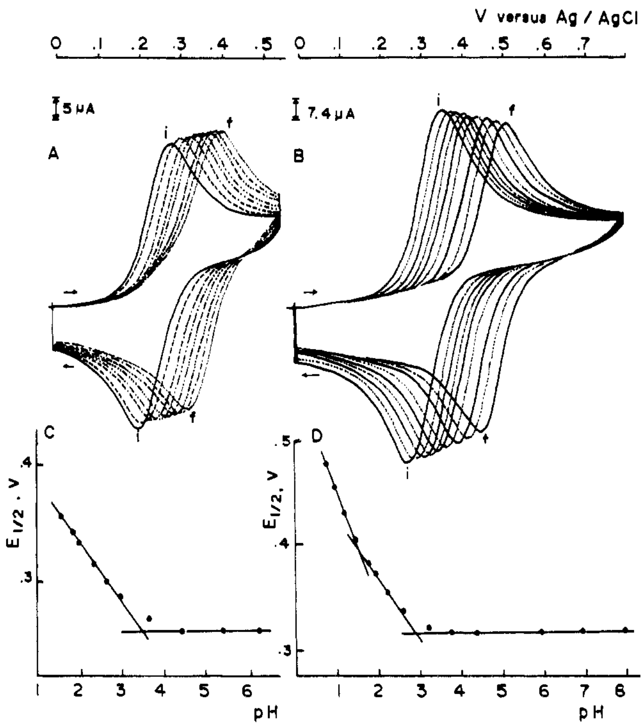

Figure 3. Cyclic voltammograms of the (A) $[(NH_3)_5Ru(dmpz)]^{2+}$ and (B) $[(CN)_5Fe(dmpz)]^{3-}$ complexes from pH 8 to 1.58 and from pH 8 to 0.70 (i–f), respectively, with the corresponding plots of $E_{1/2}$ vs. pH ([NaCl] = 0.10 M, 25 °C).

Excited-State pK_a. Calculation of the pK_a* of each complex was carried out by using eq 16,[1,7] where pK_a(gs) is the ground-state

$$pK_a^* = pK_a(\mathrm{gs}) + 2.86(\nu_1 - \nu_2)/RT \qquad (16)$$

pK_a, ν_1 is the frequency in wavenumbers of the absorption band of the unprotonated form, and ν_2 is the frequency of the corresponding absorption band in the protonated form. The results are shown in Table I.

The pK_a* values of the cyanometalates are 6 orders of magnitude higher than that of the ruthenium(II)–ammine analogue. The difference may be associated with the metal–ligand interactions in the excited states; however, there are two additional points to be considered in the present system. The MLCT transition energies used in eq 16 are strongly dependent on the potential diagrams, so that the differences of nuclear configuration between the ground and excited states of ML and MLH would increase the calculated pK_a*. The second point is that, in the derivation of eq 16, the entropy changes for the ground- and excited-state reactions have been considered the same. This kind of approximation may be reasonable for ruthenium(II) ammines and related complexes; however, it seems unlikely for the cyanometalates, which are very strongly dependent on solvent interactions.[8]

Conclusion

The basicity of the $[(CN)_5Fe(dmpz)]^{3-}$ and $[(NH_3)_5Ru(dmpz)]^{2+}$ complexes increases, respectively, by 1 and 2 orders of magnitude with respect to the free dmpz ligand (Table I). The pK_a of the $[(CN)_5Ru(dmpz)]^{3-}$ complex is similar to that of dmpz. Therefore, the extent of metal-to-ligand back-bonding, based on the relative pK_a values, increases along the series

$$Ru(CN)_5L^{3-} < Fe(CN)_5L^{3-} < Ru(NH_3)_5L^{2+}$$

in agreement with the NMR work reported by Johnson and Shepherd, for the related pz complexes.[9] Protonation on the cyanides decreases the pK_a of the coordinated dmpz ligand. Since the pK_a of $[HNC(CN)_4Fe(pz)]^{2-}$ is 1.9,[4] the pK_a of 0.065 measured by Johnson and Shepherd[3] should be ascribed to the diprotonated species $[HNC(CN)_4Fe(pzH)]^-$, rather than to $[(CN)_5Fe(pzH)]^{2-}$.

