A Green Complex from the Reaction of a Binuclear Copper(II) Complex of 2-Hydroxy-1,4-butanediamine-*N,N,N',N'*-tetraacetic Acid and H_2O_2

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Synopsis. Spectrophotometric studies have revealed that a green complex is formed by the reaction of a blue binuclear copper(II) complex of 2-hydroxy-1,4-butanediamine-*N,N,N',N'*-tetraacetic acid and H_2O_2, although analogous binuclear complexes of 2-hydroxy-1,3-propanediamine- and 3-hydroxy-1,5-pentanediamine-*N,N,N',N'*-tetraacetic acids are unreactive to H_2O_2.

New binuclear copper complexes which can interact with O_2 and related small compounds are of great interest as models for the active sites of Type III copper-containing proteins and as candidates for catalysts in oxidative synthetic reactions.[1,2] We recently reported the preparation of three analogous binuclear copper(II) complexes of amine-*N*-polycarboxylic acids with μ-alkoxide bridges at pH<6 as model complexes for Type III copper with respect to bridging ligands.[3] In this study, the reactivity of these three complexes with H_2O_2 has been investigated spectrophotometrically.

Experimental

Materials. The binucleating ligands used here are 2-hydroxy-1,3-propanediamine-, 2-hydroxy-1,4-butanediamine-, and 3-hydroxy-1,5-pentanediamine-*N,N,N',N'*-tetraacetic acids, which will be hereafter abbreviated as AC_3OH, AC_4OH, and AC_5OH, respectively. AC_3OH is commercially available. AC_4OH and AC_5OH were synthesized and purified by our own method which will be reported elsewhere in detail. The concentration of H_2O_2 in a commercial 30 wt% solution was determined precisely by redox titration with a standardized $KMnO_4$ solution. The sample solutions for spectral measurements were prepared by dissolving 2.5 mM AC_nOH (n=3, 4, or 5), 5.0 mM $Cu(ClO_4)_2$, 0.50 M $NaClO_4$, 0.05 M $Na_2B_4O_7$, and the desired amount of H_2O_2 in water and then by adjusting the solutions to pH 10.1 (1 M=1 mol dm^{-3}).

Measurements. UV and visible absorption spectra were recorded at 5.0±0.1 °C with a Shimadzu Model UV-240 spectrophotometer using 10 and 1-mm quartz cells.

Results and Discussion

In this study, it has been found that, when H_2O_2 is added to the blue aqueous solutions of the binuclear copper(II) complexes of AC_3OH, AC_4OH, and AC_5OH[3] at pH>7, only the solution of the second complex produces an intense green color. UV and visible absorption spectra for this complex system at varying H_2O_2 concentrations were measured at 5.0 °C in order to depress the formation of by-products as efficiently as possible (Fig. 1). In these spectra at $[H_2O_2]/[\text{the } Cu_2\text{-}AC_4OH \text{ complex}]<20$, there are two isosbestic points at 288 and 790 nm, indicating that there exists a reaction equilibrium. We analyzed these spectral changes at a constant pH of 10.1 on the assumption of the following equilibrium:

$$\text{Complex } \mathbf{1} + H_2O_2 \rightleftharpoons \text{Complex } \mathbf{2} + H^+ \quad (1)$$

where Complexes **1** and **2** are $[Cu_2(AC_4O)(OH)]^{2-}$ and $[Cu_2(AC_4O)(O_2)]^{3-}$ respectively and where K'=[Complex **2**][Complex **1**]$^{-1}$[H_2O_2]$^{-1}$. The analyses could be done at three wavelengths of 350, 600, and 650 nm, as exemplified by Fig. 2. The results thus analysed are summarized in Table 1.

