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SHORT-LIVED HETERONUCLEAR COPPER(II)-XYLENOL ORANGE-COBALT(II) AND COPPER(II)-XYLENOL ORANGE-NICKEL(II) COMPLEXES

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Short-lived heteronuclear intermediates $[Cu^{II}(XO)Co^{II}]$ and $[Cu^{II}(XO)Ni^{II}]$ are detected by a rapid-scan spectrophotometer upon mixing Cu^{2+} ion with a Co(II)- or a Ni(II)-complex of 3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresolsulfonphthalein (Xylenol Orange, XO) in weakly acid solution.

In the course of the reactions of Cu^{2+} ion with the mononuclear 1 : 1 complexes of Co(II) and Ni(II),1) short-lived heteronuclear species $[Cu^{II}(XO)Co^{II}]$ and $[Cu^{II}(XO)Ni^{II}]$ were detected by rapid-scan spectrometry.

Figure 1 shows the change of rapid-scan spectra observed for the reaction of Cu^{2+} ion with Co(II)-XO complex. The measurements were carried out with a Union Giken rapid-scan stopped-flow spectrophotometer model RA-1300 at 25.0 °C and $I = 0.1\ mol\cdot dm^{-3}$ ($NaClO_4$). A solution containing $8 \times 10^{-4}\ mol\cdot dm^{-3}$ Co^{2+} ion and $3.2 \times 10^{-5}\ mol\cdot dm^{-3}$ XO was rapidly mixed with a $2 \times 10^{-3}\ mol\cdot dm^{-3}$ solution of Cu^{2+} ion at pH 4.32 by stopped-flow technique. The absorption peak at 584 nm of $Co^{II}XO$ rapidly increases with blue shift. The spectra have an isosbestic point at 502 ± 1 nm. Curves 1-4 in Fig. 1 correspond to the fast step of the formation of the intermediate. After ca. 0.2 s, the absorption around 580 nm decreases gradually with further blue shift and reaches equilibrium in ca. 20 s. The spectra have another isosbestic point at 516 ± 1 nm. The feature of the final spectrum indicates the formation of Cu_2XO complex with an absorption maximum at ca. 574 nm.2) The fast and the slow process were clearly discriminated on the stopped-flow signals measured at 584 nm. The apparent rate constants for the fast process in the reactions of Cu^{2+} ion with $Co^{II}XO$ and $Ni^{II}XO$ were in the same order of magnitude as that for the reaction of Cu^{2+} ion and free ligand XO.3) The conditional stability constants $K = [Cu^{II}(XO)M^{II}]/[Cu^{2+}][M^{II}XO]$ measured at 584 nm and at pH 4.30 ± 0.06 are shown in Table 1. They were evaluated from the increments of the absorbance at 584 nm for the fast reactions, the solutions containing $4 \times 10^{-4}\ mol\cdot dm^{-3}$ Co^{2+} or Ni^{2+} ion and 1.0, 2.0, and $3.2 \times 10^{-5}\ mol\cdot dm^{-3}$ XO being rapidly mixed with an $8 \times 10^{-3}\ mol\cdot dm^{-3}$ solution of Cu^{2+} ion at pH 4.30 ± 0.06 by stopped-flow technique.

These results indicate that the short-lived species observed in the fast processes are the heteronuclear species $[Cu^{II}(XO)Co^{II}]$ and $[Cu^{II}(XO)Ni^{II}]$ formed by coordination of Cu^{2+} ion to a vacant site of the coordinated XO in the 1 : 1 complex (Fig. 2).

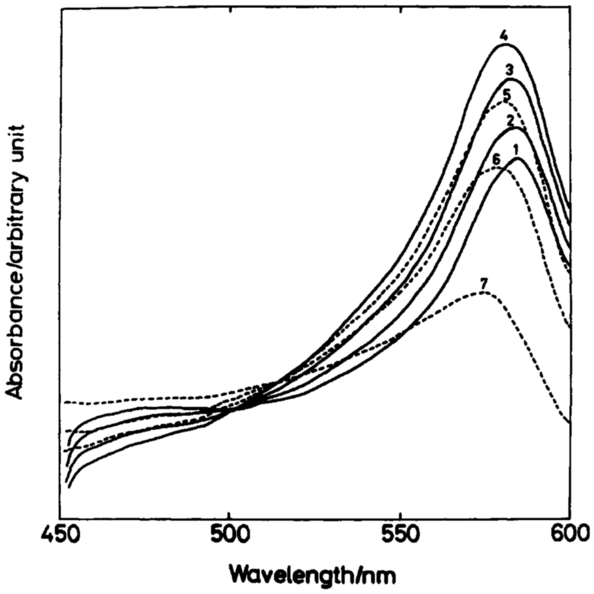

Fig. 1. Rapid-scan spectra for the reaction of Cu^{2+} ion with Co(II)-XO complex. Recorded at (1) 0-2, (2) 6-8, (3) 18-20, (4) 78-80, (5) 395-400 ms, (6) 0.8-1.0, and (7) 15.8-16.0 s after the solution containing 8×10^{-4} mol·dm^{-3} Co^{2+} ion and 3.2×10^{-5} mol·dm^{-3} XO was mixed with a 2×10^{-3} mol·dm^{-3} solution of Cu^{2+} ion at pH 4.32, at 25.0 °C, and I = 0.1 mol·dm^{-3} ($NaClO_4$).

Table 1. The Conditional Stability Constants Measured at 584 nm, at pH 4.30 ± 0.06, at 25.0 °C, and I = 0.1 mol·dm^{-3}.

Intermediate	K/mol^{-1}·dm^3
$Cu^{II}(XO)Co^{II}$	250 ± 2
$Cu^{II}(XO)Ni^{II}$	251 ± 7

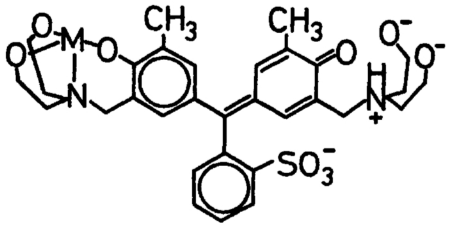

Fig. 2. Structure of the coordinated XO in the 1 : 1 complex of Co(II) or Ni(II).

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