Registry No. dmpz, 108-50-9; $[(CN)_5Fe(dmpz)]^{3-}$, 97431-16-8; $[(CN)_5Ru(dmpz)]^{3-}$, 97431-17-9; $[(NH_3)_5Ru(dmpz)]^{2+}$, 97431-18-0.

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Kinetics of the Metal Ion Catalyzed Ester Hydrolysis of *O*-Acetyldi-2-pyridyl Ketoxime

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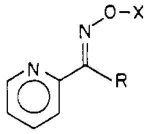
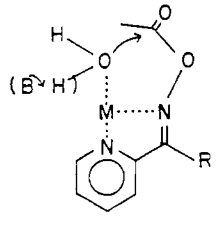
Kinetic studies on the metal ion catalyzed reactions of acyl derivatives disclosed various catalytic features.[1,2] In addition, possible catalytic roles of metal ions in metalloenzymes were proposed from these studies. Previous investigation on the metal ion catalyzed ester hydrolysis of the acetyl esters (**1**, **2**) of pyridyl



A

1: $\mathrm{X} = \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3},\ \mathrm{R} = \mathrm{H}$
1a: X = H, R = H
2: $\mathrm{X} = \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3},\ \mathrm{R} = \mathrm{CH_3}$
2a: $\mathrm{X} = \mathrm{H},\ \mathrm{R} = \mathrm{CH_3}$
3: $\mathrm{X} = \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$, R = 2-pyridyl
3a: X = H, R = 2-pyridyl

oximes **1a** and **2a** established the mechanism of B.[3-6] In this



B

R = H or CH_3
M = Zn(II) or Cu(II)

mechanism, the metal-bound water molecule or hydroxide ion makes a nucleophilic attack at the complexed ester linkage. Support for this mechanism came from the reactivity–selectivity relationship,[4] steric acceleration by the methyl substituent in **2**,[5] and the bimolecular participation of hydroxozinc(II) ion in the hydrolysis of **2**.[5]

We have extended the study to *O*-acetyldi-2-pyridyl ketoxime (**3**), in an attempt to gain further insight into the nature of the steric compression[5] in the metal ion catalyzed hydrolysis of the oxime esters. Ester **3** is the only analogue of **1** and **2** to which

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Table I. Kinetic Parameters for the Zn(II)-Catalyzed Hydrolysis of **1–3**[a]

	1[b]	**2**[c]	**3**[d]
k_W, 10^{-2} M^{-1} s^{-1}		4.5 ± 0.2	2.5 ± 0.2
k_{OH}, 10^6 M^{-2} s^{-1}	1.7 ± 0.1	15 ± 1	3.3 ± 0.1
k_{te}, 10^{15} M^{-4} s^{-1}		41 ± 1	3.9 ± 0.1
k_{sp}^{OH},[e] M^{-1} s^{-1}	15[f]	8.2[f]	15

[a] Measured at 25 °C and ionic strength 1.0 (with NaCl) in the presence of 0.8% (v/v) CH_3CN. [b] Reference 3. Only the k_{OH} path was observed apparently due to the slow rates of the other paths. [c] Reference 5. [d] This study. [e] Second-order rate constant for the spontaneous alkaline hydrolysis. [f] Calculated from the data reported in ref 7.

a bulkier substituent is introduced without causing any uncertainty in the configuration around the imine double bond. The presence of an extra pyridyl nitrogen in **3**, however, provides an additional binding site for the metal ion and should complicate the mechanistic analysis of the metal ion catalyzed hydrolysis of the ester.

Results and Discussion

Kinetic results obtained at pH 4.5–7.0 for the Zn(II)-catalyzed hydrolysis of **3** were analyzed in the same way as those[5] of the Zn(II)-catalyzed hydrolysis of **2**, and the pseudo-first-order rate constant (k_0) is represented by eq 1. The values of kinetic

$$k_0 = k_W[\mathrm{Zn(II)}] + k_{OH}[\mathrm{Zn(II)}][\mathrm{OH^-}] + k_{te}[\mathrm{Zn(II)}]^2[\mathrm{OH^-}]^2 \qquad (1)$$

parameters of eq 1 obtained for **3** are summarized in Table I together with those obtained previously for **1** and **2**.

