

Synthesis of Naphthol-Containing Polyamines and Determination of Stability Constants of Their Metal Complexes by Potentiometric Titration

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(Received Feb. 24, 1997)

나프톨을 포함하는 폴리아민의 합성 및 전위차 적정에 의한 금속착물의 안정도상수 결정

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대구대학교 화학과

(1997. 2. 24. 접수)

Abstract: The new naphthol-containing hexadentate ligands, 1,12-bis(2-naphthol)-2,5,8,11-tetraazadodecane 4HCl (nptr) and 1,14-bis(2-naphthol)-2,6,9,13-tetraazatetradodecane 4HCl (npptr) were synthesized and characterized by elemental analysis, IR, NMR, and mass spectrometry. Acid dissociation constants and stability constants of Co(II), Ni(II), Cu(II), and Zn(II) complexes were determined at 25.0 °C and ionic strength (μ)=0.10M(KNO₃) by potentiometry. The relationship between basicity and stability constants of ligands containing aliphatic amines and 2-naphthol were studied.

요약: 새로운 여섯 자리 리간드 1,12-bis(2-naphthol)-2,5,8,11-tetraazadodecane 4HCl(nptr)와 1,14-bis(2-naphthol)-2,6,9,13-tetraazatetradodecane 4HCl(npptr)을 합성하고 원소분석, 적외선분광법, 핵자기공명법 및 질량스펙트럼으로 분석하였다. 합성된 리간드의 산해리상수와 코발트(II), 니켈(II), 구리(II) 및 아연(II)의 착물 안정도상수를 25°C, 0.1M(KNO₃) 이온강도에서 전위차적정법으로 측정하였다. 지방족 아민과 2-naphthol을 가지는 리간드의 염기도와 안정도상수의 관계를 알아보았다.

Key words: synthesis, basicity, stability constants, potentiometry

1. Introduction

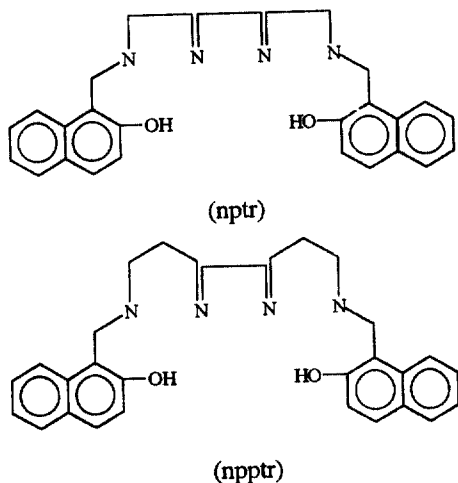
Many metal complexes containing schiff base ligands have been synthesized and studied for dioxygen uptake^{1,2} and oxidative catalyst.³⁻⁵ The ligands involving derivatives of phenol and aliphatic amine have been prepared by the schiff base

condensation of salicylaldehyde with aliphatic amines.⁶⁻¹³ The schiff base ligands and their metal complexes were highly unstable in moisture. Conversely, the metal complexes of ligands which are obtained by hydrogenation of -C=N bond in schiff base are soluble and stable in water. Compared to the imine linkages in schiff base com-

pound, the $\text{CH}_2\text{-NH}$ linkages in amine phenols are inert to hydrolytic decomposition and also provide a greater overall flexibility to the ligand.¹⁴⁻¹⁶ This increased flexibility allows the ligand to adjust to the demands of the metal ion and hence to contribute to the overall higher stability of the metal complex. It is important to prevent rapid demetalation or complex decomposition if the ligand is to be used as an effective chelating agent for the treatment of metal overload.¹⁷

The long open-chain ligands from 2-hydroxy-1-naphthaldehyde with triethylenetetramine and N, N-bis(3-aminopropyl)ethylenediamine have been synthesized by hydrogenation of imine linkages in schiff bases.

