faster than the initial complex. The character of this interaction, interesting especially from the point of view of the oxidase catalytic effect of the complex [14], has not been studied in detail.

This paper deals with the study of interactions of  $\text{Cu(TAAB)}^{2+}$  as an acid understood in the Lewis sense. The purpose of the paper is to give the characterization of such interactions, to detect the reaction site on the complex particle and to know the reasons for the Cu(II) redox reactions.

### Experimental

$\text{Cu(TAAB)(NO}_3)_2$  was synthesized as described previously [15];  $\text{Cu(TAAB)NO}_3$  was prepared following a literature method [16]. All other chemicals used were reagent-grade. Solvents were purified by double distillation and dried under molecular sieves Linde 5 Å. Argon was employed as an inert gas. The supporting electrolyte used in the electrochemical measurements was 0.1 M  $\text{NaClO}_4$ . Kinetic measurements were made in Britton–Robinson buffer solutions with constant ionic strength of 0.1 M ( $\text{KNO}_3$ ).

The electronic spectra were monitored with a Specord UV–Vis spectrometer (Zeiss, Jena). The infra-red spectra were measured with the Specord IR spectrophotometer (Zeiss, Jena). Potentiometric measurements were made with the potentiometer OP-205 (Radelkis, Budapest).

Voltammetric measurements were made with the Polarographic analyser PA-2 (Laboratorní přístroje, Prague). The indicating electrode used was the vitreous carbon disc electrode as well as the platinum disc microelectrode. The reference electrode used was the saturated calomel electrode with the bridge filled with 0.1 M NaClO<sub>4</sub> in the corresponding solvent. The auxiliary electrode used was the extensive platinum electrode. Changes of dioxygen concentration were measured voltammetrically with the Polarograph OH-202 (Radelkis, Budapest) with the mercury drop electrode ( $t_1 = 5.4$  s,  $w_r = 7.7 \times 10^{-4}$  g s<sup>-1</sup>,  $h = 53$  cm) and with the saturated calomel electrode.

Coulometric measurements were made with the potentiostat Type OH-405 and with the integrator Type OH-404 (Radelkis, Budapest). The working electrode used was the double platinum net, the reference electrode being the same as in the voltammetric measurements; the auxiliary electrode used was the graphite electrode. All measurements were made at the constant temperature 25.0 °C.

## Results and Discussion

### Influence of Solvent

With respect to the restricted solubility of the macrocyclic complex the systematic study could be made only in solvents with a certain polarity. The cyclic voltammograms of Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> represent a pair of peaks corresponding to the one-electron reduction and subsequent oxidation of the complex particle. In water and partly also in ethanol and methanol, as well, the picture is more complicated due to adsorption of the complex. The difference of peak potentials  $\Delta E_p$  lies within the range 0.07 up to 0.14 V and the peak current ratio  $i_{pa}/i_{pc}$  is near to one (Table I). Both redox processes are quasi-reversible which is in accordance with the statement for acetonitrile [17]. The halfwave potential (calculated as the arithmetic mean of  $E_{pc}$  and  $E_{pa}$  potentials) markedly

TABLE I. Electrochemical Data of Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> in Various Solvents<sup>a</sup>

Solvent	Donor number (kcal mol <sup>-1</sup> )	$E_{1/2}$ (V)	$\Delta E_p$
Nitrobenzene	4.4	0.24	0.090
Acetonitrile	14.4	0.13	0.100
Water	18.0	0.05	0.070
Methanol	19.0	0.11	0.095
Ethanol	20.0	0.09	0.145
Dimethylformamide	26.6	0.05	0.080
Dimethylsulphoxide	29.8	-0.03	0.085

<sup>a</sup>0.1 M NaClO<sub>4</sub> supporting electrolyte, platinum disk as a working electrode,  $E_{1/2}$  V vs. 4 M LiCl SCE,  $\Delta E_p$  given for scan rate 0.1 V s<sup>-1</sup>.

depends on the solvent used (Table I). In the solvent mixture the potential was measured lying between the values determined in the pure solvents. In the control measurement of the redox pair ferrocenium/ferrocene the difference  $\Delta E_p = 0.06$  up to 0.09 V, where  $E_{1/2}$  changed depending upon the kind of solvent within the range 0.400 up to 0.470 V.

