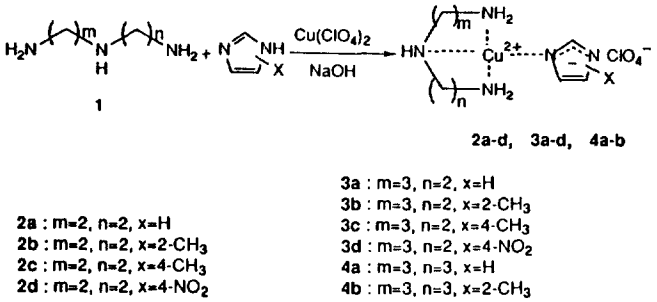
monohydroxy chelate of BIPY, which is less basic than TMED, has greater affinity for an additional donor atom than is the analogous chelates of the aliphatic diamines; hence dimer formation takes place more easily in the case of the aromatic compounds. The dimers of these chelate compounds were known to possess negligible catalytic activity.[5,12]

References

1. T-Wagner-Jauregg, Heckley, Jr., B. E.; Lies, T. A.; Owens, O. O.; Proper, R. *J. Am. Chem. Soc.* **1955**, *77*, 922.
2. Courtney, R. C.; Gustafson, R. L.; Westerback, S. J.; Hyytiainen, H.; Chaberek, Jr., S. C.; Martell, A. E. *J. Am. Chem. Soc.* **1957**, *79*, 3030.
3. Fowkes, F. M.; Ronay, G. S.; Ryland, L. B. *J. Phys. Chem.* **1958**, *62*, 867.
4. Epstein, J.; Rosenblatt, D. H. *J. Am. Chem. Soc.* **1958**, *80*, 3596.
5. Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1962**, *84*, 2309.
6. Gulick, W. M.; Geske, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 2928.
7. Menger, F. M.; Gan, L. H.; Johnson, E.; Durst, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 2800.
8. Morrow, J. R.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 3387.
9. Scheller-Krattiger, V.; Siegel, H. *Inorg. Chem.* **1986**, *25*, 2628.
10. Epstein, J.; Mosher, M. A. *J. Phys. Chem.* **1968**, *72*, 622.
11. Albizo, J. M.; Ward, J. R. *Catalysis of Soman Hydrolysis by HEPES*; CRDEC-TR-226, U. S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Groung, MD **1988**.
12. Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 525.



Scheme 1.

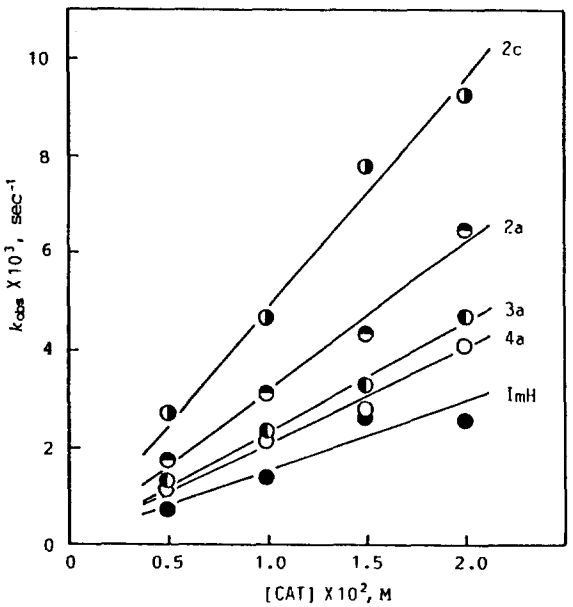


Figure 1. Plots of [CAT] *vs.* k_{obs} for the hydrolysis of *p*-nitrophenyl acetate at 25℃ (pH 7.0).

Catalysis of Triamine-copper(II)-imidazolate Complexes for Ester Hydrolysis

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Imidazole and imidazolate as catalysts for ester hydrolyses have aroused many worker's interest,[1] since they have an essential active site of several hydrolytic enzymes.[2] Recently imidazole when co-ordinated to a copper(II) complex of diethylenetriamine (**2a**) was reported to exhibit a marked increase in catalytic effect on the hydrolysis of *p*-nitrophenyl benzoate.[3]

In this work, we have synthesized nine additional derivatives of triamine-copper(II)-imidazolate complexes (**2b-4b** in Scheme 1), and examined their catalytic activity to the hydrolysis of *p*-nitrophenyl acetate (NPA).