This study deals with the new hexadentate ligands 1,12-bis(2-naphthol)-2,5,8,11-tetraazadodecane $\cdot 4\text{HCl}$ (nptr) and 1,14-bis(2-naphthol)-2,6,9,13-tetraazatetradecane $\cdot 4\text{HCl}$ (npptr). Proton dissociation constants and stability constants of the ligands with transition metal ions are determined by potentiometric titration.



2. Experimental

2.1. Synthesis

1,12-Bis(2-naphthol)-2,5,8,11-tetraazadodecane tetrahydrochloride(nptr $\cdot 4\text{HCl}$) : 2-Hydroxy-1-naphthalde-

hyde 3.44g(0.02mol) and triethylene tetramine-1.46g, (0.01mol) were dissolved in 30mL of absolute methanol and refluxed for 6h under nitrogen atmosphere. The brown solution was concentrated with a rotary evaporator. The remaining brown oil was dissolved 50mL of methanol. Sodium borohydride(1.51g, 0.04mol) was added in small portions to the solution and the mixture stirred for another 12h. The reaction mixture was neutralized to pH 7.0~7.5 with concentrated hydrochloric acid in an ice bath and filtered to remove the white solid formed. The brown filtrate was further acidified to pH 1 and allowed to stand at 4°C for 2 days. The brown solid formed were filtered off, washed with methanol(95%) and air-dried. Yield: 63%. Anal. Cald for $\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_2\text{Cl}_4$: C, 55.64 : H, 6.29 : N, 9.27. Found: C, 55.24 : H, 6.72 : N, 9.53. $^1\text{H-NMR}(\text{D}_2\text{O-DMSO-d}_6)$: δ 7.96(m), 7.65(t), 7.46(t), 4.96(d), (naphthol): 4.73(s) (naphthol-methyl): 3.58~3.50 (m) (ethylene of aliphatic amine). IR(KBr pellet, cm^{-1}) : 3420(O-H), 3047(arom., C-H), 2930(aliph., C-H), 1458(C=C), 1264(C-O). UV-vis ($\text{H}_2\text{O}, \lambda_{\text{max}}(\epsilon)$): 330(4352). Mass spectrum: (m/z) :458(M^+).

1, 14-Bis(2-naphthol)-2,6,9,13-tetraazatetradecane tetrahydrochloride(npptr. 4HCl) : To a solution of 2-hydroxy-1-naphthaldehyde(3.44g, 0.02mol) in methanol 30mL, N,N'-bis-(3-aminopropyl) ethylenediamine(1.95g, 0.01mol) and 5mL of triethyl orthoformate were slowly added with stirring. The brown solution was refluxed overnight under nitrogen atmosphere. The brown solution was concentrated with a rotary evaporator and the remaining brown oil was dissolved 50mL of methanol. Sodium borohydride(1.51g, 0.04mol) was added in small portions to the solution and the mixture stirred for another 12h. The reaction mixture was neutralized to pH 7.0~7.5 with concentrated hydrochloric acid in an ice bath and filtered to remove the white solid formed. The brown filtrate was further acidified to pH 1 and to allowed stand at 4°C for 2 days.

The brown solid formed were filtered off, washed with methanol (95%) and air-dried. Yield : 55%. Anal. Calcd for $C_{30}H_{42}N_4O_2Cl_4$: C, 56.97 ; H, 6.64 ; N, 8.86. Found: C, 56.42 ; H, 6.93 ; N, 8.58. 1H -NMR (D_2O -DMSO- d_6): δ 8.01(m), 7.73(t), 7.55(t), 7.36(d), (naphthol); 4.77(s) (naphthol methyl); 3.51(s), 3.28(m), 2.54(m). $[NH-(CH_2)_2-NH$ and $NH-(CH_2)_3-NH$ of aliphatic amine). IR(KBr pellet, cm^{-1}) : 3425(O-H), 3015(arom., C-H), 2940(aliph., C-H), 1460(C=C), 1245(C-O). UV-vis(H_2O), $\lambda_{max}(\epsilon)$): 328(4318). Mass spectrum(m/z): 486(M^+).