The shift of  $E_{1/2}$  of the complex towards the negative values of the potential shows the stability of coordination of the solvent molecule to the copper(II) complex in comparison with that of copper(I). Table I contains data on the  $E_{1/2}$  dependence on the donor number ( $DN$ ) characterizing the donor properties of solvent. In the solvents used the dependence appears to be linear with the slope  $-0.010$ . The intercept on the ordinate axis equal to 0.286 V represents the value  $E_{1/2}$  in the medium with  $DN = 0$ . With respect to the  $DN$  definition (solvation heat of SbCl<sub>5</sub>, kcal/mol [18]) the  $E_{1/2}$  dependence indicates the enthalpic nature of the solvent binding to Cu(TAAB)<sup>2+</sup>.

The electrochemical data have confirmed the assumption on interaction of Cu(TAAB)<sup>2+</sup> with the electron-donor molecules. The Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> complex is probably fully dissociated in all the solvents used and the complex cation is solvated in the axial position of copper. In some other copper complexes the coordination of water, acetonitrile, pyridine, imidazole, cyanide, etc. causes an increase in the wavelength of the d-d band with a simultaneous increase of the extinction coefficient [19–21] and for pentacoordinated copper(II) compounds the square-pyramidal or trigonal-bipyramidal structure has been proposed [22]. However, the electronic spectra are not a sufficient diagnostic criterium of the copper(II) geometric environment. The Cu(TAAB)<sup>2+</sup> spectrum in all solvents under investigation is practically identical with that in water [16]. The redox potential differences indicate the effect of apical coordination of the copper(II) state.

The  $E_{1/2}$  changes in general indicate the way to investigate the donor abilities of the solvent experimentally [18]. The Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> complex is thus appropriate for judging the donor effect of the axial molecule. For similar reasons the dioxin complexes with transition metals [23] as well as the tetraaza macrocyclic nickel complexes [18] have been used.

### Influence of Strong Base

#### (a) The Cu(TAAB)<sup>2+</sup> reaction with hydroxyl ions

The reaction of the macrocyclic complex with alkali hydroxide has been followed potentiometrically, spectrophotometrically as well as voltammetrically in aqueous as well as non-aqueous solutions. During the potentiometric titration of  $1 \times 10^{-3}$  M Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> with  $9.8 \times 10^{-3}$  M NaOH in aqueous medium without CO<sub>2</sub> a potential jump has

been recorded corresponding *ca.* to 2.5 units of pH (pH 7 up to 9.5). The potential has fixed relatively fast. The molar ratio NaOH:Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> equal to 1:1 and the value of the equilibrium constant  $1.7 \times 10^{-7}$  correspond to the inflex point of the titration curve. In excess of NaOH a red-brown precipitate has been separated. A similar potential jump and stoichiometric ratio have been observed during Cu(TAAB)<sup>2+</sup> titration with KOH in ethanolic medium but the precipitate is not formed in excess of hydroxide. In ethanolic solution alkalimetric titration of the reduced form of the complex (insoluble in water) has also been made. In this case the sharp potential jump was not observed, however, a small change of the potential compared to the blank experiment without Cu(TAAB)<sup>+</sup> has confirmed the consumption of OH<sup>-</sup> ions.

The reaction of Cu(TAAB)<sup>2+</sup> with the OH<sup>-</sup> ions is connected with the change in the visible region of the electronic spectrum. A relatively intensive absorption band is observed within 450 to 500 nm where the initial complex possesses only a few intensive shoulders. In aqueous medium the maximum of the band lies at 490 nm and at 425 nm the isosbestic point is to be found. The band intensity is proportional to the NaOH:Cu(TAAB)<sup>2+</sup> molar ratio. In the Britton-Robinson buffer solutions of pH 9 up to 11.5 the extinction coefficient of this band increases gradually with pH up to  $7600 \text{ M}^{-1} \text{ cm}^{-1}$ . The increase of optical density to the relatively stable value during some minutes shows a relatively fast chemical reaction. After a longer period (several hours) the decrease in band intensity as well as the formation of the precipitate were observed. At pH 6 up to 9, however, greater changes in the Cu(TAAB)<sup>2+</sup> spectrum were not observed.

In non-aqueous media the maximum of the given band is situated as follows: in ethanol 465 nm, in acetonitrile 455 and 500 nm and in dimethylsulphoxide 480 nm. The rate of reaction of the complex with NaOH decreases markedly on going from ethanol to dimethylsulphoxide. In ethanol and acetonitrile solutions, similar to in water, the decrease in intensity of the absorption band occurs after several hours and a new band appears at 710 nm. In dimethylsulphoxide, however, the spectrum is much more stable.