Catalytic actions of these complexes to the hydrolysis of *p*-nitrophenyl acetate, PNA + $H_2O \xrightarrow{CAT}$ AcOH + *p*-nitrophenol, were investigated by a similar method utilized for the imidazole catalyzed hydrolysis of the same substrate by Lombardo.[4] The rate law applied to this study is written in Eqs. (1)-(3), where k_o is the first-order rate constant for the uncatalyzed hydrolysis and k_{cat} is the second-order rate constant for the catalysis. Under pseudo first-order conditions in which [CAT]≫[NPA], Eq. (1) is reduced to Eq. (2) and Eq. (3). As shown several examples in Figure 1, plots of k_{obs} against [CAT] revealed straight lines. Then k_{cat} values were derived (Table 1) from slopes of the lines.

$$\text{rate} = \{k_o + k_{cat}[\text{CAT}]^n\}\ [\text{NPA}] \quad (1)$$

$$\text{rate} = k_{obs}[\text{NPA}] \quad (2)$$

$$k_{obs} = k_o + k_{cat}[\text{CAT}]^n \quad (3)$$

The first-order rate constants (k_o) for the uncatalyzed hydrolysis, obtained from intercepts of lines in Figure 1, are in the range of $4.95\text{-}5.25 \times 10^{-5}$ s^{-1}. The ring size of complexes seems to affect the catalytic activity. The complex consists

Table 1. Second-order Rate Constants (k_{cat}) for the Hydrolysis of *p*-Nitrophenyl Acetate at 25℃ (pH=7.0); [NPA]=8.13×10^{-5} M, [CAT]=$0.5\text{-}2.0\times10^{-2}$ M

Catalysts	$k_{cat}\times10$, $M^{-1}s^{-1}$
Imidazole (ImH)	1.48
4-CH_3-ImH	2.22
2a	3.12
2b	4.72
2c	4.81
2d	0.29
3a	2.28
3b	2.88
3c	2.69
3d	1.73
4a	1.99
4b	2.44

of two five-membered rings (**2a**) showed better catalytic action than that consists of one five-membered ring and one six-membered ring (**3a**) or that consists of two six-membered rings (**4a**). Substituents on imidazole ring also affected the catalytic activity. The catalytic action was promoted by the presence of an electron-donating group but suppressed by the presence of an electron-withdrawing group.

The catalyzed hydrolysis of *p*-nitrophenyl acetate has been considered to proceed *via* two distinct but kinetically indistinguishable pathways: (1) general base catalysis in which imidazolate enhances the nucleophilicity of water through partial proton abstraction from water, and (2) nucleophilic catalysis in which imidazolate nitrogen attacks directly to the carbonyl carbon of the acetate. Though both mechanisms are still controversial,[4] kinetic results suggest that imidazolate is a direct participant in the transition state and imidazole when co-ordinated to a Cu(II) complex with triamine displays a more reinforced nucleophilicity. However, the reason why the complex of smaller ring-sized (**2a**) shows better catalytic action than that of larger ring-sized (**3a** or **4a**), as observed in this work, is not clear.

Experimental

Preparation of Complexes. All monoperchlorate salts of triamine-copper(II)-imidazolate complexes (**2a-d, 3a-d** and **4a-b**) were obtained from $Cu(ClO_4)_2$, imidazole and corresponding triamine (**1**) by using a slight modification of the method reported by Sato, *et al.* for **2a** synthesis.[5] Products were identified by checking elemental analysis data and UV bands occured near 220, 260, and 330 nm presumably due to σ(Im) $\rightarrow$, π_2(Im)$\rightarrow$, and π_1(Im)$\rightarrow$Cu(II) LMCT (ligand to metal charge-transfer) absorptions respectively.[6] ^{1}H-NMR spectra (Bruker 300 MHz) of these complexes showed corresponding kinds of equivalent protons with broad peaks ranging from -13 to 41 ppm, but their resonance positions and integrals were unreliable. Analytical data are as follows.

Diethylenetriamine-copper(II)-imidazolate monoperchlorate (2a). Pale blue crystal; mp. 154-158℃ (dec.). Anal. Calcd for $C_7H_{16}N_5O_4$ ClCu: C, 25.23; H, 4.84; N, 21.01; Cl, 10.64. Found: C, 25.20; H, 4.75; N, 20.50; Cl, 10.45.

Diethylenetriamine-copper(II)-2-methylimidazolate monoperchlorate (2b). Pale blue crystal; mp. 180℃ (dec.). Anal. Calcd for $C_8H_{18}N_5O_4ClCu$: C, 27.67; H, 5.23; N, 20.17; Cl, 10.21. Found: C, 27.03; H, 5.18; N, 19.95; Cl, 9.81.

Diethylenetriamine-copper(II)-4-methylimidazolate monoperchlorate (2c). Pale blue crystal; mp. 164-165℃ (dec.). Anal. Calcd for $C_8H_{18}N_5O_4ClCu$: C, 27.67; H, 5.23; N, 20.17; Cl, 10.21. Found: C, 26.72; H, 5.19; N, 19.85; Cl, 9.92.

Diethylenetriamine-copper(II)-4-nitroimidazolate monoperchlorate (2d). Blue crystal; mp. 170℃ (dec.). Anal. Calcd for $C_7H_{15}N_6O_6ClCu$: C, 22.23; H, 4.00; N, 22.22; Cl, 9.37. Found: C, 21.52; H, 3.95; N, 21.05; Cl, 8.95.

