Several things can be considered for discrepancies of the K values and theoretical fittings. Constant efficiencies of non-radiative decay are assumed in Eq. (3), however, the efficiency of non-radiative decay usually decreases at low temperature. If the reduced efficiency of non-radiative decay is used at low temperatures, the consistency of the K values and the power law would be improved. Participation of molecular vibrations in thermal conduction of molecular crystals[2,3,20] is not considered in the simple phonon gas model. At very low temperature below θ_D, thermal conduction occurs mainly by phonons. When temperature rises to produce sufficient population of phonons, low lying vibrations are excited and complex dynamics of molecular vibrations activate. Among various vibrational relaxation processes responsible for the spatial energy transport, resonant intermolecular vibrational energy transfer is significant at low temperatures and interrupted with temperature rise.[2b] Deviation from the power law may be interpreted as the results of direct resonant intermolecular vibrational energy transfer.

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Potentiometric Study of Co(II), Ni(II), Cu(II), and Zn(II) Complexes of Pyridyl- and Pyrrolyl-Containing Triethylenetetramine Ligands

Sun-Deuk Kim*, Jun-Kwang Kim, and Woo-Sik Jung†

Department of Chemistry, Taegu University,
Kyongsan 713-714, Korea
†*Department of Industrial Chemistry,*
*Yeungnam University,*
Kyongsan 712-749, Korea

The role of transition metal ions in the redox functions of various enzymes in the living systems has been extensively studied by using synthetic model complexes.[1] Many of the complexes are those of Schiff bases which are synthesized from the condensation reaction between *ortho*-substituted aromatic aldehydes and various primary amines.[2] The Schiff base complexes which contain -CH=N bonds are usually insoluble or unstable in water. In contrast, the metal complexes of ligands which are obtained by hydrogenation of -CH=N bonds in Schiff bases are soluble and stable in water. The hydrogenation is unlikely to affect their coordination ability to form strong bonds with transition metal ions. The hydrogenated ligands are more flexible than the parent compounds and which thus can present their donor atoms to a metal atom from either a planar or a nonplanar arrangement.[3]

Martell *et al.* studied the interaction of pyridyl- and imidazolyl-containing ligands with a series of first-row transition metals and showed that the stability constants of the ligands are higher than those of the analogous aliphatic polyamines.[4~7] This study deals two ligands, 1,12-bis(2-pyridyl)-2,5,8,11-tetraazadodecane (pytrien) and 1,12-bis(2-pyrrolyl)-2,5,8,11-tetraazadodecane (pyrrotrien) as their tetrahydrochloride salts. Proton association constants and stability constants of the ligands with Co(II), Ni(II), Cu(II), and Zn(II) ions are

pytrien   pyrrotrien

Notes

Bull. Korean Chem. Soc. **1996**, Vol. 17, No. 1 81
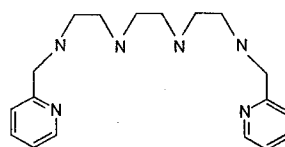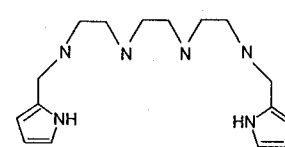
determined by potentiometry and are compared with those of the analogous ligands previously studied.

Experimental

Materials. 1,12-Bis(2-pyridyl)-2,5,8,11-tetraazadodecane Tetrahydrochloride(pytrien·4HCl) and 1,12-Bis(2-pyrrolyl)-2, 5,8,11-tetraazadodecane Tetrahydrochloride(pyrrotrien·4HCl). The ligand of pytrien·4HCl was synthesized by a modification of the method of Arulsamy *et al.*[1] Pyridine-2-carboxalde-hyde (2.14 g, 0.02 mol) and triethylenetetramine (1.46 g, 0.01 mol) were dissolved in 70 mL of absolute methanol and refluxed for 1 h under dinitrogen atmosphere. The solution was then hydrogenated at room temperature over 1 g of 10%-platinum on activated carbon for 10 h at slightly higher than 1 atom of hydrogen. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in 100 mL of methanol. The solution was acidified to pH 2 by concentrated HCl and allowed to stand at 4 °C overnight. The crude crystals formed were filtered and recrystallized by dissolving in H_2O followed by addition of methanol until the white crystal reprecipitated. The yield was 65%. The crystal gave satisfactory elemental analysis, ^{1}H- and ^{13}C NMR, and mass spectra. The preparation of pyrro-trien·4HCl was identical to that described for pytrien·4HCl. Yield: 72%. Anal. Cald for $C_{16}H_{32}N_6Cl_4$: C, 43.07; H, 6.28; N, 18.84. Found: C, 45.03; H, 6.42; N, 18.68. ^{1}H NMR (D_2O-DMSO-*d*) : δ 6.62 (t, 2H, pyrrole H), 6.26 (q, 2H, pyrrole H), 6.06 (t, 2H, pyrrole H), 4.16 (s, 4H, methylene), 3.14-3.31 (m, 12H, ethylene). ^{13}C NMR (D_2O-DMSO-*d*₆): δ 121.0, 120.4, 111.5, 109.2, 44.7, 44.0, 43.6, 42.3.