2.2. Spectroscopic measurements

The UV-visible electronic absorption spectra were recorded by a Shimadzu UV-160A spectrophotometer. 1H - and ^{13}C -NMR spectra were measured on a Bruker AM-300 spectrometer. Infrared spectra were recorded as KBr disks on a Shimadzu IR 440 spectrophotometer. Mass spectra were measured on a Kratos 25-RFA GC-Mass spectrometer.

2.3. Equilibrium constant measurement

All titrations were carried out under nitrogen atmosphere on a Metrohm 605 pH meter and a thermostat controlled titration assembly set to $25.0 \pm 0.1^\circ C$. The term pH in this work is defined as $-\log[H^+]$ and the direct pH meter reading were used in the calculations of the equilibrium constants. The value of $\log K_w$ used in the computations was -13.78 .

The ionic strength was adjusted to 0.1M by the addition of KNO_3 as supporting electrolyte, and solution concentration of ligand and metal ions were 1.00×10^{-3} M. The total volume was 50.00 ± 0.01 mL at the beginning of each potentiometric titration. The protonation and stability constants were determined from two separate potentiometric titrations. The protonation constants $\log K_H^n$ of the ligand were determined by titration of the protonated ligand with standardized KOH solution in the absence of metal ions and then by calculation

of the results on PUKAS.¹⁸ The stability constants were determined by titration of the protonated ligand with KOH solution in the presence of metal ions. The titrations were performed on 1:1 molar ratios of the ligand to the metal ion and titration curves were calculated on BEST.¹⁸ A total of 40~50 points were collected for each experimental run. It was necessary to allow more than 15 min to reach equilibrium for each equilibrium points in some pH ranges where the complexes were forming.

3. Results and discussion

The ligands nptr and npptr were synthesized by hydrogenation of the parent schiff base in absolutely anhydrous methanol solution. The ligands obtained were characterized by elemental analysis (EA), NMR, IR and mass spectrometry. ^{13}C -NMR spectra of nptr and npptr are given in Fig. 1. The symmetric hexadentate ligands carrying 4N, 2O donor possess two naphthol groups and aliphatic amine group. ^{13}C -NMR spectra of nptr and npptr ligands in D_2O -DMSO- d_6 show naphthol carbons in the range of 157.00~104.92ppm and carbons of aliphatic group in the range of 41.83~25.22ppm. The IR spectra of ligands exhibited the typical strong bands of schiff base at 1643 cm^{-1} . The bands of the ligands were disappeared by hydrogenation of imines bonds in schiff base.

3.1. Protonation constants

The potentiometric titration curves of nptr and npptr with standard KOH solution are shown in Fig. 2 and 3. The experimental pH values were plotted as a function of q values to obtain pH profiles for each system. The q value is the ratio of moles of base added per mole of ligand present and $q=4$ corresponds to the neutral form(H_2L) of the ligand. The protonation constants K_H^n are defined by $K_H^n = [H_nL] / [H][H_{n-1}L]$. The stepwise protonation constants($\log K_H^n$) and the overall

