BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 769—773 (1970)

Kinetics of the Ligand Substitution Reaction of the Copper(II)-4-(2-Pyridylazo)resorcinol Complex with (Ethylene glycol)-bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic Acid

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(Received July 21, 1969)

The kinetics of the ligand substitution reaction of the copper(II)-4-(2-pyridylazo)resorcinol complex (Cu(II)-PAR) with (ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) has been studied spectrophotometrically at pH 9—10 at $\mu=0.10$ ($NaClO_4$) and at 25.0°C. The reaction proceeds through the 1 : 1 Cu(II)-PAR complex resulting from the predissociation equilibrium of the 1 : 2 Cu(II)-PAR complex:

$$-d[CuR_2^{2-}]/dt = 10^{6.15}[CuR_2^{2-}][H^+][Y']/[HR^-] = 10^{2.9}[CuR][Y']$$

where R^{2-} refers to the divalent anion of PAR (H_2R) and Y′ the free EGTA not combined with any metal. The release of PAR from the mixed ligand intermediate RCuY is the rate-determining step. The substitution reaction for the copper(II)-PAR complex proceeds in the same mechanism with that for the zinc(II)-PAR complex. The difference in reactivity of these complexes is discussed. Cu-PAR bond is weakened in a distorted octahedron of the intermediate RCuY before the release of PAR.

Many works have been devoted to the kinetics and mechanisms of the exchange of polyaminocarboxylic acid anion (*e.g.* EDTA) between metal ions. A general mechanism has been proposed by Margerum and Bydalek[1] for the exchange of a multidentate ligand between metal ions that involves a dinuclear intermediate species, in which the multidentate ligand is partially unwound from the initially complexed metal ion and partially attached to the attacking metal ion. We have studied the substituion of metal chelates with multidentate ligands which are often involved in the complexometric titration and the solvent extraction of metal chelates.

In a previous paper,[2] the ligand substitution reaction of the zinc(II)-4-(2-pyridylazo)resorcinol complex (Zn(II)-PAR) with (ethylene glycol)bis-(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) has been reported. The reaction was found to proceed through one path involving predissociation equilibrium of the zinc(II)-PAR complex, and the possible mechanism was discussed.

It seemed worth while to extend the study to the substitution reaction involving the other metal ion, and the ligand substitution reaction of the copper(II)-4-(2-pyridylazo)resorcinol complex with (ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid

$$\text{Cu(II)-PAR} + \text{EGTA} \rightleftharpoons \text{Cu(II)-EGTA} + \text{PAR} \qquad (1)$$

was undertaken, where EGTA and PAR represent (ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid and 4-(2-pyridylazo)resorcinol respectively and are abbreviated as H_4Y (hexadentate) and H_2R (tridentate) respectively. This paper gives the results.

Results

It is necessary to determine the stability constants of copper(II)-PAR complexes in connection with

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[1] T. J. Bydalek and D. W. Margerum, *J. Amer. Chem. Soc.*, **83**, 4326 (1961); *Inorg. Chem.*, **1**, 852 (1962); **2**, 678 (1963); **2**, 683 (1963).

[2] M. Tanaka, S. Funahashi and K. Shirai, *Inorg. Chem.*, **7**, 573 (1968).

the equilibria involved in the substitution reaction. Thus the stability constants of the copper(II)-PAR complexes have been determined spectrophotometrically at $\mu=0.10$ ($NaClO_4$) and at 25.0°C:

$$[CuHR^+]/[Cu^{2+}][HR^-] = 10^{9.90\pm0.05},$$

$$[CuHR^+]/[CuR][H^+] = 10^{5.00\pm0.05},$$

$$[CuR]/[Cu^{2+}][R^{2-}] = 10^{17.20\pm0.05},$$

$$[CuR_2{}^{2-}]/[CuR][R^{2-}] = 10^{9.1\pm0.2}.$$

Details will be reported elsewhere.[3]

Methods of preparation of the reagents and kinetic measurements have been described previously.[2-4]

Under the present experimental conditions the copper(II) forms with PAR quantitatively the 1 : 2 complex $CuR_2{}^{2-}$. The absorbance of the copper(II)-PAR complex is constant over a pH range 9 to 10. The molar absorption coefficient is 6.87×10^4 at 515 nm. The dominant species of PAR is the singly charged species (HR^-), and the species of EGTA involves Y^{4-}, HY^{3-} and H_2Y^{2-}. The copper(II)-EGTA complex is the 1 : 1 complex CuY^{2-} ($K_{CuY}=10^{17.8}$).[5] Equilibrium (1) is much favored to the right so that the substitution reaction of the copper(II)-PAR complex with EGTA goes substantially to completion and the reverse reaction can be neglected.