Stock solutions of the metal ions were prepared from reagent grade nitrate salts and standardized by titration with EDTA using Murexide as an indicator.

Spectroscopic Measurements. The UV-visible electronic absorption spectra were recorded on a Shimadzu UV-160A spectrophotometer. ^{1}H- and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer and reported as δ in ppm relative to DMSO-*d*₆ (2.49 ppm for ^{1}H and 39.7 ppm for ^{13}C). Mass spectra were obtained on a Kratos 25-RFA GC-Mass spectrometer. Infrared spectra were recorded as KBr disks on a Shimadzu IR 440 spectrophotometer.

Equilibrium Measurement. All titrations were carried out under dinitrogen atmosphere using a Metrohm 605 pH meter. In all cases, the ligand was present at 1.00×10^{-3} M concentration. Solutions were adjusted to 0.10 M ionic strength by the addition of KNO_3 and maintained at 25.0 ± 0.1 °C. The proton association constants ($K_H{}^n$) of the ligand (L) were determined by titration of the protonated ligand with standardized KOH in the absence of the complexing metal ions and then by calculation of the results by the aid of a computer program of PUKAS.[8] The constants $K_H{}^n$ are defined by $[H_nL]/[H][H_{n-1}L]$.

The stability constants were determined by titration of the protonated ligand with KOH in the presence of the metal ions. The titrations were performed on 1 : 1 molar ratios of the ligand with metal ions. Titration curves were calculated by a computer program of BESTA.[8] Two stability constants obtained were defined as follows:
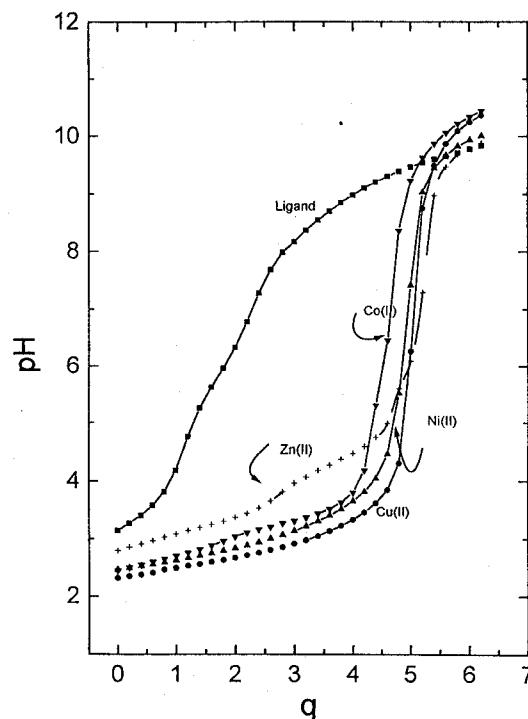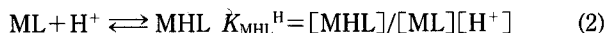
$$M + L \rightleftharpoons ML \quad K_{ML} = [ML]/[M][L] \quad (1)$$

Figure 1. Potentiometric equlibrium curves for 1 : 1 molar ratios of pytrien with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions at 25 °C. $T_L = T_M = 1.00 \times 10^{-3}$ M; ionic strength = 0.10 M (KNO_3). *q* is the number of equivalents of KOH added.

$$ML + H^+ \rightleftharpoons MHL \quad K_{MHL}{}^H = [MHL]/[ML][H^+] \quad (2)$$

where [M], [ML], [MHL], and [L] represent, respectively, the equilibrium concentrations of the free metal ion, of the 1 : 1 metal chelate, of the protonated 1 : 1 metal chelate, and of the free ligand in its most basic form.