The voltammetric picture of the complex does not change with an increase in alkalinity. In aqueous buffer solutions of pH 3 up to 10 the quasi-reversible redox process on platinum as well as on vitreous carbon is characterized by constant value  $E_{1/2} = 0.05 \text{ V}$ . The dependence of anodic and cathodic peak potential difference  $\Delta E_p$  on the scan rate within the range 0.02–0.50 V s<sup>-1</sup> is unchanged within the whole interval pH 3 up to 10 and leads to the value of the rate constant of electrode reaction  $k_{s,h} = 1.8 \times 10^{-3} \text{ cm s}^{-1}$  under the assumption of diffusion coef-

ficient  $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . The stable value of the Cu(TAAB)<sup>2+</sup> reduction potential within the pH range 3–10 confirms that the OH<sup>-</sup> ion does not participate in the process of electron exchange.

The Cu(TAAB)<sup>2+</sup> interaction with OH<sup>-</sup> is reversible. After acidification of the alkaline solution of the complex through the addition of perchloric acid, brown CuTAAB<sup>2+</sup> is obtained. Reversibility has also been noted in non-aqueous media in the interaction of the blue reduced form of the complex with OH<sup>-</sup>. In strong alkaline solution, however, the disproportionation of copper(I) occurs and after acidification with HClO<sub>4</sub> brown Cu(TAAB)<sup>2+</sup> is observed.

The experiments carried out have confirmed the acid character of the complex. Titrations in alcoholic solution have also been made as the determination of weak acids is usually made in this medium. It is, however, possible that in alkaline solution ethanolate also reacts with the electrophilic complex. The macrocyclic complex possesses more reaction centres for the hydroxyl ion (central atom, ligand). In order to detect the reaction site of the complex particle the red-brown reaction product has been characterized.

#### (b) Characterization of the red-brown reaction product

The product of the reaction of Cu(TAAB)<sup>2+</sup> with excess of NaOH in water non-buffered medium has been isolated in the solid state and purified. *Anal.*, C, 59.85; H, 4.18; N, 10.41; Cu, 11.90%. In comparison with the initial Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub> the carbon content and that of hydrogen has been increased by 5% and 0.8%, respectively and the nitrogen content has been decreased markedly by 3.3%. This analysis stands in good agreement with data calculated for Cu[TAAB-(OH)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub>: C, 61.33; H, 4.01; N, 10.23; Cu, 11.59%, which may be expected on the basis of analogy with the products of other reactions of nucleophilic addition to Cu(TAAB)<sup>2+</sup> [24, 25]. The lower found carbon content is due to the difficult combustibility of the complex.

The data of the infra-red spectrum of the reaction product are given in Table II together with those for Cu(TAAB)(NO<sub>3</sub>)<sub>2</sub>. The assignments of bands has been made following ref. 17. In the reaction product the shift of benzene ring absorption bands, the decrease in intensity of the C=N vibration band, a new strong band at  $1525 \text{ cm}^{-1}$  as well as three new broad bands in the range 3300–3600 cm<sup>-1</sup> are observed. A similar character of spectrum change has been described in refs. 24 and 26 and has been explained through the formation of a partly delocalized system of bonds with the nucleophilic addition of the substituent to the C–N bond in copper, nickel and palladium complexes with the TAAB ligand. Through the reaction of Pd(TAAB)<sup>2+</sup> with OH<sup>-</sup> Pd[TAAB-(OH)<sub>2</sub>] formation has been proposed, however, the OH band data were not given [26].

TABLE II. Infrared Spectral Data of the Complexes in Nujol (band maxima in  $\text{cm}^{-1}$ )

Assignment	Cu(TAAB)(NO <sub>3</sub> ) <sub>2</sub>	Cu[(TAAB)(OH) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub>
OH		3550, 3400, 3300 broad
Benzene I	1620sh, 1605s	1615sh, 1605s
Benzene II	1585s	1575s
C=N	1560s	1555sh, w, 1525s
Benzene III	1520sh, 1485s	1510sh, w, 1490sh, 1485sh
Benzene IV	1460vs, 1440sh	1460 doublet, s, 1445sh

TABLE III. Spectral and Voltammetric Data of the Complexes<sup>a</sup>

Solvent	Cu(TAAB)(NO <sub>3</sub> ) <sub>2</sub>		Cu[(TAAB)(OH) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub>	
	$\lambda_{\text{max}}$ (ε)	$E_{1/2}$	$\lambda_{\text{max}}$ (ε)	$E_{1/2}$
Acetonitrile	470sh (1000)	0.13	465 (7500)	0.13
Dimethylsulphoxide	480sh (500)	-0.03	470 (10000)	-0.03

<sup>a</sup> $\lambda_{\text{max}}$  in nm, ε in  $\text{M}^{-1} \text{cm}^{-1}$ ,  $E_{1/2}$  in V vs. 4 M LiCl SCE.