***N*-(2-Aminoethyl)-1,3-propanediamine-copper(II)-imidazolate monoperchlorate (3a).** Blue crystal; mp. 166-168℃ (dec.). Anal. Calcd for $C_8H_{18}N_5O_4ClCu$: C, 27.67; H, 5.23; N, 20.17; Cl, 10.21. Found: C, 26.47; H, 5.10; N, 19.61; Cl, 10.01.

***N*-(2-Aminoethyl)-1,3-propanediamine-copper(II)-2-methylimidazolate monoperchlorate (3b).** Pale blue crystal; mp. 175-179℃ (dec.). Anal. Calcd for $C_9H_{20}N_5O_4ClCu$: C, 29.92; H, 5.58; N, 19.38; Cl, 9.81. Found: C, 29.05; H, 5.62; N, 20.05; Cl, 10.03.

***N*-(2-Aminoethyl)-1,3-propanediamine-copper(II)-4-methylimidazolate monoperchlorate (3c).** Blue crystal; mp. 188℃ (dec.). Anal. Calcd for $C_9H_{20}N_5O_4ClCu$: C, 29.92; H, 5.58; N, 19.38; Cl, 9.81. Found: C, 30.03; H, 6.02; N, 20.15; Cl, 10.25.

***N*-(2-Aminoethyl)-1,3-propanediamine-copper(II)-4-nitroimidazolate monoperchlorate (3d).** Blue cryatel; mp. 193℃ (dec.). Anal. Calcd for $C_8H_{17}N_6O_6ClCu$: C, 24.50; H, 4.37; N, 21. 43; Cl, 9.04. Found: C, 23.80; H, 4.03; N, 20.35; Cl, 8.62.

3,3′-Iminobispropylamine-copper(II)-imidazolate monoperchlorate (4a). Blue crystal; mp. 152.5-154℃ (dec.). Anal. Calcd for $C_9H_{20}N_5O_4ClCu$: C, 29.92; H, 5.58; N, 19.38; Cl, 9.81. Found: C, 28.94; H, 5.22; N, 18.13; Cl, 9.02.

3,3′-Iminobisproylamine-copper(II)-2-methylimidazolate monoperchlorate (4b). Pale blue crystal; mp. 155.5-158℃ (dec.). Anal. Calcd for $C_{10}H_{22}N_5O_4ClCu$: C, 32.00; H, 5.91; N, 18.66; Cl, 9.45. Found: C, 31.01; H, 5.03; N, 15.75; Cl, 9.03.

Kinetic Procedure. Rates of hydrolysis of *p*-nitrophenyl acetate in the presence corresponding triamine-Cu(II)-imidazolate complexes as catalyst were measured by monitoring the appearance of *p*-nitrophenoxide, a hydrolysis product, at 405 nm. A Kontron Uvikon 860 UV-Visible Spectrophotometer fitted with an external recorder was used. Temperature was controlled to within ± 0.1℃ with a Julabo SN Circulator. Kinetics were performed at an ionic strength of 0.1 M which was adjusted with KCl. The pH of the reactant buffer (pH=7.0) was measured before and after the reaction with a Corning pH Meter 220. Pseudo first-order rate constants (k_{obs}'s) were obtained from the slopes of linear plots of in A_∞/A_∞-At against t, where A_∞ is the optical density of the reaction mixture measured at infinity time (more than ten half-lives).

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References

1. (a) Bruice, T. C.; Benkovic, S. *Bioorganic Mechanisms*, Benjamin, W. A., New York, 1966; Vol. 1, p 46-66; (b) Overberger, C. G.; Pierr, T. S.; Vorchheimer, N. Lee, J.; Yaroslavsky, S. *J. Am. Chem. Soc.* **1965**, *87*, 296.
2. (a) Wilson, T. B.; Bergmann, F. *J. Biol. Chem.* **1950**, *186*, 683; (b) Hammond, R. B.; Gutfreund, H. *Biochem. J.* **1955**, *61*, 187; (c) Gutfreund, H., *Trans. Faraday Soc.* **1955**, *51*, 441; (d) Mounter, L. A. *J. Biol. Chem.* **1956**, *219*, 677.
3. Sato, M.; Ohmae, K.; Nagae, S.; Nakaya, J. *J. Chem. Soc., Chem. Commun.* **1987**, 839.
4. Lambardo, A. *J. Chem. Educ.* **1982**, *59*, 887.
5. Sato, M.; Nagae, S.; Ohmae, K.; Nakaya, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1947.
6. Fawcett, T. G.; Bernarducci, E. E.; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 2598.
7. Kim, C. S.; Kim, T. S.; *J. Korean Chem. Soc.* **1993**, *37*, 265.