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Synthesis, Protonation Constants and Stability Constants for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} Ions of 1,15-bis(2-pyridyl)-2,5,8,11,14-pentaazapentadecane

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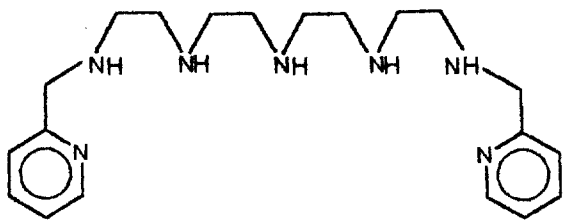
1. Introduction

The spent nuclear fuel contains large and potentially valuable sources of metals(such as Ru, Rh, and Pd, all metals in scare abundance on earth) and radiation. One of the separation methods is the solvent extraction process in which the fuels are dissolved in nitric acid and contacted with an organic solvent which selectively extracted the desired elements. The purex process, which is one of the solvent extraction processes, is the only nuclear fuel reprocessing method which has been applied to commercial plants.[1] However, this process has the disadvantage to induce the production of a large amount of waste involving organic solvents which are of potential danger of explosion. From an environmental point of view the volume reduction of radioactive waste is of particular importance in nuclear energy. The troublesome problem of the reduction may be solved by availability of the ion-selective extractant, which is soluble and stable in aqueous concentrated nitric acid.

We have been developing the separation method in nuclear waste using new ion-selective extractants in water. In our basic program long open-chain polyamines, which are soluble and stable in water, have been synthesized by hydrogenation of -CH=N bonds in Schiff bases.[2,3] In order to get further insight into the chemistry of the polyamines we have synthesized a new potentially heptadentate N_7 ligand 1, 15-bis(2-pyridyl)-2, 5, 8, 11, 14-pentaazapentadecane (pytetren) as its pentahydrochloride salt. The ligand contains two pyridyl moieties and five aliphatic amines. Proton association constants and stability constants of the ligand with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions are determined by potentiometry and compared with those of analogous N_6 ligands.



pytetren

2. Experimental

2.1. Synthesis

The ligand of 1, 15-bis(2-pyridyl)-2, 5, 8, 11, 14-pentaazapentadecane(pytetren) was prepared as its salt(pytetren·5HCl) by the method described in the previous paper.[2,3] Pyridine-2-carboxaldehyde(2.

14g, 0.02mol) and tetraethylenepentamine(1.89g, 0.01mol) were dissolved in a mixture of 50mL of absolute methanol and 5mL triethyl orthoformate and then refluxed for 3h under dinitrogen atmosphere.

The solution was hydrogenated at room temperature over 1g of 10% platinum on activated carbon for 15h 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 100mL of methanol, and the solution was saturated with hydrogen chloride until no additional colorless precipitate formed 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 pytetren ligand is very stable in air and water. Yield: 4.21g(76%). Anal. Cald for $C_{20}H_{38}N_7Cl_5$: C, 43.36: H, 6.87: N, 17.70. Found: C, 43.59: H, 7.02: N, 17.46. ^{1}H-NMR(D_2O-DMSO-d_6) :δ 8.37(d, 2H, pyridine H), 7.82(t, 2H, pyridine H), 7.37(m, 4H, pyridine H), 4.28(s, 4H, pyridylmethyl), 3.25(m, 16H, ethylene). ^{13}C-NMR(D_2O-DMSO-d_6) :δ 151.4, 149.7, 140.0, 125.4, 124.5, 51.5, 45.2, 44.4, 44.0, 43.9.

2.2. 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 (2.49ppm for ^{1}H and 39.7 ppm for ^{13}C). 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

Protonation constants(K_H^n) and stability(K_{ML})