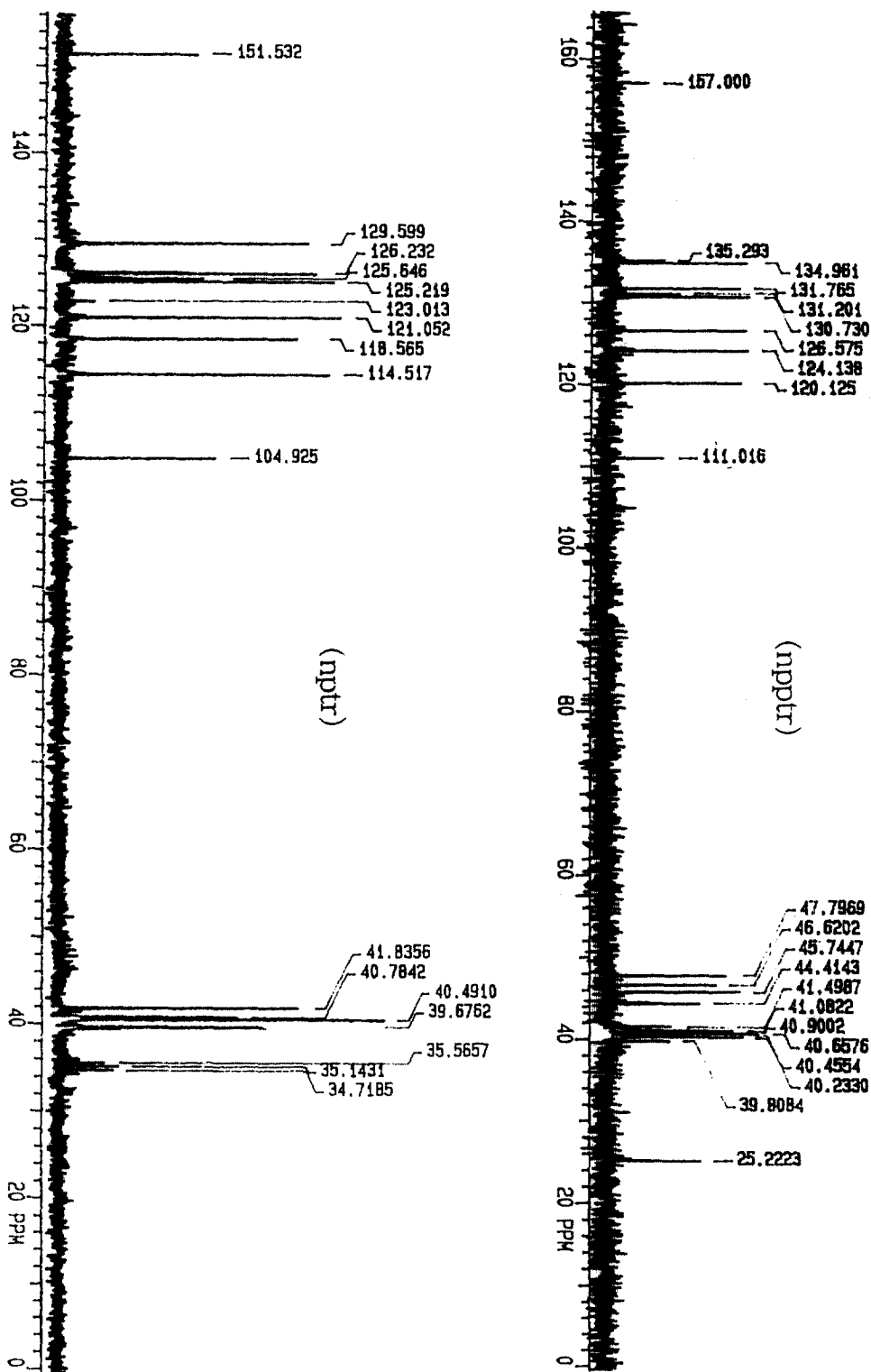


Fig. 1. ^{13}C -NMR spectrums of nptr and nppt

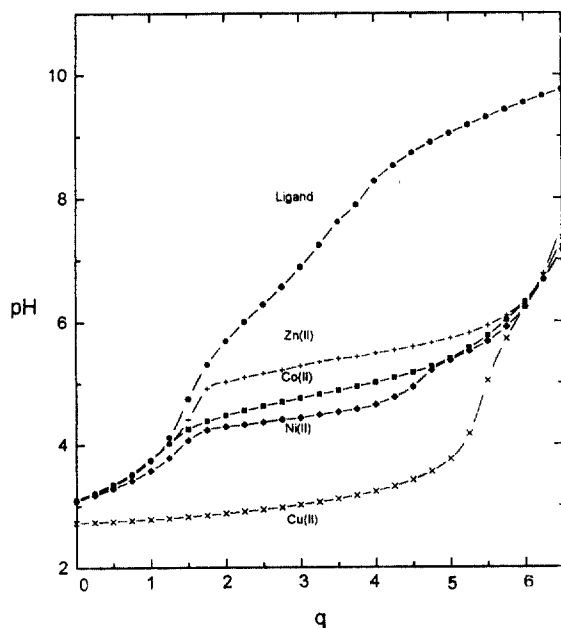


Fig. 2. potentiometric equilibrium curves of nptr and nptr-metal ion systems. $t=25.0^{\circ}\text{C}$; $\mu=0.10\text{M}(\text{KNO}_3)$; q =moles of base added per mole of ligand

