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# Thermochromism of Metal Chelates with Triphenylmethane Complexons in Aqueous Solutions. III. Copper(II)-Methylthymol Blue and -Methylxylenol Blue Systems[†]

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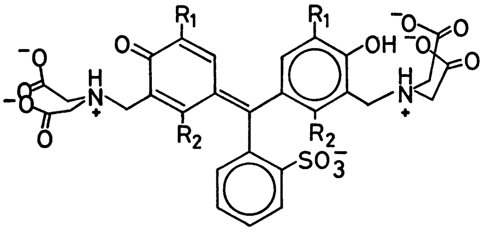
(Received December 20, 1979)

Reversible thermochromisms of copper(II) complexes with 3,3′-bis[bis(carboxymethyl)aminomethyl]thymolsulfonphthalein (Methylthymol Blue; MTB) and 3,3′-bis[bis(carboxymethyl)aminomethyl]-*p*-xylenolsulfonphthalein (Methylxylenol Blue; MXB) were studied in aqueous solutions. The thermochromisms of these complexes were primarily ascribed to the temperature-dependence of the protolytic equilibria between a complex species AH having an uncoordinated free phenolic hydroxyl group and a complex species A having a coordinated phenolate group: $AH \rightleftarrows A+H$. The equilibrium constants $K$ of the reactions at 25 °C were determined to be $p(K/\text{mol dm}^{-3})=4.66$ for Cu(II)–MTB and 4.78 for Cu(II)–MXB. The thermodynamic parameters $\Delta H$ and $\Delta S$ for the reactions were calculated to be $26\pm2$ kJ mol$^{-1}$ and $-6\pm3$ J K$^{-1}$ mol$^{-1}$ (298 K) for both complexes, respectively. The rate constants of the proton dissociation of the phenolic hydroxyl group in the complexes AH were estimated to be $1.6\times10^5$ and $1.8\times10^5$ s$^{-1}$ for Cu(II)–MTB and Cu(II)–MXB, respectively. The thermodynamic and kinetic data are discussed in terms of the effects of the substituents in the ligand molecules on the thermochromism.

The complexes of the multidentate ligands of the triphenylmethane complexons with various bivalent metal ions were found to be thermochromic in aqueous media.[1] In the previous papers, the thermochromism observed for the Cu(II)–Xylenol Orange (XO) system was interpreted in terms of the temperature-dependence of a protolytic equilibrium between a complex species AH having an uncoordinated free phenolic hydroxyl group and a complex species A having a coordinated phenolate group:

$$AH \rightleftarrows A + H.^{1)} \qquad (1)$$

In the present paper we study the thermochromisms observed for the Cu(II) complexes of the similar ligands MTB and MXB by means of a spectrophotometric and a temperature-jump method. The data obtained for the thermochromisms of Cu(II) complexes of the ligands will be compared with that for the Cu(II)–XO system in relation to the differences in alkyl substituents in the ligand molecules (see Fig. 1).



MTB : $R_1 = CH(CH_3)_2$, $R_2 = CH_3$

MXB : $R_1 = CH_3$, $R_2 = CH_3$

XO : $R_1 = CH_3$, $R_2 = H$

Fig. 1. The structural formulae of the ligands.

## Experimental

*Materials.* All chemicals used were of analytical grade, unless otherwise specified. Water was deionized and distilled.

Methylthymol Blue and Methylxylenol Blue were synthesized by Mannich condensation from Thymol Blue or *p*-Xylenol Blue, iminodiacetic acid (IDA), and formaldehyde, respectively.[2] The crude samples of the synthesized MTB and MXB purified beforehand by means of cellulose column chromatography were finally purified by means of high-performance liquid chromatography as in the case of XO.[3] The purity of the specimens of the ligands was confirmed by elemental analyses and melting point measurements. The purified ligands were used as a free acid form. Stock solutions of the ligands ($1.0\times10^{-3}$ mol dm$^{-3}$) were prepared by dissolving a desired amount of MTB and MXB in water. It should particularly be emphasized that for the quantitative studies the use of the highly purified specimens of the ligands was essential. In the pH range above 8.8, the color of the solutions of the ligands faded within one or two days because of the decomposition, whereas the solutions of the ligands were very stable in the acidic media.