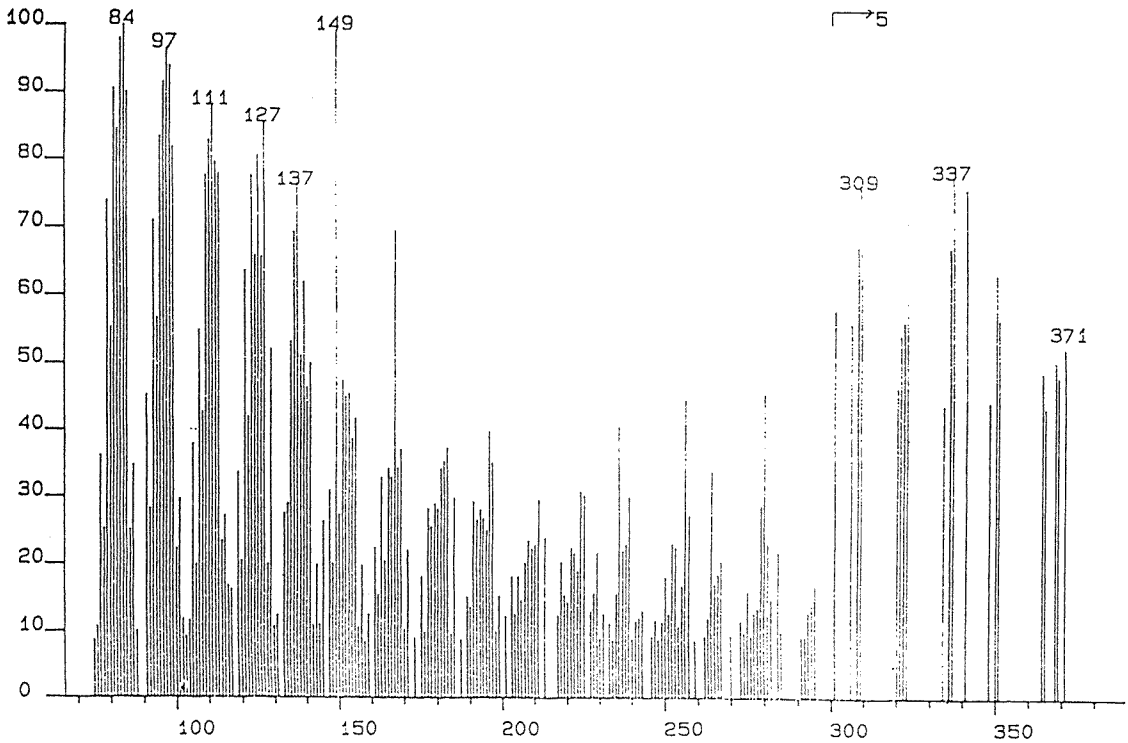


Fig. 1. Mass spectrum of pytetren.

and chelate protonation(K_{MHL}^{H}) constants for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} of the ligand(L) were determined by the method described in the previous paper.[2]

3. Results and discussion

The ligand pytetren was synthesized by the hydrogenation of the parent Schiff base, which was prepared in absolutely anhydrous methanol solution. If the solution contains a small amount of water as an impurity, the product is contaminated by by-products. The ligand obtained was characterized by elemental analysis(EA), ^{1}H- and ^{13}C-NMR, and IR, and mass spectrometry. The mass spectrum (*Fig.* 1) of pytetren measured as its pentahydrochloride salt gave its parent peak(m/e=371), which corresponds to $[pytetren]^{+}$ ion.

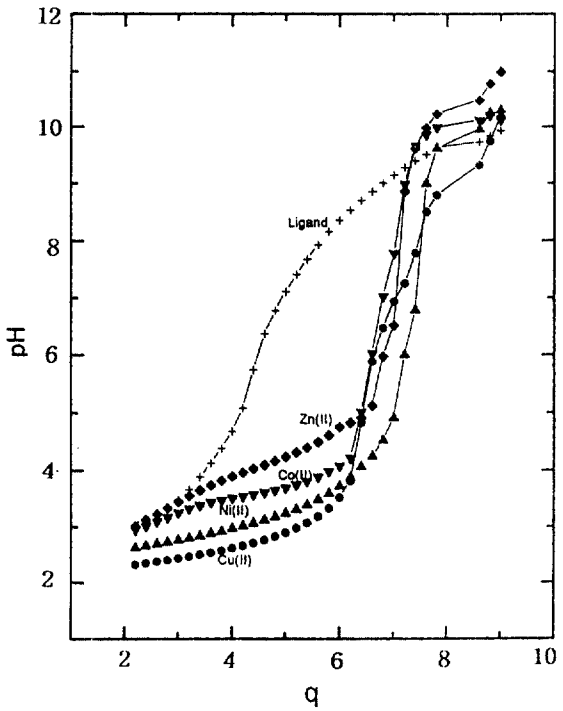


Fig. 2. Potentiometric equilibrium curves for 1:1 Molar ratios of pytetren with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions at 298.1 K. $T_L=T_M=1.00\times10^{-3}$ mol dm^{-3}; ionic strength=0.100 mol dm^{-3}(KNO_3). q is the number of equivalent of KOH added.