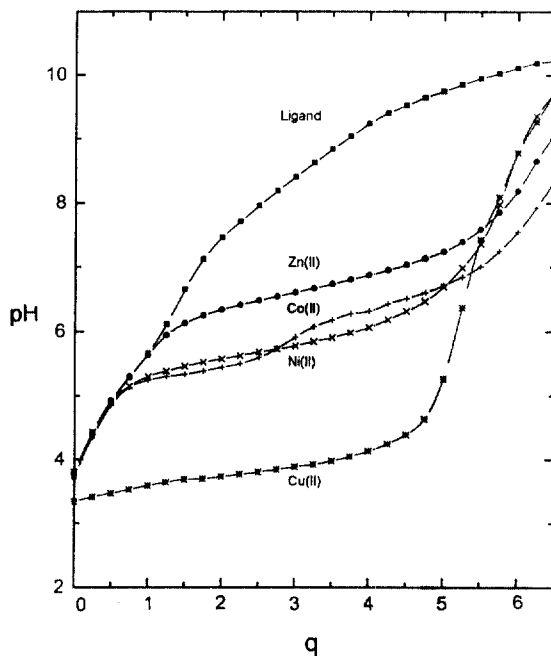


Fig. 3. Potentiometric equilibrium curves of npptr and npptr-metal ion systems. $t=25.0^{\circ}\text{C}$; $\mu=0.10\text{M}(\text{KNO}_3)$; q =moles of base added per mole of ligand

protonation constant ($\log \beta$) are listed in Table 1. The ligands were isolated as tetrahydrochlorides and the six basic groups are protonated. The overall protonation constants of the ligands reflect their total basicities. The protonation constant of npptr is greater than that of nptr. The presence of propylenic spacers between the nitrogen atoms yields higher basicity than that of ethylenic ones because of reduced repulsions between polyamine sites.^{19,20} Thus K_H^3 , K_H^4 , K_H^5 , and K_H^6 of ligands are the proton dissociation constants of the secondary amino group while K_H^1 , and K_H^2 reflect the basicity of naphtha oxygen atoms. The base strength of aliphatic nitrogen is lower than their naphtha oxygens. The protonation constants of the two

naphthol hydroxyl groups represent the basicity of the aliphatic amino groups. This interpretation is substantiated by the fact that in nptr and npptr strong intramolecular hydrogen bond are formed involving participation of the naphthol hydroxyl groups and unprotonated aliphatic amino group. Hydrogen bonding ultimately results in a weakening of the proton affinity of the aliphatic amino groups and increasing the stability of the naphthol O-H bond. The base strength of ligands are in the order of nptr and npptr. The sixth protonation constant of nptr is appreciably lower than that of npptr. This can be ascribed as the last protonation of nptr should take place at the central

Table 1. Ligand dissociation constants for nptr and npptr at 25.0°C in 0.10M KNO_3

	$\log K_H^1$	$\log K_H^2$	$\log K_H^3$	$\log K_H^4$	$\log K_H^5$	$\log K_H^6$	$\log \beta$
nptr	10.27	9.55	8.21	6.80	5.23	3.03	43.09
np ptr	10.62	10.50	9.87	8.93	7.46	6.24	53.62