The reaction product is well soluble in non-polar organic solvents which confirms its electroneutral character. The electronic spectrum shows the absorption band within the range 450–500 nm (Table III) the intensity of which in acetonitrile decreases during several hours. This decrease is the same as in the case of alkalimetric titration (see part (a)). The band is again similar to that of Cu[TAAB(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] for which  $\lambda_{\text{max}} = 450 \text{ nm}$ ,  $\epsilon = 17\,200 \text{ M}^{-1} \text{cm}^{-1}$  have been determined [24]. Voltammetric data of the product are given in Table III. No change of redox behaviour after the addition of OH groups as well as the marked influence of solvent as in the case of Cu(TAAB)<sup>2+</sup> follow from these. Axial positions in the complex particle are thus accessible to the solvent molecule.

#### (c) Chemical redox reactions of the complex

The observed acid properties of the copper complex make it possible to explain the reciprocal dependence of the rate of Cu(TAAB)<sup>2+</sup> reduction by ascorbic acid (A) on the H<sup>+</sup> concentration documented by experimental data in ref. 11. Considering the constant  $K_2 = 1.7 \times 10^{-7}$  corresponding to the jump on the potentiometric titration curve of the complex, the relation for rate constant of the Cu(TAAB)<sup>2+</sup> reduction has for the pH range 2.5 up to 7 the form

$$k_{\text{obs}} = \frac{k_1 K_1 c(\text{A})}{K_1 + c(\text{H}^+)} + \frac{k_2 K_1 K_2 c(\text{A})}{(K_1 + c(\text{H}^+))(K_2 + c(\text{H}^+) )}$$

where  $K_1 = 9.12 \times 10^{-5}$  is the dissociation constant of ascorbic acid [27],  $k_1 = 7.08 \text{ M}^{-1} \text{s}^{-1}$  [12] and  $k_2 = 5 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$  for 25.0 °C where  $c(\text{Cu}$

(TAAB)<sup>2+</sup>) =  $3 \times 10^{-5} \text{ M}$  and  $c(\text{A})$  up to  $4 \times 10^{-3} \text{ M}$  were used. For pH < 3.5 the pH influence of  $k_{\text{obs}}$  is thus connected with the first degree of dissociation of ascorbic acid (the monoanion of the latter reacts). At higher pH the reaction of ascorbate anion with the monodeprotonized form of the macrocyclic complex (see part (d)) must be considered where the first member of the right part of the rate equation may be neglected with respect to the inequality  $k_1 \ll k_2$ . The equation is afterwards that of a straight line going through the origin of the coordinate system (the correlation coefficient  $r = 0.9996$ ). With respect to the determined agreement of electrode reduction rates of pursued forms of the complex the difference in rates of their chemical reduction is obviously affected by the mechanism of the chemical reaction.

The increased rate of chemical reduction of Cu(TAAB)<sup>2+</sup> could be manifested in its catalytic activity [14]. Through the polarographic monitoring of the concentration of dissolved dioxygen ( $E = -0.45 \text{ V}$ ,  $c(\text{Cu(TAAB)}^{2+}) = 3 \times 10^{-5} \text{ M}$ ,  $c(\text{A}) = 3 \times 10^{-3} \text{ M}$ , pH 6–8, 25.0 °C) it has been found that in spite of a substantially higher rate of complex reduction in neutral and weak alkaline medium the increase in rate of catalytic oxidation of ascorbic acid does not occur. The same fact has been noted in studying the Cu(TAAB)<sup>2+</sup> reaction with hydroxylamine [13]. The cause of this is obviously the method of reoxidation of the Cu(I) complex.

To explain the reoxidation of the Cu(I) complex we have carried out electrochemical experiments. For the coulometric reduction of Cu(TAAB)<sup>2+</sup> at -0.3 V and for subsequent oxidation of the formed Cu(TAAB)<sup>+</sup> at +0.3 V after saturation of the solution by dioxygen, the same charge in water (buffer solution

of pH 4.0), dimethylsulphide as well as in ethanol has been consumed corresponding to the exchange of one electron per complex particle. The same result has been obtained with KOH addition in double molar quantity against the Cu complex. This confirms that the copper(I) complex is stable against dioxygen both in weakly acidic and weakly alkaline medium under voltammetric as well as coulometric conditions. In comparison with many other Cu(I) complexes this behaviour of  $\text{Cu}(\text{TAAB})^+$  is peculiar.