Results and Discussion

Synthesis. Two ligands obtained were characterized by elemental analysis, mass spectrometry, and IR and NMR spectroscopy. The absence of a strong C=N stretching band (1645 cm⁻¹) of the parent Schiff bases in IR spectra confirmed the successful reduction of the aldimino groups of the Schiff bases. It was found from the elemental analysis that the products were isolated as tetrahydrochloride salts. Four aliphatic amino groups are likely to be protonated. The mass spectra of pyrrotrien measured as its tetrahydrochloride salt gave its parent peak (m/e = 304), which corresponds to [pyrrotrien]⁺ ion. The ligand was also well characterized by ^{1}H- and ^{13}C NMR spectra. Four ^{13}C signals at >109 ppm and four ^{13}C signals at the higher field correspond to carbons on pyrrolyl moieties and aliphatic branches, respectively.

Equilibrium Constants. The potentiometric equilibrium curves for free ligands are shown in Figures 1 and 2, which were obtained by measuring the pH of aqueous solution of the ligands as a function of 3the moles (q) of KOH added per mole of ligand. The ligand protonation constants calculated from the curves are listed in Table 1, along with corresponding values for triethylene-tetramine (trien), 1,6-bis(2-pyridyl)-2,5-diazahexane(pyen), and 1,12-bis(2-pyri-
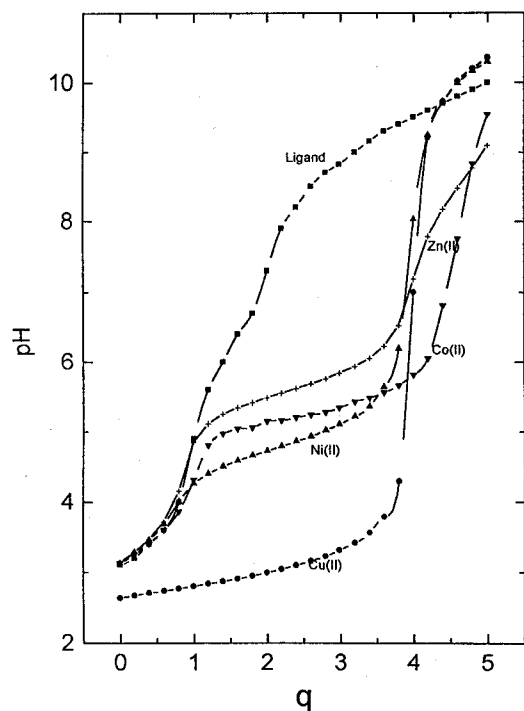
Figure 2. Potentiometric equlibrium curves for 1 : 1 molar ratios of pyrrotrien with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions at 25 °C. $T_L = T_M = 1.00 \times 10^{-3}$ M; ionic strength=0.10 M (KNO$_3$). q is the number of equivalents of KOH added.

Table 1. Ligand Protonation Constants for trien, pyen, pydien, pytrien, and pyrrotrien at 25 °C

Ligand	$\log K_H^1$	$\log K_H^2$	$\log K_H^3$	$\log K_H^4$	$\log K_H^5$	Ref
trien	9.92	9.20	6.67	3.32		4
pyen	8.23	5.45	1.81	1.62		4
pydien	8.88	7.04	3.82	1.44		5
pytrien	9.08	8.78	7.51	5.42	2.99	This work
pyrrotrien	8.94	8.67	6.18	3.79		This work

dyl)-2,5,8,11-triaza-nonane (pydien). The values from K_H^1 to K_H^4 for pytrien and pyrrotrien represent protonation of aliphatic amine groups and are similar each other. The one lowest value for pytrien represents protonation of one of pyridyl groups, in view of the fact that the nitrogen atom on the pyridyl moiety is less basic than that on aliphatic amines because the former is more *s*-characteristic than the latter.[9] The fourth protonation constant is much lower than the first three protonation constants for pytrien and pyrrotrien, as for trien. This seems to be the result of the strong electrostatic repulsions between protonated aliphatic nitrogen atoms: the reasoning should apply to the case of pydien, where the third protonation constant is much lower than the first two protonation constants.