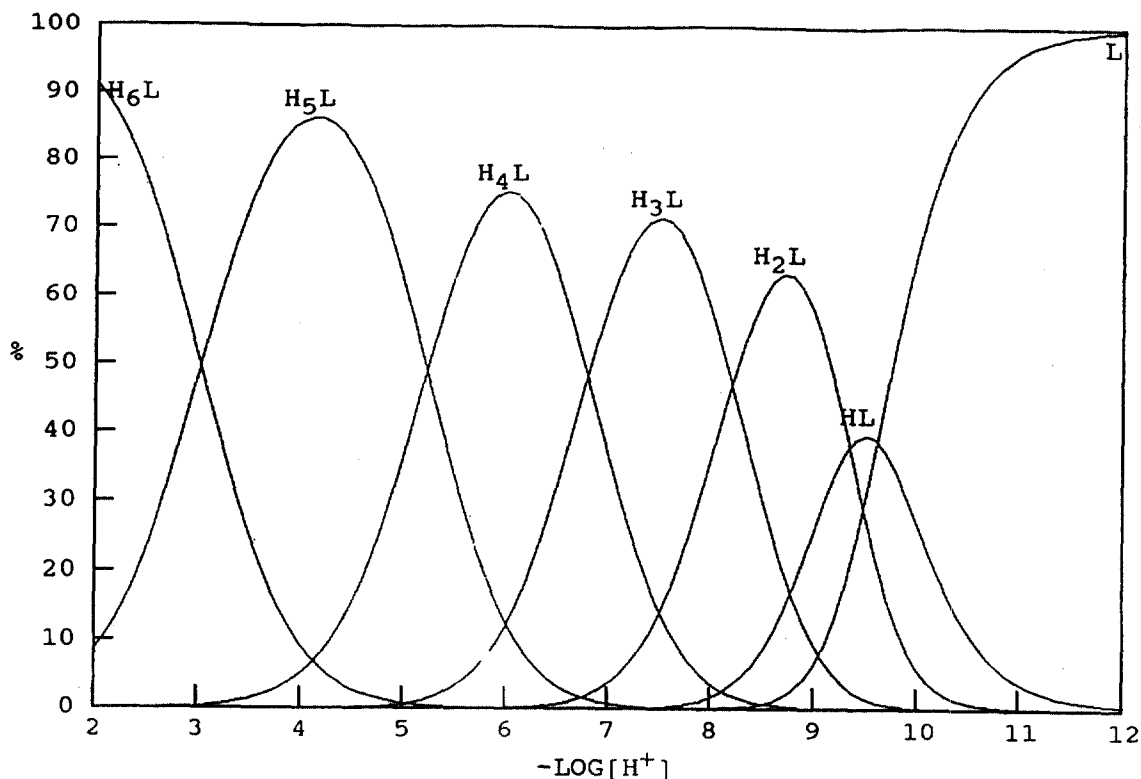
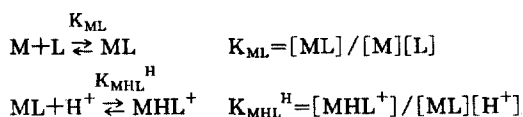


Fig. 4. Distribution of nptr species in the absence of metal ions

ethylenic nitrogens which are separated from the adjacent amine groups by an ethylenic. The effects of the charge repulsions on the protonation constants of the polyamines are reflected in the distribution diagrams for nptr and nptr (Fig. 4 and 5). Thus, the first protonations of nptr and nptr show pH 2~3 and pH 3~6 range.

3.2. Stability constants of the complexes

Stability constants were defined as follows:



where [M], [ML], [MHL⁺], and [L] represent 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 respectively. Complexation of the metal ions with a ligand resulted in a complete displacement of the hydrogen ions from the protonated polyamine. The metal-ligand potentiometric equilibrium curves are shown in Fig. 2 and 3. The constants listed in Table 2, were determined by using computer program BEST. At pH values above 8, there seems to be some additional reactions involving the formation of hydroxo complexes. This is the indication that the neutralization curves of the ligand in the presence of the complexing metal ion do not match with the titration curves for the metal-free compound. The stability constants for two ligands given in Table 2 are found as an order of Co(II) < Ni(II) < Cu(II)