For the reaction with large excesses of PAR and EGTA the rate law can be expressed as

$$-\frac{[CuR_2{}^{2-}]}{dt} = k_{0(H,R,Y)}[CuR_2{}^{2-}], \tag{2}$$

where $k_{0(H,R,Y)}$ is the conditional rate constant[6] involving concentration of PAR, EGTA and hydrogen ion. The rate plots of $\log{(E_0-E_\infty)/(E_t-E_\infty)}$ *vs.* t were linear at least for over 90% of reaction. The conditional rate constant $k_{0(H,R,Y)}$ was determined from the slope of the straight line. The values of conditional rate constants at various concentrations of PAR, at a concentration of EGTA, and at constant pH are given in Table 1 (Runs No. 1—9). These data indicate clearly a linear relationship between $k_{0(H,R,Y)}$ and the reciprocal concentration of PAR with the zero intercept. In Fig. 1, the values of $k_{0(H,R,Y)}$ determined at various pH's and concentrations of EGTA and PAR are plotted against the hydrogen ion concentration and some data of $k_{0(H,R,Y)}$ are tabulated in Table 1. It is evident from Fig. 1 that $k_{0(H,R,Y)}$ is linearly related to hydrogen ion concentration and that the rate increases with increasing EGTA concentration. The plots give the zero intercept (Figs. 1 and 2). The substitution reaction is of first order with respect to EGTA and hydrogen ion. Thus the rate law is given by

$$-\frac{d[CuR_2{}^{2-}]}{dt} = k_0\frac{[CuR_2{}^{2-}][H^+][Y']}{[HR^-]}. \tag{3}$$

TABLE 1. FIRST ORDER CONDITIONAL RATE CONSTANTS $k_{0(H,R,Y)}$
At 25.0°C and $\mu=0.10$ ($NaClO_4$), $C_{Cu}=1.00\times10^{-6}$M.

Run No.	10^4C_R (M)	10^3C_Y (M)	pH	$k_{0(H,R,Y)}$ (sec^{-1})
1	1.00	1.00	9.52	3.8
2	1.50	1.00	9.52	2.9
3	2.00	1.00	9.52	2.2
4	3.00	1.00	9.52	1.7
5	1.00	1.00	9.30	6.3
6	1.50	1.00	9.30	4.8
7	2.00	1.00	9.30	3.7
8	1.50	1.00	9.16	6.7
9	2.00	1.00	9.16	5.2
10	1.00	1.00	9.08	11.1
11	1.00	1.00	9.20	8.38
12	1.00	1.00	9.35	4.75
13	1.00	1.00	9.60	2.79
14	1.00	1.00	9.78	1.87
15	1.00	1.00	10.06	0.767
16	1.50	1.00	9.10	8.33
17	1.50	1.00	9.19	6.25
18	1.50	1.00	9.35	4.13
19	1.50	1.00	9.55	2.21
20	1.50	1.00	9.72	1.38
21	2.00	1.00	9.09	6.33
22	2.00	1.00	9.19	4.79
23	2.00	1.00	9.35	2.96
24	2.00	1.00	9.54	1.73
25	3.00	1.00	9.07	5.13
26	3.00	1.00	9.32	2.50
27	3.00	1.00	9.52	1.46
28	1.00	0.500	9.11	5.75
29	1.00	0.500	9.31	3.42
30	1.00	0.500	9.76	0.792
31	1.00	1.50	9.14	13.8
32	1.00	1.50	9.32	8.83
33	1.00	1.50	9.45	6.42
34	1.00	1.50	9.60	3.75
35	1.00	2.00	9.17	16.7
36	1.00	2.00	9.27	13.8
37	1.00	2.00	9.41	9.25

This rate law is consistent with the reaction mechanism:

$$CuR_2{}^{2-} + H^+ \rightleftharpoons CuR + HR^-, \tag{4}$$

$$CuR + Y' \rightleftharpoons RCuY \rightleftharpoons CuY^{2-} + HR^-. \tag{5}$$

EGTA reacts with CuR in equilibrium with $CuR_2{}^{2-}$. Substituting the equilibrium constants in Eq. (4),

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[3] S. Funahashi, S. Yamada and M. Tanaka, to be published.