Copper(II) perchlorate and sodium perchlorate were prepared and purified as described previously.[1] Acetate and phosphate buffer solutions were used for the Cu(II) complexes and the free ligands, respectively.

*Measurements.* The equilibria were measured with Hitachi recording spectrophotometers Model ESP-3T and Model 323 equipped with a cell thermostated at various temperatures. A 1 cm quartz cell was used. The kinetic measurements were carried out with a Union Giken co-axial-cable temperature-jump apparatus Model RA-105.[4] The pH values of the solutions were adjusted with the buffer solutions and measured with a Hitachi-Horiba pH-meter Model F-7SS. Temperature of the solution was measured with a copper-constantan thermocouple and a millivoltmeter within ±0.2 °C. The ionic strength of the solution was adjusted to 0.1 mol dm$^{-3}$ with sodium perchlorate.

Melting point was measured with a Rigaku Denki differential scanning calorimeter Model 8001 SL/C.

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[†] Presented in part at the 29th Annual Meeting on Coordination Chemistry, Hamamatsu, October 1, 1979, Abstracts, p. 82.

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## Results and Discussion

In the previous papers we ascribed the thermochromism observed for the Cu(II)–XO system primarily to the temperature-dependence of the protolytic equilibrium (1) based on the similarity of the temperature-dependence and the pH-dependence of the absorption spectra and on the results of molar-ratio method carried out at various temperatures.[1] Quite similar features were observed for the thermochromisms of the Cu(II) complexes of MTB and MXB.

As compared with XO these ligands contain two additional methyl groups $R_2$ and two isopropyl groups $R_1$ for MTB and two methyl groups $R_1$ for MXB (see Fig. 1). The effects of such structural factors in the ligand molecules on the phenomena of thermochromisms of their metal chelates are discussed in relation to the thermodynamic functions and the kinetic data.

*Equilibria.* Figures 2(a) and 2(b) show the typical examples of the temperature-dependence of the visible absorption spectra of the aqueous solution of Cu(II)–MTB at pH 4.36 and of Cu(II)–MXB at pH 4.57, respectively, the solutions containing $3.0\times10^{-5}$ mol dm$^{-3}$ ligand and $2.4\times10^{-4}$ mol dm$^{-3}$ $Cu^{2+}$ ion. The absorption spectra change reversibly with a distinct isosbestic point at 504 nm for Cu(II)–MTB and at 509 nm for Cu(II)–MXB. As the temperature rises the absorbances at 450 nm for Cu(II)–MTB and at 460 nm for Cu(II)–MXB decrease accompanied with a large increase in the absorbance at 600 nm for both systems. For the temperature-rise from 20 to 78 °C the absorbance at 600 nm increases about two-fold, the color changing from dark yellowish brown to dark blue for both systems. The increase of the absorbances at 600 nm was much the same as that of the Cu(II)–XO system at 574 nm under similar conditions. For the Cu(II) complexes of MTB and MXB the features of the temperature-dependences of the absorption spectra at a constant pH were all the same as those