Protonation and stablity constants of pytetren have been investigated in 0.100mol dm^{-3} KNO_3 at 298.1K. The potentiometric equlibrium curves for the free ligand is shown in *Fig.* 2, together with those for 1:1 molar ratios of pytetren with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions. The ligand protonation constants(K_H^n) calculated from the curve are as follows: log K_H^1=9.36, log K_H^2=9.12, log K_H^3=8.09, log K_H^4=6.62, log K_H^5=4.02, log K_H^6=2.54. Since the nitrogen atom on the pyridyl moiety is less basic than that on aliphatic amines, the constants from K_H^1 to K_H^5 correspond those of protonation of aliphatic amine groups. The fact that the larger the difference between K_H^{n-1} and K_H^n the higher n is due to the stronger the electrostatic repulsion between protonated nitrogen atoms. For pytetren with five aliphatic nitrogens, the first four protonation occurs at the nitrogen atom adjacent to one of the protonated nitrogens. Therefore the difference between K_H^3 and K_H^4 is larger than those between K_H^1 and K_H^2 or between K_H^2 or between K_H^2 and K_H^3. *Fig.* 3 shows the distribution diagram for pytetren as a function of pH.

Titrations of pytetren · 5HCl in the presence of the ions Co(Ⅱ), Ni(Ⅱ), Cu(Ⅱ), and Zn(Ⅱ) with KOH yield neutralization curves which are shown in *Fig.* 2. The chelate stability constants(K_{ML}) obtained are listed in *Table* 1, along with those of N_6 ligands such as 1, 12-bis(2-pyridyl)-2, 5, 8, 11-tetraazadodecane(pytrien)[2], 1, 12-bis(2-pyrrolyl)-2, 5, 8, 11-tetraazadodecane(pyrrotrien)[2], 1-amino-13-(2-pyridyl)-3, 6, 9, 12-tetraazatridodecane(aptatd)[3], 4, 8, 5, 11, 15-tetraazaoctadecane-1, 18-diamine(taoda)[4], and N,N^1-dimethyl-3, 6, 9, 12-tetraazatetradecane-1, 14-diamine(Me_2linpen).[5~7] As expected on the basis of the general Irving-Williams order, the stability constants for all ligands given follow the order Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The stability constants of pytetren are much higher than those of any N_6-containing ligand in *Table* 1. Assuming that the sum of protonation constants of a ligand reflects its total basicity[8], the plots of log K_{ML} against

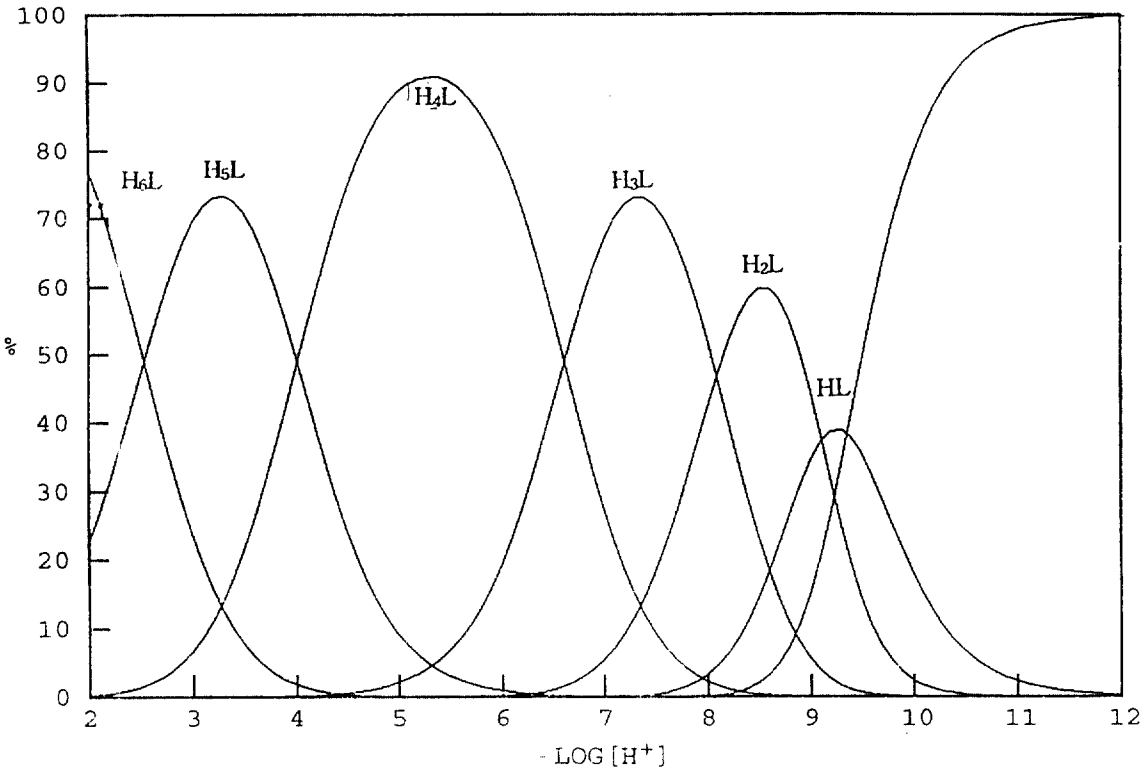


Fig. 3. Distribution diagram for pytetren as a function of pH. [pytetren] = 1.00×10^{-3} mol dm^{-3}