[4] S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

[5] J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).

[6] M. Tanaka, S. Funahashi and K. Shirai, *Anal. Chim. Acta*, **39**, 437 (1967).

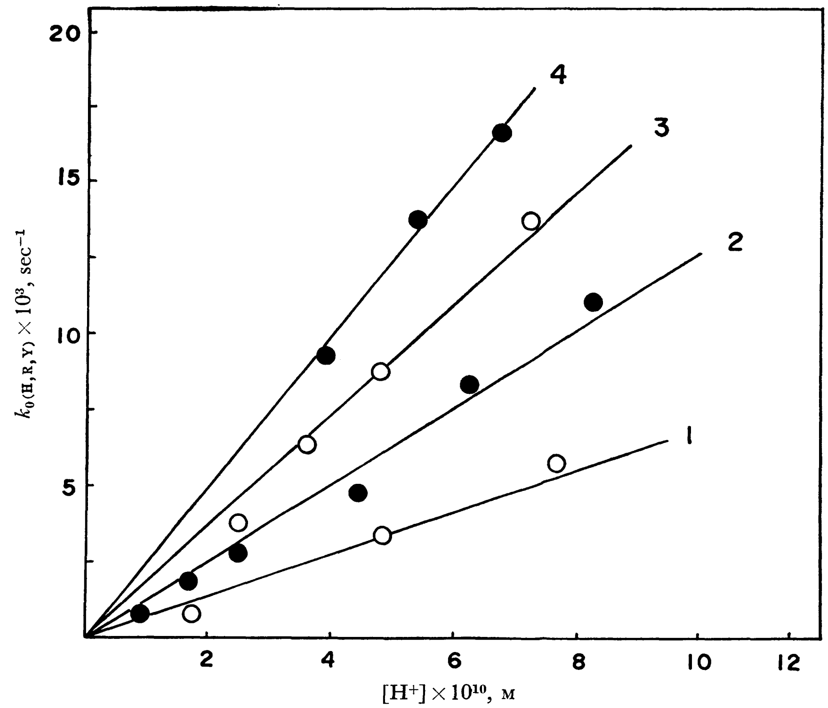

Fig. 1. $k_{0(\mathrm{H,R,Y})}$ as a function of hydrogen ion concentration.
$C_{\mathrm{Cu}}=1.00\times 10^{-6}$M; $C_{\mathrm{R}}=1.00\times 10^{-4}$M; $C_{\mathrm{Y}}=1$, 5.00×10^{-4}M; 2, 1.00×10^{-3}M; 3, 1.50×10^{-3}M; 4, 2.00×10^{-3}M; $\mu=0.10$ ($\mathrm{NaClO_4}$); temperature, 25.0°C