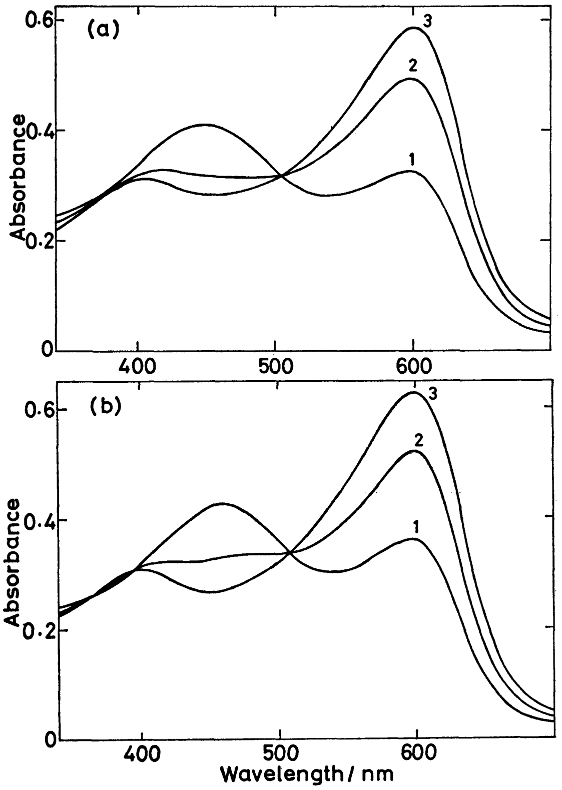

Fig. 2. Temperature-dependence of the absorption spectra of the Cu(II) complexes.
(a) Cu(II)–MTB. At 29 (1), 58 (2), and 77 °C (3). [Cu]$=2.4\times10^{-4}$ mol dm$^{-3}$; [MTB]$=3.0\times10^{-5}$ mol dm$^{-3}$. $I=0.1$ mol dm$^{-3}$ ($NaClO_4$). At pH$=4.36\pm0.02$. (b) Cu(II)–MXB. At 28 (1), 54 (2), and 78 °C (3). [Cu]$=2.4\times10^{-4}$ mol dm$^{-3}$; [MXB]$=3.0\times10^{-5}$ mol dm$^{-3}$. $I=0.1$ mol dm$^{-3}$ ($NaClO_4$). At pH$=4.57\pm0.02$.

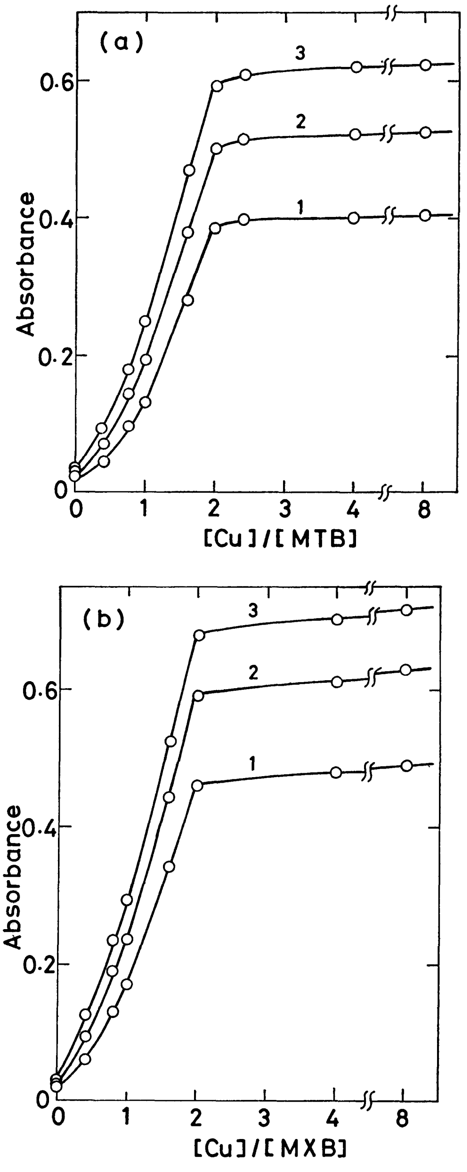

Fig. 3. Molar-ratio method at 600 nm for Cu(II) complexes at various temperatures.
(a) Cu(II)–MTB. At 25 (1), 50 (2), and 70 °C (3), [MTB]$=3.0\times10^{-5}$ mol dm$^{-3}$. pH$=4.57\pm0.02$. $I=0.1$ mol dm$^{-3}$ ($NaClO_4$). (b) Cu(II)–MXB. At 25 (1), 50 (2), and 70 °C (3). [MXB]$=3.0\times10^{-5}$ mol dm$^{-3}$. pH$=4.88\pm0.02$. $I=0.1$ mol dm$^{-3}$ ($NaClO_4$).

of the pH-dependences of the absorption spectra at a constant temperature.[5-9] The wavelengths of the absorption maxima and the isosbestic points observed for the two dependencies of the spectra were found to be all the same. Namely, also in the cases of the Cu(II) complexes of MTB and MXB the effect of heating the solutions essentially corresponds to the effect of the increase in pH of the same solutions.