Now, it seems probable that Complex **2** contains a peroxide ion, as shown in Eq. 1, because the absorption spectra of Fig. 1 have been satisfactorily analyzed

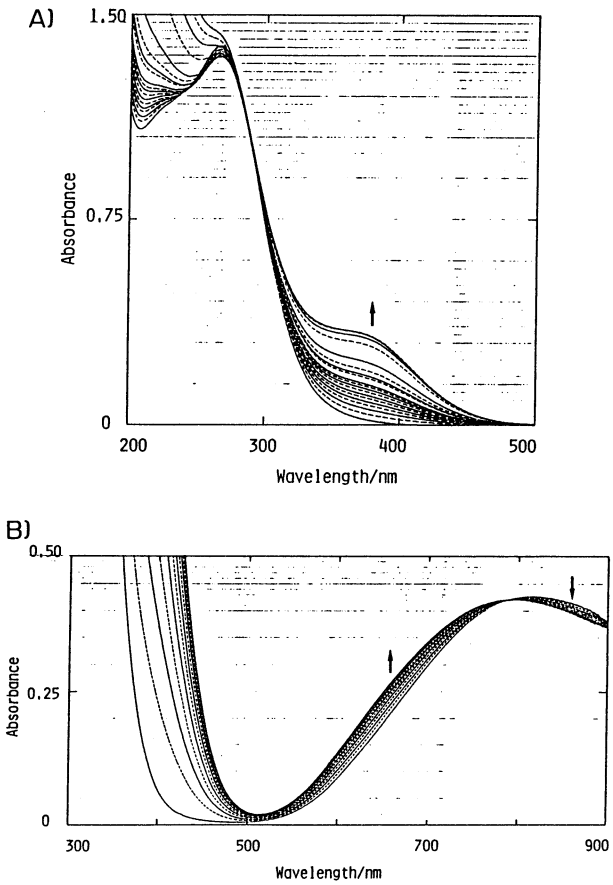

Fig. 1. UV (A) and visible (B) absorption spectra for the system of the Cu_2-AC_4OH complex (Complex **1**) and H_2O_2 in aqueous solutions at pH 10.1 at 5.0 °C (0.05 M $Na_2B_4O_7$ buffer; $[NaClO_4]$= 0.50 M; $[Cu(ClO_4)_2]$=5.114 mM; $[AC_4OH]$=2.557 mM; A), 1-mm quartz cells; B), 10-mm quartz cells). The spectra changed along the direction of arrows with increasing concentrations of H_2O_2, the concentrations being varied from 0 to 0.127 M for A and to 1.02 mM for B.

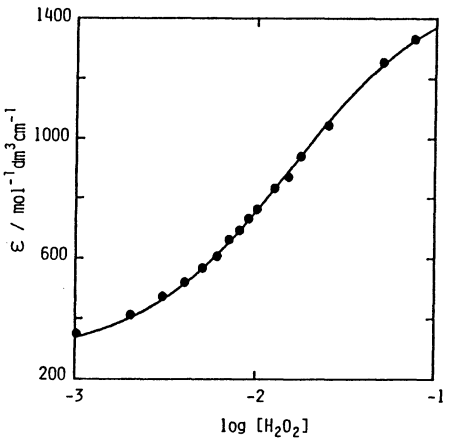

Fig. 2. Plots of molar extinction coefficients (ε) at 350 nm in Fig. 1(A) against the concentration of H_2O_2: darked circle, experimental; solid line, calculated with the parameter values listed in Table 1.

Table 1. Results[a] of Absorption Spectral Measurements for the Reaction System of Complex **1** and H_2O_2

Wavelength / nm	ε_1	ε_2	log K'
350	264.9	1533	1.84
600	35.35	88.8	1.83
650	75.83	140.6	1.84

a) ε_1 and ε_2 are the molar extinction coefficients (mol^{-1} dm^{-3} cm^{-1}) of Complexes **1** and **2**, respectively (see text as to Complexes **1** and **2** and K').

on the assumption of Eq. 1. Furthermore, it is obvious that Complex **2** shows two spectral pesks around 370 nm ($\varepsilon \approx 2000$) and 650 nm ($\varepsilon \approx 150$). Interestingly, this complex is quite similar to oxyhemocyanin and its analogues in the spectral band positions and in their intensity ratio.[4] However these bands of the present complex are too weak in intensity compared with those of oxyhemocyanin and its analogues. It is an interesting fact that H_2O_2 does not react with the binuclear copper(II) complexes of AC_3OH and AC_5OH, but only with that of AC_4OH, suggesting that the reactivity is severely dependent upon small structural variations of the binuclear complexes, for instance, the relative positions and asymmetrical environments of the two cupric ions. This study also shows that model complexes for the active sites of oxyhemocyanin and its analogues may be stably produced even in aqueous solutions at room temperature, contrary to the general belief that a hydrophobic environment is desirable for the dioxygen binding center in the biological systems and their model complexes.[1]

References

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