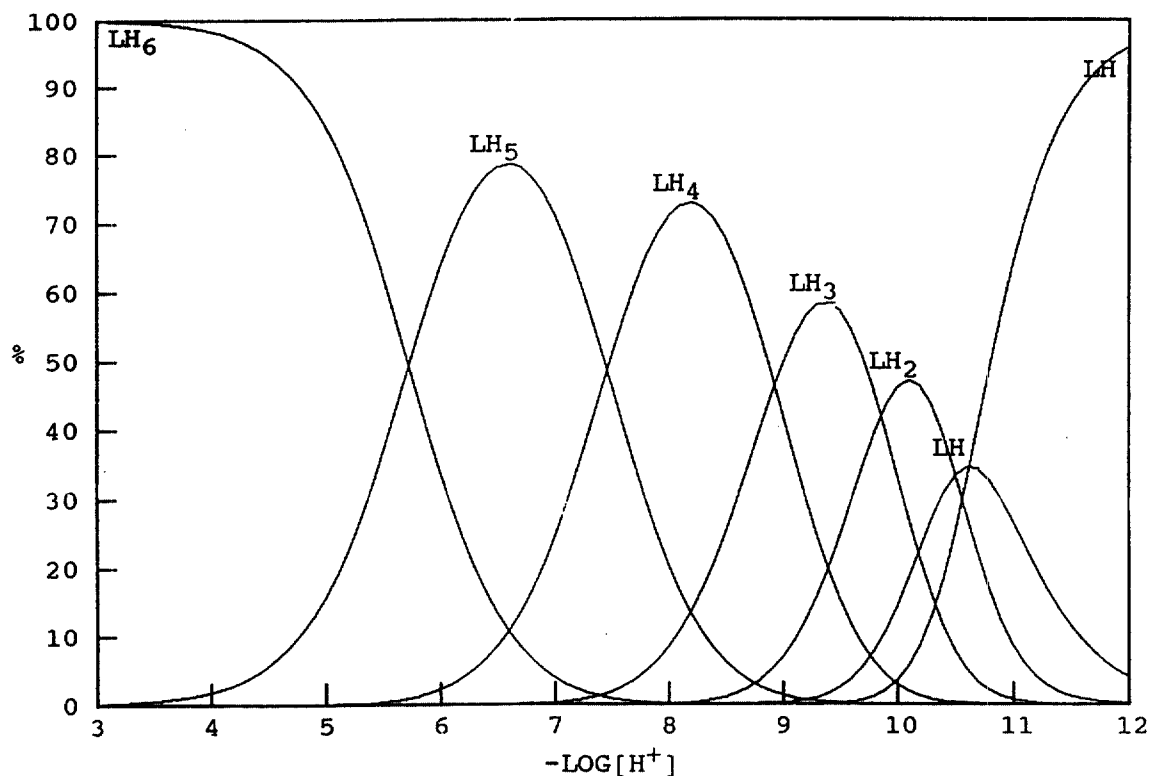


Fig. 5. Distribution of npptr species in the absence of metal ions

Table 2. Stability constants for Co(II), Ni(II), Cu(II), and Zn(II) complexes of nptr and npptr at 25.0 °C in 0.100mol KNO₃

Ligand	Equilibrium constant	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
nptr	logK _{ML}	17.97	19.89	27.12	16.59
	logK _{MHL} ⁺	8.77	9.50	9.86	9.01
npptr	logK _{ML}	18.38	20.21	28.26	17.97
	logK _{MHL} ⁺	8.80	9.73	10.11	8.76

>Zn(II) in the accordance with the general Irving-Williams order.²¹ The high stability constants for the first-row transition metal ions for nptr and npptr ligands could be due to the polydentate effect, flexibility of ligands and the high basicity of ligands. Compared to the stability of nptr-metal complexes, the higher stability of the

npptr-metal complexes may be attributed to its higher basicity and the more flexible arrangement of ligand due to two propylenic spacers

Acknowledgement

This research was supported by the Taegu Uni-

versity Grant, 1997.

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