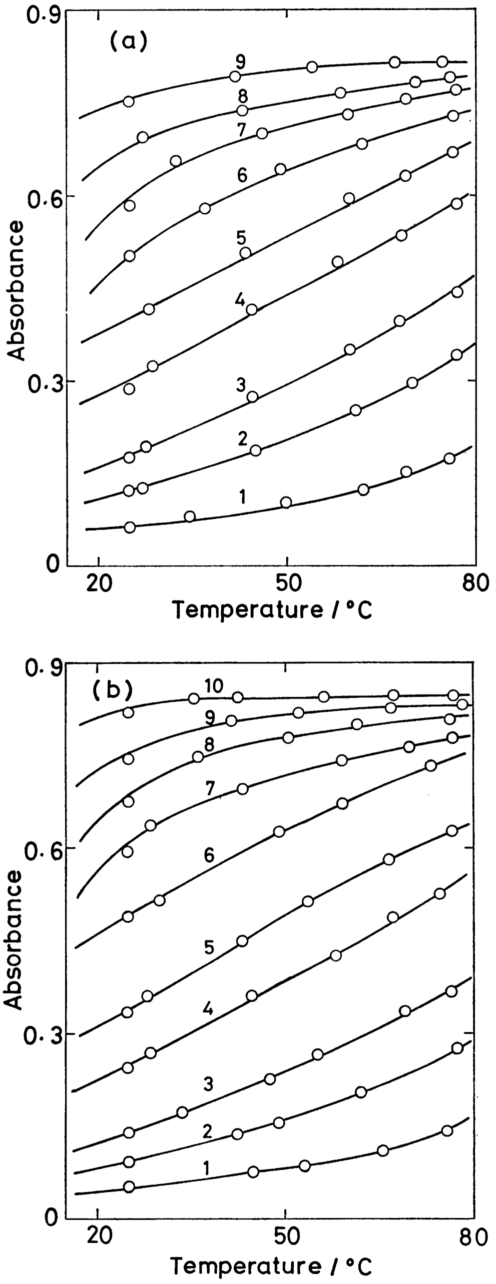

Fig. 4. The temperature-dependence of the absorbance at 600 nm of the Cu(II) complexes at various pH's.
(a) Cu(II)-MTB. At pH 3.26 (1), 3.71 (2), 3.99 (3), 4.36 (4), 4.59 (5), 4.90 (6), 5.20 (7), 5.47 (8), and 6.10 (9). [Cu]$=2.4\times10^{-4}$ mol dm$^{-3}$; [MTB]$=3.0\times10^{-5}$ mol dm$^{-3}$. $I=0.1$ mol dm$^{-3}$ (NaClO$_4$). (b) Cu(II)-MXB. At 3.24 (1), 3.69 (2), 4.00 (3), 4.33 (4), 4.57 (5), 4.88 (6), 5.18 (7), 5.44 (8), 5.70 (9), and 6.08 (10). [Cu]$=2.4\times10^{-4}$ mol dm$^{-3}$; [MXB]$=3.0\times10^{-5}$ mol dm$^{-3}$. $I=0.1$ mol dm$^{-3}$ (NaClO$_4$).

Figures 3(a) and 3(b) show the results of molar-ratio method measured at 600 nm, at various temperatures, and at pH 4.57 for Cu(II)-MTB and at 4.88 for Cu(II)-MXB, respectively. The metal-to-ligand ratio of the complex species formed in the solution for both systems was found to be invariably 2: 1 irrespective of the temperature.[1]

From the results described above, we concluded that the observed thermochromisms of Cu(II) complexes of MTB and MXB are also ascribed to the temperature-dependence of the protolytic equilibrium between two 2: 1 complex species, *i.e.*, between the low-temperature and the high-temperature form of a 2 : 1 complex species (see equilibrium (1)).