The values of $\log K_H^n$ increase in pyen, pydien, pytrien, and pyrrotrien as the aliphatic amine chain becomes longer. The four highest ligand protonation constants for pytrien are comparable with those for trien. Martell *et al.* explained the lowered values of $\log K_H^n$ for pydien compared with dien

Table 2. Stability Constants for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} Complexes of pyen, pydien, pytrien, and pyrrotrien at 25 °C

Ligand	Equlibrium Constant	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ref
pyen	$\log K_{ML}$	12.8	12.7	16.3	11.5	4
pydien	$\log K_{ML}$	14.73	19.20	20.85	13.71	5
	$\log K_{MHL}^H$	2.28		1.83		
pytrien	$\log K_{ML}$	17.02	23.03	24.15	16.03	This
	$\log K_{MHL}^H$	6.42	6.51	6.07	5.21	work
pyrrotrien	$\log K_{ML}$	12.28	13.46	20.77	11.08	This
	$\log K_{MHL}^H$	2.58	3.28	5.85	1.85	work

in terms of the inductive effect of the two pyridyl groups.[5,6] The values of $\log K_H^1$ and $\log K_H^2$ are smaller for pytrien than for trien but the values of $\log K_H^3$ and $\log K_H^4$ are larger for pytrien than for trien. Thus the difference in log-K_H^n values between pytrien and trien is likely to be hard to be explained by only the inductive effect of the two pyridyl groups of pytrien.

Titrations of pytrien·4HCl and pyrrotrien·4HCl in the presence of the ions Co(II), Ni(II), Cu(II), and Zn(II) with KOH yield neutralization curves which are shown in Figures 1 and 2. These curves are representative of the overlapping equilibria defined by Eqs. 1 and 2. The chelate stability constants (K_{ML}) and the chelate protonation constants (K_{MHL}^H) obtained are listed in Table 2. In addition, corresponding values of pyen and pydien are given for comparison. For each metal complex the stability constant of pyrrotrien is much smaller than that of pytrien and close to that of pyen except for Cu^{2+} complex, suggesting that pyrrotrien is a tetra-coordinated ligand.

The stability constants show the increase expected on going from tetra- to hexa-coodinated ligands for all metal complexes. On the assumption that the sum of protonation constants of a ligand reflects 4its total basicity, the plots of $\log K_{ML}$ against ΣK_H^n were almost linear for three pyridyl-containing ligands in Table 2 and the line for each metal ion was drawn above the line formed by the aliphatic poly-amine ligands. This enhanced stability is partially attributed to bonding between the pyridyl π or π* orbitals and the d orbitals of Co(II), Ni(II), and Cu(II) ions.[6] But the enhanced stability of Zn(II) ion with the d^{10} electronic configuration is not likely to be due to the strong bonding because the d orbitals of the zinc is too low in energy to overlap strongly with ligand orbitals. This indicates that there may be other factors associated with the more rigid ring structure of pytrien relative to an aliphatic amine.[7]

The chelate protonation constants (K_{MHL}^H) are close to the protonation constants K_H^4 and much higher than one would predict for the protonation of a pyridyl group in the free ligand. This is well explained by considering the one-protonated complexes MHL, where one aliphatic amine adjacent to the pyridyl moiety and not one pyridyl nitrogen is protonated and two potentially coordinating groups involving the pyridyl group are dangling in solution.

Recently Arulsamy *et al.* showed that the geometry of Ni (pytrien)$^{2+}$ is six-coordinate pseudooctahedral, with pyridine nitrogen atoms mutually *cis* and *trans* to amine nitrogen

atoms, while that of Mn(pytrien)$^{2+}$ is trigonal prismatic.[1] The UV-vis spectra of M(pytrien)$^{2+}$ (M=Co and Cu) in aqueous solution were measured and their absorption maxima in the visible region are as follows: Co, 471 nm (ε=18 M^{-1}cm^{-1}); Cu, 591 nm (ε=94 M^{-1}cm^{-1}). It is still uncertain whether M(pytrien)$^{2+}$ (M=Co and Cu) are pseudooctahedral or trigonal prismatic. The crystal structures of M(pytrien)$^{2+}$ (M=Co, Cu, and Zn) are to be determined.