In the aprotic medium of dimethylsulphoxide the reaction of  $\text{Cu}(\text{TAAB})^+$  with superoxide  $^{\cdot}\text{O}_2^-$  has been confirmed. The cyclic voltammogram obtained at the polarization of the platinum electrode up to  $-1.0$  V has contained neither  $\text{Cu}(\text{TAAB})^+$  nor  $\text{O}_2^-$  counter peaks which can be observed on voltammograms of  $\text{Cu}(\text{TAAB})^{2+}$  and  $\text{O}_2$ , respectively. The same status has been found in the solution containing a small excess of KOH. Fast reoxidation of blue  $\text{Cu}(\text{TAAB})^+$  by superoxide to brown  $\text{Cu}(\text{TAAB})^{2+}$  has also been confirmed under coulometric conditions. Acids ( $\text{HClO}_4$ , phenol) as well as the easily oxidizable substrate (glucose) that cause the destruction of superoxide have made the reoxidation of copper(I) complex impossible by which it has been confirmed that  $^{\cdot}\text{O}_2^-$  is the true oxidizing agent.

In aqueous acid and weak alkaline media catalysis of the electrode reduction of dioxygen in the presence of  $\text{Cu}(\text{TAAB})^{2+}$  has been found, which has been explained through the interaction of Cu(I) complex with the primary product of  $\text{O}_2$  reduction [28]. In spite of the known instability of superoxide in water solutions [29] we assume in agreement with refs. 30 and 31 that the Cu(I) complex is reoxidized at the catalytic oxidation of the substrates in the aqueous weak acidic solutions by the  $\text{HO}_2^{\cdot}$  radical formed in a chemical way [14]. The reaction of  $\text{HO}_2^{\cdot}$  with  $\text{Cu}(\text{TAAB})^+$  is sufficient in these solutions to compete with the  $\text{HO}_2^{\cdot}$  disproportionation. For the first reaction the rate constant is estimated  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  [32] whilst for the second reaction as  $k(\text{HO}_2^{\cdot}) = 8.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  [29].

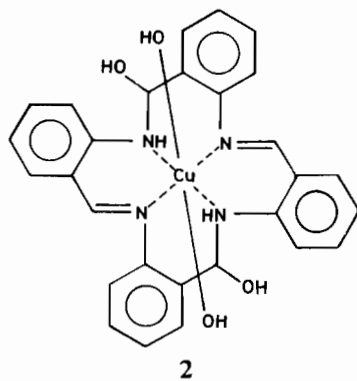
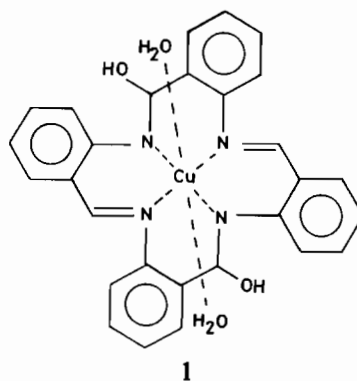
However, in neutral and weak alkaline media besides the change of the Cu complex superoxide also deprotonizes ( $\text{p}K_a = 4.69$  [29]). However the reoxidation of most metals and complexes through  $^{\cdot}\text{O}_2^-$  does not occur because in contrast to  $^{\cdot}\text{HO}_2$  the  $^{\cdot}\text{O}_2^-$  must be probably coordinated in the first coordinating sphere of metal [29]. This is apparently the cause of the decrease in the catalytic effect of the complex in our case.

#### (d) Proposal of reaction products

The experiments have confirmed the more complicated character of the reaction of Cu(II) as well as Cu(I) complexes with a strong base. In neutral and weak alkaline solutions the copper complexes react as very weak monoprotic acids. This acid character is

due to the deprotonization of the  $\text{H}_2\text{O}$  molecule bonded in the axial position or due to binding of the  $\text{OH}^-$  in this position. This reaction does not lead to a change in the electronic spectrum which is determined predominantly by the macrocyclic ligand. As a consequence of the presence of  $\text{OH}^-$  in the axial position a high rate of Cu(II) complex reduction by the ascorbic anion as well as by hydroxylamine is observed.

At higher  $\text{OH}^-$  concentrations the  $\text{Cu}[(\text{TAAB})(\text{OH})_2](\text{H}_2\text{O})_2$  adduct is formed. The equilibrium constant of adduct formation is rather low indicating the dependence of optical density on pH. The adduct formation reaction rate depends on the reaction medium. Localization of OH groups on the macrocyclic ligand has been confirmed. However, experimental data do not allow us to decide between structures 1 and 2.



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