Figures 4(a) and 4(b) show the temperature-dependences of the absorbances at 600 nm of the solutions of the 2 : 1 Cu(II) complexes of MTB and MXB at various pH values. Upon heating the solutions at pH higher than 5.5 or lower than 3.7 the absorbances of both systems increase only slightly. The marked increase in the absorbance was observed for both systems only in a narrow pH range, *e.g.*, between pH 4.0 and 4.9 for Cu(II)-MTB and between pH 4.3 and 5.1 for Cu(II)-MXB (see Figs. 4(a) and 4(b)).

From the temperature-dependences of the absorbance the pH-dependences of the absorbance at various temperatures were derived as reproduced in Figs. 5(a) and 5(b). From these figures the p*K* values for the Eq. 1 were calculated at 25, 35, 50, and 70 °C. The

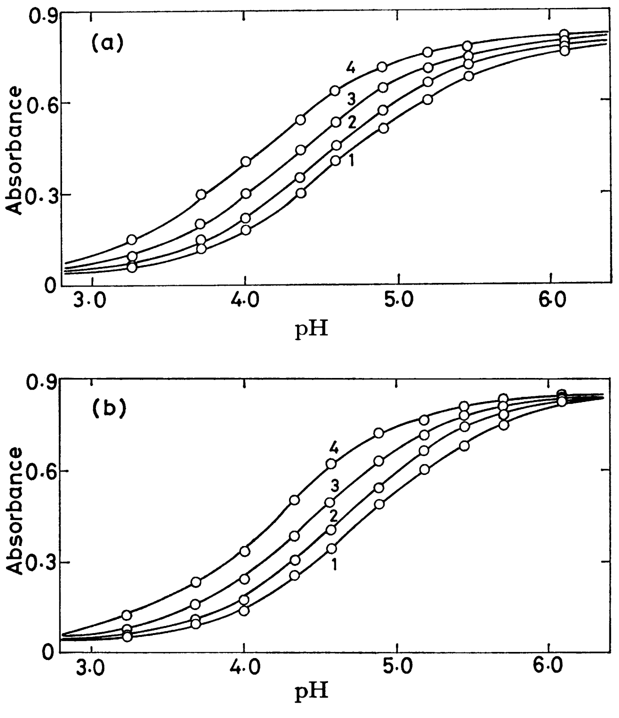

Fig. 5. The pH-dependence of the absorbance at 600 nm of the Cu(II) complexes at various temperatures.
(a) Cu(II)-MTB. At 25 (1), 35 (2), 50 (3), and 70 °C (4). [Cu]$=2.4\times10^{-4}$ mol dm$^{-3}$; [MTB]$=3.0\times10^{-5}$ mol dm$^{-3}$. $I=0.1$ mol dm$^{-3}$ (NaClO$_4$). (b) Cu(II)-MXB. At 25 (1), 35 (2), 50 (3), and 70 °C (4). [Cu] $=2.4\times10^{-4}$ mol dm$^{-3}$; [MXB]$=3.0\times10^{-5}$ mol dm$^{-3}$. $I=0.1$ mol dm$^{-3}$ (NaClO$_4$).

Table 1. Temperature-dependence of the acid-dissociation constants for the Cu(II) complexes and the free ligands at $I=0.1$ mol dm$^{-3}$ (NaClO$_4$)[a)]

| $T$/°C | 15 | 25 | 35 | 50 | 70 |
|---|---|---|---|---|---|
| Cu(II)–MTB | | 4.66 | 4.54 | 4.34 | 4.10 |
| Cu(II)–MXB | | 4.78 | 4.65 | 4.45 | 4.20 |
| Cu(II)–XO[b)] | 4.62 | 4.40 | 4.27 | 4.11 | 3.83 |
| MTB | 6.94 | 6.87 | 6.81 | | |
| MXB | 7.05 | 6.98 | 6.90 | | |
| XO[b)] | 6.66 | 6.57 | 6.50 | | |

a) p($K$/mol dm$^{-3}$) for the complexes. p($K_a$/mol dm$^{-3}$) for the free ligands. b) See Ref. 1.

data were summarized in Table 1 together with those for Cu(II)–XO.