The metal ion catalyzed hydrolysis of oxime esters **1** and **2** proceeds through the formation of the metal complex of the substrates, according to the scheme of eq 2 in which S and Ox

$$\mathrm{SH^+} \overset{K_a^S}{\rightleftharpoons} \mathrm{S} \xrightleftharpoons{\mathrm{M(II)},\, K_f^{MS}} \mathrm{M^{II}S} \xrightarrow{k_{cat}} \mathrm{M^{II}Ox} + \mathrm{CH_3COOH} \qquad (2)$$

stand for the ester substrate and the oxime, respectively.[3-5] Breakdown of $M^{II}S$ occurs through the attack of metal-bound water molecule or hydroxide ion. For the Zn(II)-catalyzed hydrolysis of **3**, k_{cat} represents the sum of the catalytic constants of the three paths ($k_{cat}^W + k_{cat}^{OH}[\mathrm{OH^-}] + k_{cat}^{te}[\mathrm{Zn(II)}][\mathrm{OH^-}]^2$) indicated by eq 1. The expression of k_0 for eq 2 derived under the condition of $[\mathrm{M(II)}] \gg [\mathrm{S}]_0$ is eq 3. For the Zn(II)-catalyzed

$$k_0 = \frac{k_{cat}K_f^{MS}[\mathrm{M(II)}]/(1 + [\mathrm{H^+}]/K_a^S)}{1 + K_f^{MS}[\mathrm{M(II)}]/(1 + [\mathrm{H^+}]/K_a^S)} \qquad (3)$$

reactions, K_f^{MS} values are not sufficiently large and eq 3 becomes eq 4 when $[\mathrm{H^+}] \ll K_a^S$.[3,5] If eq 4 is applied to **3**, each of the

$$k_0 = k_{cat}K_f^{MS}[\mathrm{M(II)}] \qquad (4)$$

parameters indicated in eq 1 contains both the formation constant (K_f^{MS}) and the respective catalytic constant (i.e., k_{cat}^W, $k_{cat}^{OH}[\mathrm{OH^-}]$, and $k_{cat}^{te}[\mathrm{Zn(II)}][\mathrm{OH^-}]^2$). Unless these constants are separately estimated, the stability and reactivity of $Zn^{II}S$ cannot be compared for **1–3**. Thus, although the values of the kinetic parameters for the Zn(II)-catalyzed hydrolysis of **3** lie between the corresponding values of **1** and **2**, direct comparison of these values does not lead to meaningful mechanistic information.

The k_0 for the Cu(II)-catalyzed hydrolysis of **3** manifested saturation behavior with respect to [Cu(II)], and the kinetic results obtained at pH 2 and 2.5 were analyzed in terms of eq 5, a linear

$$\frac{1}{k_0} = \frac{1}{k_{cat}} + \left(\frac{(1 + [\mathrm{H^+}]/K_a^S)}{k_{cat}K_f^{MS}}\right)\left(\frac{1}{[\mathrm{Cu(II)}]}\right) \qquad (5)$$

Table II. Kinetic Parameters for the Cu(II)-Catalyzed Hydrolysis of **1–3**[a]

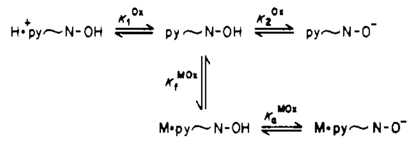
	1[b]	**2**[c]	**3**[d]
k_{cat}^W,[e] 10^{-3} s^{-1}	17 ± 1	>700[f]	2.8 ± 0.1
$K_f^{CuS}/(1 + [H^+]/K_a^S)$, M^{-1}			490 at pH 2.0 900 at pH 2.5
K_f^{CuS}, M^{-1}	76 ± 2	[f]	1500 ± 10

[a] Measured at 25 °C and ionic strength 0.3 (with NaCl) in the presence of 0.8% (v/v) CH_3CN. K_a^S values are listed in Table III. [b] Reference 4. [c] Reference 5. [d] This study. [e] k_{cat} value for the water attack at $Cu^{II}S$. [f] Exact values were not measured because the reaction was too fast.