Table 1. Stability Constants for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} Complexes of N_6- and N_7-Containing ligands at 298.1K in 0.100mol dm^{-3} KNO_3

Ligand	Equilibrium Constant	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ref
pytrien	log K_{ML}	17.02	23.03	24.15	16.03	2
	log K_{MHL}^{H}	6.42	6.51	6.07	5.21	
pyrrotrien	log K_{ML}	12.28	13.46	20.77	11.08	2
	log K_{MHL}^{H}	2.58	3.28	5.85	1.85	
taoda[a]	log K_{ML}	10.30	12.23	19.35	10.53	4
Me_2linpen[a]	log K_{ML}	14.8	18.2	21.6	14.0	5, 6, 7
aptatd	log K_{ML}	18.00	21.31	23.62	15.60	3
pytetren	log K_{ML}	22.67	26.25	28.46	19.90	This
	log K_{MHL}^{H}	6.80	8.44	8.86	8.14	work

[a]In 0.15mol dm^{-3} $NaClO_4$

ΣK_H^n were almost linear for pyridyl-containing ligands involving the ligands enumerated in *Table* 2 of Reference 2.

The chelate protonation constants K_{MHL}^{H}, which are defined by [MHL]/[ML][H^+], are also given in *Table* 1. The constants for Ni^{2+}, Cu^{2+}, and Zn^{2+}

chelates are much larger with pytetren than with pytrien, whereas the constant for Co^{2+} chilate is similar in magnitude with each other.

The UV-vis spectra of $[M(pytetren)]^{2+}$ (M=Co, Ni, and Cu) in aqueous solution were measured and their maxima in the visible region are as follows: Co, 479nm; Ni, 514nm; Cu, 621nm. It is uncertain which of seven nitrogen atoms are coordinated to the first-row transtion metals.

Acknowledgement.

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References

1. G. R. Choppin, J. Rydberg, "Nuclear Chemistry," Pergamon Press, Chap. 20, Oxford, U. K., 1980.
2. S.-D. Kim, J.-K. Kim, and W.-S. Jung, *Bull. Korean Chem. Soc.*, **17**, 80(1996).
3. S.-D. Kim, J.-K. Kim, and W.-S. Jung, and K.-C. Chung, *Bull. Korean Chem. Soc.*, in press.
4. J. A. Aguilar, A. Bianchi, E. Garcia-Espana, S. V. Luis, J. M. Llinares, J. A. Ramirez, and C. Soriano, *J. Chem. Soc., Dalton Trans.*, 637(1994).
5. J. Arago, A. Bencini, A. Bianchi, E. Garcia-Espana, M. Micheloni, P. Paoletti, J. A. Ramirez, and P. Paoli, *Inorg. Chem.*, **30**, 1843(1991).
6. J. Arago, A. Bencini, A. Bianchi, E. Garcia-Espana, M. Micheloni, P. Paoletti, J. A. Ramirez, and A. Rodriguez, *J. Chem. Soc., Dalton Trans.*, 3077 (1991).
7. A Bencini, A. Bianchi, V. Fusi, P. Paoletti, B. Valtancoli, A. Andres, A. Arago, and E. Garcia-Espana, *Inorg. Chim. Acta*, **204**, 221(1993).
8. W. R. Harris, I. Murase, J. H. Timmons, and A. E. Martell, *Inorg. Chem.*, **17**, 889(1978).

Abstract: The new potentially heptadentate N_7 ligand 1, 15-bis(2-pyridyl)-2, 5 8, 11, 14-pentaazapentadecane(pytetren) has been synthesized and characterized by EA, IR, NMR, and mass spectrometry. Its proton association constants(log K_H^n) and stability constants(log K_{ML}) for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were determined at 298.1K and ionic strength=0.100M(KNO_3) by potentiometry: log K_H^1=9.36, log K_H^2=9.12, log K_H^3=8.09, log K_H^4=6.62, log K_H^5=4.02, log K_H^6=2.54; log $K_{ML}(Co^{2+})$=22.67, log $K_{ML}(Ni^{2+})$=26.25, log $K_{ML}(Cu^{2+})$=28.46, log $K_{ML}(Zn^{2+})$=19.90

Key words: protonation constant, stability constant, potentiometry