The p$K_a$ values of the phenolic proton of the free ligands MTB and MXB also were obtained at various temperatures by the same procedure as in the case of XO[1)] (Table 1).

The temperature-dependences of the absorption spectra of the free ligands in neutral region were smaller compared with those in the Cu(II) complexes in weakly acidic region. For the temperature-rise from 25 to 45 °C the absorbance at 600 nm of the free ligands MTB at pH 6.85 and MXB at pH 6.95, *viz.*, near the p$K_a$ values of the phenol proton of the free ligands, increased only by 11% for MTB and 14% for MXB; the absorbance at 600 nm of Cu(II) complexes of MTB at pH 4.60 and MXB at pH 4.80 increased by so large as 28 and 37%, respectively.

Table 2. Thermodynamic functions for the protonation of the Cu(II) complexes and the free ligands

| | $\Delta H$ | $\Delta S$ |
|---|---|---|
| | kJ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ (298 K) |
| Cu(II)–MTB | $25\pm2$ | $-6\pm3$ |
| Cu(II)–MXB | $26\pm2$ | $-6\pm3$ |
| Cu(II)–XO[a)] | $26\pm2$ | $1\pm3$ |
| MTB | $12\pm2$ | $-92\pm3$ |
| MXB | $13\pm2$ | $-91\pm3$ |
| XO[a)] | $14\pm1$ | $-78\pm1$ |

a) See Ref. 1.

The thermodynamic parameters $\Delta H$ and $\Delta S$ for the Eq. 1 for Cu(II) complexes, and for the acid-dissociation of the phenol proton for the free ligands were graphically determined by plotting the values of log $K$ and log $K_a$ against $1/T$, respectively. The obtained values are listed in Table 2 together with the corresponding values for the Cu(II)–XO complex and the free ligand XO.

The positive values of $\Delta H$ show that the thermochromic changes of the Cu(II) complexes of MTB and MXB also are endothermic.

The values of $\Delta H$ for the Cu(II) complexes were about twice as large as that for the free ligands; the thermochromism was not observed for the free ligands.

A relationship is observed between the thermodynamic data and the position of alkyl substituents in the ligand molecule. Namely, the thermodynamic data for the three ligands, MTB, MXB, and XO, indicate that the effect of the substituents R$_2$ at meta position to the phenol group is reflected on the values of $\Delta S$, but the effect of the substituents R$_1$ at ortho position is not (see Table 2). Similar relationship was also observed for the Cu(II) complexes of these ligands.

Bolton and co-workers reported the increase in values of p$K_a$ and $\Delta S$ caused by the presence of meta-methyl substituents in phenols.[10)]

The difference in the substituents R$_1$ at ortho position to the phenol group did not affect the thermodynamic functions.

As described in our previous report,[1)] the data obtained in the present study also show that the values of $\Delta S$ for the equilibrium (1) differ much from those for the protolytic equilibrium in the free ligands. The small values of $\Delta S$ for the Cu(II) complexes would be ascribed to the compensation of the increase in the entropy by water molecules released from the coordination sphere of the metal ion upon coordination of the phenolate oxygen and the decrease in the entropy by the hydration of a dissociated proton.[1)] Similar discussions have been reported by Desai and Milburn[11)] for the complex formation of Fe(III) with phenols, and by Wright *et al.*[12)] and Brunetti *et al.*[13)] for the protonation of EDTA and its bivalent metal complexes.

Molar absorptivities of the ligands MTB and MXB were found to depend on the temperature. In the pH region between 3.5 and 3.9 corresponding to the p$K_a$ of the carboxyl proton of the ligands[6,8,9)] where the absorption spectra of the free ligands show no pH-dependency, a definite temperature-dependence of the spectra was clearly observed. This temperature-dependence of the absorbance would be attributed to the change in molar absorptivity of the ligands and might also contribute to the thermochromism of the Cu(II) complexes, though the effect is not so strong.