Table III. Values of the Thermodynamic Parameters for the Oximes and the Oxime Esters[a]

param[b]	**1/1a**	**2/2a**	**3/3a**[c]
pK_1^{Ox}	3.6,[d] 3.8[e]	4.2[f]	3.0[g]
pK_2^{Ox}	10.0,[h] 10.2[d]	10.8[i]	10.0
pK_a^S	2.3[j]	2.9[k]	2.3[g]
pK_a^{ZnOx}	6.5[h]	7.0[i]	6.7
K_f^{ZnOx}	150[h]	420[i]	70
pK_a^{CuOx}	3.2[e]	3.5[f]	[l]
K_f^{CuOx}	5.4 × 10^4 [e]	7.8 × 10^5 [f]	1.4 × 10^3

[a] Standard deviations for p*K* values are ±0.1 and those for K_f are ±10% of the K_f values. Unless noted otherwise, the values were measured at 25 °C in the presence of 0.8% (v/v) CH_3CN. Ionic strength was maintained at 1.0 (0.3 for Cu(II) complexes) with NaCl. [b] K_a^S is defined by eq 2, and others as follows:



[c] This study. [d] Reference 8. Conditions are not specified. [e] Reference 9. Measured at 25 °C and ionic strength 0.3 (with $NaClO_4$) in the presence of 3.2% (v/v) CH_3CN. [f] Reference 10. [g] This p*K* may reflect the protonation of the pyridyl group located at the syn position relative to the oxime hydroxyl group. In that case, the p*K* for the other pyridyl group should be smaller than this value. [h] Reference 11. Measured at 25 °C with 0.01 M 2,6-lutidine. [i] Reference 6. [j] Reference 4. [k] Reference 5. [l] Spectral properties were not suitable for the spectroscopic titration.

transform of eq 3. As described previously for the Cu(II)-catalyzed hydrolysis of **1**,[4] the plot of $1/k_0$ against 1/[Cu(II)] produced a straight line. From the intercept and the slope of the straight line, k_{cat} and K_f^{MS} were calculated. Values of the kinetic parameters for the Cu(II)-catalyzed reactions are summarized in Table II. The K_f^{MS} for **3** is much greater than that for **1**, while k_{cat} is smaller for **3** compared with that for **1**. The value of $k_{cat}K_f^{MS}$ is 3.3 times greater for **3** than for **1** as the values of kinetic parameters for the Zn(II)-catalyzed reaction.

As **3** contains an additional coordination site, whether the K_f^{MS} values for Cu^{II}(**1**) and Cu^{II}(**3**) reflect the formation of the same type of complex is not clear from the kinetically measured parameter values. Therefore, several thermodynamic parameters were measured for the oxime esters and the oximes in order to clarify the binding mode in Cu^{II}(**3**) and are summarized in Table III.

The pK_1^{Ox} for **1a–3a** reflects the relative inductive effects on the pyridyl nitrogen atom exerted by the various R groups of A. Thus, the electron density on the pyridyl nitrogen atom is lower in **3a** than in **1a** or **2a** (CH_3 > H > pyridyl). The magnitude of K_f^{ZnOx} or K_f^{CuOx} for **1a–3a** reflects the same inductive effects. In

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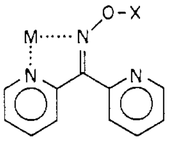
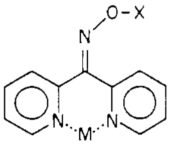
addition, the ionization (pK_a^{ZnOx}) of the oxime hydroxyl group of **3a** is enhanced upon formation of the Zn(II) complex to the same extent as that of **1a** or **2a**. Therefore, the metal complexes of **3a** should be assigned to C instead of D.