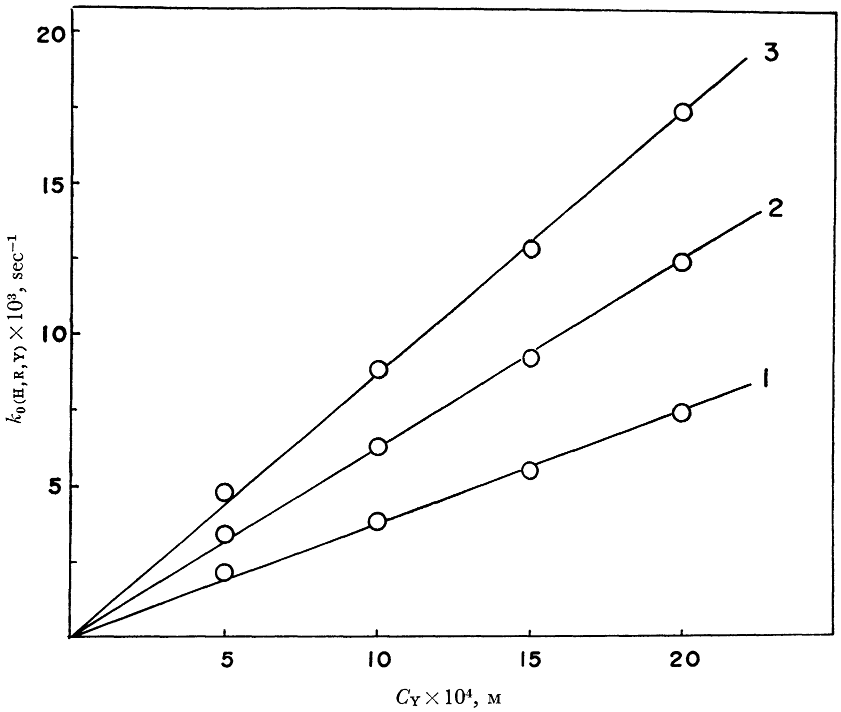

Fig. 2. $k_{0(\mathrm{H,R,Y})}$ as a function of EGTA concentration.
$C_{\mathrm{Cu}}=1.00\times 10^{-6}$M; $C_{\mathrm{R}}=1.00\times 10^{-4}$M; pH=1, 9.52; 2, 9.30; 3, 9.16; $\mu=0.10$($\mathrm{NaClO_4}$); temperature, 25.0°C

the rate law can be rewritten as

$$-\frac{\mathrm{d}[\mathrm{CuR_2}^{2-}]}{\mathrm{d}t} = k_0\frac{K^{\mathrm{R}}_{\mathrm{CuR_2}}}{K^{\mathrm{H}}_{\mathrm{HR}}}[\mathrm{CuR}][\mathrm{Y'}]$$
$$= k[\mathrm{CuR}][\mathrm{Y'}], \qquad (6)$$

where

$$K^{\mathrm{R}}_{\mathrm{HR}} = [\mathrm{HR^-}]/[\mathrm{R^{2-}}][\mathrm{H^+}] = 10^{12.30}\text{[6]}.$$

Under the present experimental conditions, Y^{4-}, HY^{3-} and H_2Y^{2-} are present. However, we observe no variation of the rate with varying proportion of these species of EGTA. The rate constants k_0 and k determined in this investigation are $1.4\pm0.4\times10^6$ M^{-1} sec^{-1} and $8.8\pm0.3\times10^2$ $\mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$, respectively.

Discussion

Margerum and Rosen[7] have recently shown a clear evidence for a series of intermediates in equilibrium with one another in the reaction of EDTA with mono- and bis(diethylenetriamine)-nickel(II) complexes. We have reported the kinetics of the ligand substitution reaction of the zinc(II)-4-(2-pyridylazo)-resorcinol complex with (ethylene glycol)bis(2-aminoethyl ether)-*N*,*N*,*N'*,*N'*-tetraacetic acid. The substitution reaction of copper(II)-PAR proceeds through the same mechanism with that of zinc(II)-PAR, *i. e.*, the cleavage of PAR bonded to the central metal in the mixed ligand intermediate, RMY, should be rate-determining (M denotes Zn or Cu).[2]

We assume the 1 : 1 M-PAR complex and EGTA are in rapid equilibrium with the mixed ligand complex in which EGTA is bonded to the central metal ion with a segment of EGTA and the rate-determining step is the loss of PAR from the mixed ligand intermediate. Since PAR is not as flexible as aliphatic polyamines, it is not likely that EGTA reacts with PAR complexes *via* a stepwise removal of donor atoms of PAR from the central metal as postulated previously in the substitution of polyamine complexes of nickel with EDTA.[8] As soon as one donor atom of PAR is removed from the central metal ion in the intermediate RMY, the other two will also be detached. This step should be the rate-determining step. Thus the reaction of ZnR and CuR with EGTA is given by

$$\mathrm{MR} + \mathrm{Y'} \underset{}{\overset{K_{\mathrm{RMY}}}{\rightleftharpoons}} \mathrm{RMY} \xrightarrow{k_{\mathrm{R}}{}^{\mathrm{M}}} \mathrm{MY^{2-}} + \mathrm{HR^-}, \qquad (7)$$

where $K_{\mathrm{RMY}}=[\mathrm{RMY}]/[\mathrm{MR}][\mathrm{Y'}]$ is the stability constant of the intermediate. If the reaction follows the mechanism given in Eq. (7), the experimentally determined rate constants, k^{M}, can be equated with the corresponding rate constants for metal-PAR bond rupture, $k_{\mathrm{R}}{}^{\mathrm{M}}$, by

$$k^{\mathrm{M}} = K_{\mathrm{RMY}}k_{\mathrm{R}}{}^{\mathrm{M}}. \qquad (8)$$

According to the proposed mechanism, the rate law (6) can be rewritten as

$$-\frac{\mathrm{d}[\mathrm{MR_2}^{2-}]}{\mathrm{d}t} = k^{\mathrm{M}}[\mathrm{MR}][\mathrm{Y'}]$$
$$= \frac{k^{\mathrm{M}}}{K_{\mathrm{RMY}}}[\mathrm{RMY}] = k_{\mathrm{R}}{}^{\mathrm{M}}[\mathrm{RMY}]. \qquad (9)$$