*Kinetics.* The temperature-jump studies were carried out for the Cu(II) complexes of MTB and MXB, and the free ligands, according to the procedure used in the case of Cu(II)–XO.[1)] Only one relaxation signal of an increasing absorbance at 600 nm was observed in 5—10 μs region for the Cu(II) complexes in acidic solutions; the corresponding signal for the ligands in nearly neutral solutions was observed in 10—20 μs region. The relaxation times for the protolytic changes can be expressed by

$$\tau^{-1} = k_1 + k_{-1}([\bar{\mathrm{H}}]+[\bar{\mathrm{A}}]), \qquad (2)$$

where $k_1$, $k_{-1}$, and $[\bar{\ }]$ denote the forward and the backward rate constants and equilibrium concentrations, respectively. The kinetic data were listed in Table 3 together with those for Cu(II)–XO and the ligand XO.

The values of $k_1$ and $k_{-1}$ for the acid-dissociation of phenol proton of the free ligands differ from those of XO. The values of quotient, $k_1/k_{-1}$, for free ligands were determined to be $10^{-6.7}$ and $10^{-6.9}$ mol dm$^{-3}$ for MTB and MXB, respectively. These values are in good agreement with the values of $K_a$ determined by the equilibrium measurements, though the errors are large. The kinetic data for the free ligands, MTB and

Table 3. The protonation-deprotonation rate constants for the Cu(II) complexes and the free ligands, at 25 °C and $I=0.1$ mol dm$^{-3}$ (NaClO$_4$)

| | $\frac{k_1}{10^4\ \mathrm{s}^{-1}}$ | $\frac{k_{-1}}{10^{10}\ \mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{s}^{-1}}$ |
|---|---|---|
| Cu(II)-MTB | 16 | — |
| Cu(II)-MXB | 18 | — |
| Cu(II)-XO[a] | 20 | — |
| MTB | 0.2±0.8 | 0.9±0.5 |
| MXB | 0.2±0.8 | 1.5±0.5 |
| XO[a] | 1.0±0.6 | 3.0±0.1 |

a) See Ref. 1. —: For the complexes the values of $\tau^{-1}$ did not depend on the sum of equilibrium concentrations, $[\bar{\mathrm{H}}]+[\bar{\mathrm{A}}]$.

MXB, would suggest that the differences in the values of $K_a=k_1/k_{-1}$ observed may primarily be ascribed to the differences in the values of $k_{-1}$. This indicates that isopropyl substituent R$_1$ at ortho position to the phenol group slows down the rate of the proton recombination to somewhat larger extent compared with the methyl substituent R$_1$ at the same position.

For the Cu(II) complexes of MTB and MXB the values of $k_1$ estimated for reaction (1) were found to be in the same order of magnitude as that for Cu(II)–XO, *i.e.*, *ca.* $2\times10^5\ \mathrm{s}^{-1}$. The values of $\tau^{-1}$, reciprocal of the relaxation times, for the protonation-deprotonation of the Cu(II) complexes of MTB, MXB, and XO are essentially independent of the sum of the equilibrium concentrations of proton and the chelate species involved. These results may be attributed to (1) an instrumental problem that the values of $\tau$ derived from the exponential signals for the Cu(II) complexes would reflect the time constant $\tau_c$ for the temperature-rise of our apparatus; (2) a possibility of a mechanism involving a contribution of a sort of intramolecular rate-determining step to the recombination of the phenolate with a central Cu(II) ion. The problems on the ambiguity of these possibilities are still open and will be reported elsewhere.

For the kindness in the DSC measurements, the authors thank Professor Yoshio Matsunaga. They also thank Professor Mitsuo Shimoji and Professor Yoshio Nakamura for aid in the use of a spectrophotometer for the measurements at high temperatures.

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5) The values of the molar absorptivity for Cu(II) complexes of MTB and MXB at 600 nm, and the free ligands at 610 nm were determined to be $2.7\times10^4$, $2.9\times10^4$, $2.0\times10^4$, and $2.3\times10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively. These values were found to be reasonable by comparing with the corresponding values by other authors.[6—9]

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