C: X = H

E: $X = \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3}$



D: X = H

F: $X = \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3}$

The 600-fold smaller value of K_f^{CuS} for **1** (Table II) compared with K_f^{CuOx} for **1a** is due to the greater electron-withdrawing effect of the acetoxy group compared with the hydroxyl group and the consequently lower electron density on the coordinating nitrogen atom in the acetyl ester. On the other hand, K_f^{CuS} (1500 M^{-1}) for **3** is similar to K_f^{CuOx} (1400 M^{-1}) for **3a**. This cannot be explained if these values are assigned to E and C, respectively. Instead, an alternative binding mode of F is required to explain the large value of K_f^{CuS} for **3**.[12]

Although the metal complexation of **3** produces F as the major species, F cannot be the productive intermediate for the ester hydrolysis. The only catalytic role of the metal ion proposed in F is to lower the pK_a of the leaving oxime, leading to the enhanced leaving ability of the oxime. The decrease in the pK_a of the leaving oxime should be smaller in F compared with E or B. The decrease in the pK_a of the oxime group in B alone did not account for the large rate acceleration observed with **1** and **2**,[3-5] and additional catalytic factors illustrated by B were needed to explain the observed results. Therefore, E should be present in the metal-catalyzed hydrolysis of **3** as the productive intermediate, and the scheme of eq 6 is better suited than eq 2 for the metal-catalyzed hydrolysis of **3**.

$$\mathrm{H(3)^+} \xrightleftharpoons{\mathrm{p}K_a^{\mathrm{S}}} \mathbf{3} \xrightleftharpoons{K_f^{\mathrm{MS}},\ \mathrm{M(II)}} \mathrm{F} \xrightleftharpoons{K_{\mathrm{MS}}} \mathrm{E} \xrightarrow{k'} \mathrm{C} + \mathrm{CH_3COOH} \quad (6)$$

For eq 6, the observed value of k_{cat} corresponds to $k'K_{\mathrm{MS}}$. As K_{MS} is smaller than 1, k' should be greater than the $k_{\mathrm{cat}}^{\mathrm{W}}$ value listed in Table II. At present, k' for **3** cannot be compared correctly with $k_{\mathrm{cat}}^{\mathrm{W}}$ for **1** or **2**. Consequently, it is not clear whether the additional pyridyl ring in **3** exerts greater steric compression[5] in the transition state compared with the hydrogen or methyl (R in B) of **1** or **2**.

Experimental Section

O-Acetyldi-2-pyridyl ketoxime (**3**) was prepared by reacting di-2-pyridyl ketoxime (**3a**)[9] with an excess amount of acetic anhydride for 2 h at 80 °C. The residue obtained after evaporation of the excess acetic anhydride was recrystallized from ethyl acetate–hexane, mp 81–82 °C.

Kinetic measurements were performed as described previously.[3-5] Thermodynamic measurements were performed by spectral titration as reported previously.[7]

Acknowledgment. This work was supported by a grant from the Korea Science and Engineering Foundation.

Registry No. 3, 97571-67-0; Zn(II), 23713-49-7; Cu(II), 15158-11-9.

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(12) Assignment of K_f^{CuOx} for **3a** to C indicates that K_f for the Cu(II) complex D is smaller than 1400 M^{-1} and, consequently, smaller than K_f^{CuS} for F. The greater K_f for F compared with that for D may be attributed to π back-bonding.[13-16] The acetoxy group in F could enhance the back-bonding through electronic effects. In addition, a steric effect to shorten the metal–N bonds[17] in F by the introduction of the acetoxy group is possible.

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Additions and Corrections

1985, Volume 24

Lechosław Latos-Grażyński: Proton Nuclear Magnetic Resonance Characterization of Chloro(*N*-methyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) and Chloro(*N*-methyloctaethylporphyrinato)nickel(II) Complexes.

Page 1683. In the second column, last paragraph, line 16, the expression for the line width ratio is incorrect. The correct version is as follows: $r_{12}^{-6}:r_{22}^{-6}:r_{23}^{-6}:r_{42}^{-6}$.—Lechosław Latos-Grażyński

Paul R. Sharp* and Kevin G. Frank: Reactions of WCl_2L_4 (L = a Phosphine). 2. Tungsten(IV) and Tungsten(V) Hydride Complexes.

Page 1808. The following reference to another preparation of $WH_2Cl_2(PMe_3)_4$ was inadvertently omitted: Chiu, K. W.; Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803–810. We thank Prof. G. Wilkinson for bringing this omission to our attention.—Paul R. Sharp