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Oxidative Dehydrogenation of an Octahedral Nickel(II) Complex of Saturated Tetraaza Macrocycle Containing N-(2-Hydroxyethyl) Pendant Arms: Synthesis of a Square-Planar Nickel(II) Complex of Unsaturated Macrocycle

Shin-Geol Kang*, Seong-Jin Kim, and Kiseok Ryu

Department of Chemistry, Taegu University, Kyungsan 713-714, Korea

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Some transition metal(II) complexes of polyaza macrocyclic ligands containing coordinated secondary amino groups can be chemically oxidized to metal(II) complexes with increased ligand unsaturation.[1~7] It has been suggested that metal(III) state is an intermediate in the oxidative dehydrogenation reaction.[1~6] The reaction is assisted by the central metal ion and is strongly affected by the nature of metal ion, the ligand structure, the oxidizing agent, and the reaction condition such as temperature.[1~7]

The introduction of additional functional pendant arms such as hydroxyl, carboxylato, and amino groups into polyaza macrocyclic compounds often causes a considerable change in chemical properties and structures.[8~20] Recently, we reported the synthesis and crystal structure of the octahedral nickel(II) complex [Ni(A)]$^{2+}$ in which two N-(2-hydroxyethyl) pendant arms are coordinated to the central metal ion.[8] The cyclic voltammetric study indicated that the octahedral complex [Ni(A)]$^{2+}$ is more easily oxidized to Ni(III) state than the square-planar complex [Ni(C)]$^{2+}$ containing two N-ethyl pendant arms.[8,21] In this work, we attempted the synthesis of the diimine complex [Ni(B)]$^{2+}$ from the oxidative dehydrogenation reaction (eq. (1)) of [Ni(A)]$^{2+}$ to further investigate the effects of the hydroxyethyl groups on the reaction and on the properties of the diimine complex. Interestingly, it was found that the hydroxyl groups of [Ni(B)]$^{2+}$ are not directly involved in coordination. This note reports the synthesis and properties of the new diimine complex.

$$[Ni(A)]^{2+} \xrightarrow{\ HNO_3\ } [Ni(B)]^{2+} \tag{1}$$
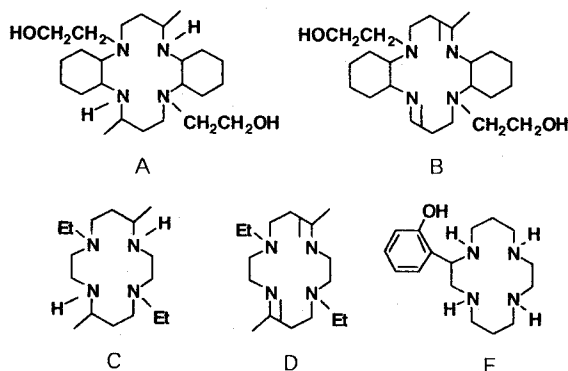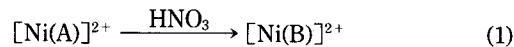
Experimental

Measurements. Infrared spectra were recorded as ether KBr pellets or Nujol mulls on a Shimadzu IR-440 spectrophotometer, conductance measurements with a Metrohm Herisau Conductometer E518, visible absorption spectra with a Shimadzu UV-440 spectrophotometer, and NMR spectra with a Bruker WP 300 FT NMR spectrometer. Magnetic susceptibilities were measured with a Johnson Matthey MK-1 magnetic susceptibility balance. Molar susceptibilities were corrected for diamagnetism of the ligand and the anions by use of Pascal's constants. Elemental analyses were performed at the Korea Basic Science Institute, Seoul, Korea. Cyclic voltammograms were recorded using a Yanaco p-1000 voltammetric analyzer equipped with a FG-121B function generator and a Watanabe X-Y recorder.

Materials. All chemicals used in syntheses were of reagent grade and were used without further purification. The complex [Ni(A)](ClO$_4$)$_2$ was prepared as described previously.[8]

Caution!. Perchlorate salts of metal complexes with organic ligands are explosive and should be handled with great caution.

Synthesis. [Ni(B)](ClO$_4$)$_2$. To an acetonitrile-water (1 : 1) suspension (20 mL) of [Ni(A)](ClO$_4$)$_2$ (1.0 g) was added an excess amount of *conc.* HNO$_3$ (*ca.* 5 mL) with stirring. The mixture was heated on a steam bath (*ca.* 70 °C) for 1 hr. After the resulting orange solution was cooled to room