It is interesting to compare the ratio $k^{\mathrm{Cu}}_{\mathrm{R}}/k^{\mathrm{Zn}}_{\mathrm{R}}$ with the ratio of rate constants of dissociation of PAR from CuR and ZnR. Unfortunately, experimental K_{RMY} values are not available for the system studied. Consequently, it is necessary to rely on estimates. The second stability constants, $K^{\mathrm{X}}_{\mathrm{MX_2}}=[\mathrm{MX_2}]/[\mathrm{MX}][\mathrm{X}]$, for copper(II) and zinc(II) with various tridentate ligand similar to PAR and a segment of EGTA are compared. Plots of $\log K^{\mathrm{X}}_{\mathrm{CuX_2}}$ *vs.* $\log K^{\mathrm{X}}_{\mathrm{ZnX_2}}$ are shown in Fig. 3. The plots lie close to a straight line with a slope of unity and zero intercept: the value of $K^{\mathrm{X}}_{\mathrm{CuX_2}}$ does not seem to differ appreciably from $K^{\mathrm{X}}_{\mathrm{ZnX_2}}$. Thus it appears reasonable to assume $K_{\mathrm{RCuY}}\cong K_{\mathrm{RZnY}}$. Then

$$\frac{k_{\mathrm{R}}{}^{\mathrm{Cu}}}{k_{\mathrm{R}}{}^{\mathrm{Zn}}} = \frac{k^{\mathrm{Cu}}/K_{\mathrm{RCuY}}}{k^{\mathrm{Zn}}/K_{\mathrm{RZnY}}} = \frac{k^{\mathrm{Cu}}}{k^{\mathrm{Zn}}} = 10^{-1.5}, \qquad (10)$$

where the value of k^{Zn} is 2.4×10^4 M^{-1} sec^{-1} at 25.0°C and $\mu=0.10$.[2]

The release of a water molecule from an aquo metal ion is the rate-determining step in the complex formation.[9-12] Though the rate constants for formation of CuR and ZnR are not yet available, they will very probably be comparable to the rate constants $k^{\mathrm{M}}_{\mathrm{H_2O}}$ of the substitution of coordinated water molecules of corresponding aquo metal ion M. Therefore, the rate of dissociation of CuR and ZnR can be estimated from the stability constants and the rate constants of formation of these complexes. We have immediately the ratio of the rate constants of dissociation of PAR from the 1 : 1 M-PAR complexes:

$$\frac{k^{\mathrm{Cu}}_{\mathrm{H_2O}}/K^{\mathrm{R}}_{\mathrm{CuR}}}{k^{\mathrm{Zn}}_{\mathrm{H_2O}}/K^{\mathrm{R}}_{\mathrm{ZnR}}} = 10^{-4.5} \qquad (11)$$

where the values of $k^{\mathrm{Cu}}_{\mathrm{H_2O}}$ and $k^{\mathrm{Zn}}_{\mathrm{H_2O}}$ are 2×10^8 sec^{-1} at 25°C[13] and 3×10^7 sec^{-1} at 25°C[14], respectively, and the value of $K^{\mathrm{R}}_{\mathrm{ZnR}}$ is $10^{11.9}$ at 25°C and

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6) W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962).

7) D. W. Margerum and H. M. Rosen, *Inorg. Chem.*, **7**, 299 (1968).

8) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

9) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

10) M. Eigen and N. Tamm, *ibid.*, **66**, 93 (1962).

11) M. Eigen and R. W. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C. (1965).

12) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

13) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

14) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

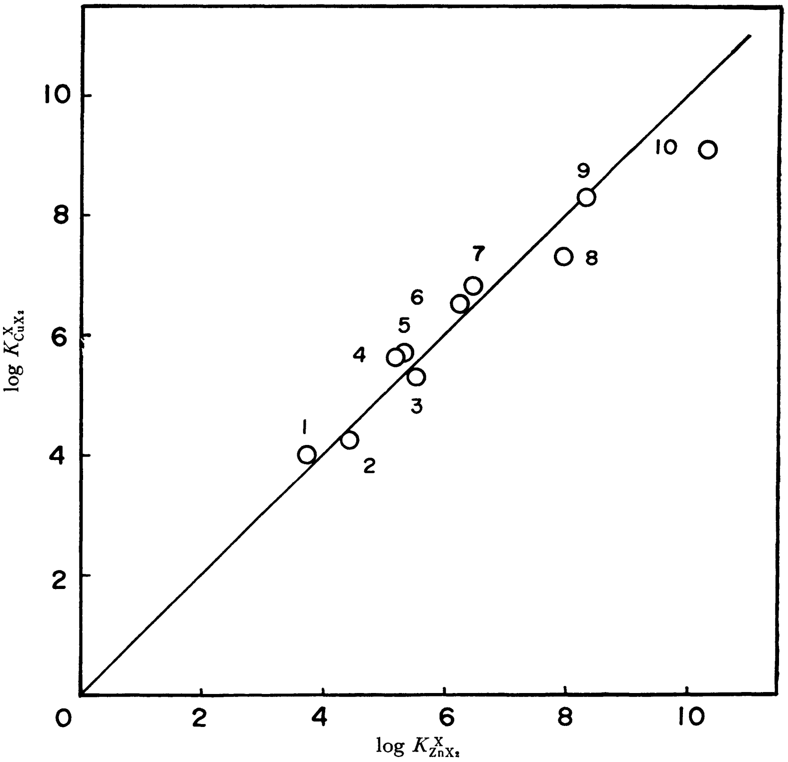

Fig. 3. log $K^X_{CuX_2}$ as a function of log $K^X_{ZnX_2}$.
1, *N*-2-hydroxyethyliminodiacetic acid; 2, *N*-(2-methoxyethyl)iminodiacetic acid;
3, diethylenetriamine; 4, iminodiacetic acid;
5, *N*-(3-hydroxypropyl)iminodiacetic acid; 6, *N*-(3,3-dimethylbutyl)iminodiacetic acid;
7, *N*-methyliminodiacetic acid;
8, 2-(2-pyridylazo)-4-methoxyphenol (G. Nakagawa and H. Wada, private communication, 1968);
9, 2-(2-pyridylazo)-4-methylphenol (G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **83**, 1190 (1962));
10, 4-(2-pyridylazo)resorcinol (Ref. 2).
Data from L. G. Sillén and A. E. Martell, "Stability Constants of Metal Complexes," Special Publication No. 17, The Chemical Society, London, 1964, except where indicated otherwise.

$\mu=0.10$.[2] The ratio of dissociation rate of PAR from M-PAR (Eq. (11)) is by three orders of magnitude lower than the ratio of the rate constants of dissociation of PAR from the intermediates (Eq. (10)). This difference points to the possible change of the structure of the assumed intermediate RMY during the reaction. Since the *d* electron configuration of copper(II) ion is $(t_{2g})^6(e_g)^3$, we expect to find four short bonds coplanar with the metal atom and two longer ones completing a distorted octahedron (Jahn-Teller distortions). We know that zinc(II) ion with the configuration d^{10} is spherical. In 1 : 1 Cu-PAR complex, PAR is coordinated in the same plane with the central metal and two of the three water molecules in the complex are coordinated weakly with copper. These water molecules are substituted by EGTA in the formation of the intermediate RCuY. The bond Cu-PAR should then be necessarily forced to be longer and weaken in the distorted octahedron of the intermediate before the cleavage of Cu-PAR bond. In other words, the dissociation of PAR in the mixed ligand intermediate RCuY should be strongly driven due to Jahn-Teller distortions.[15]

The financial support given by the Ministry of Education is gratefully acknowledged.

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[15] The stepwise stability constants of the zinc(II)-PAR complexes are different by less than a factor of 10^2: $K^R_{ZnR}=10^{11.9}$ and $K^R_{ZnR_2}=10^{10.3}$.[2] The second stability constant of the copper(II)-PAR complex, however, is smaller than the first by a factor of 10^8. The greatly reduced stability of the 1 : 2 copper(II)-PAR complex must be attributed to Jahn-Teller distortions.