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Protonation and Stability Constants for Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ of the Open-Chain Polyamine 1-Amino-13-(2-pyridyl)-3,6,9,12-tetraazatridecane. Crystal Structure of Its Nickel(II) Complex

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The new unsymmetric N₆ ligand 1-amino-13-(2-pyridyl)-3,6,9,12-tetraazatridecane (aptatd) containing one pyridyl group has been synthesized and characterized by EA, IR, and NMR. Its proton association constants (log $K_{\rm H}^{n}$) and stability constants (log $K_{\rm ML}$) for Co(II), Ni(II), Cu(II), and Zn(II) ions were determined at 298.1 K and ionic strength 0.100 mol dm⁻³ (KNO₃) in aqueous solution by potentiometry: log $K_{\rm H}^{1}$ =8.80, log $K_{\rm H}^{2}$ =8.49, log $K_{\rm H}^{3}$ =6.84, log $K_{\rm H}^{4}$ =4.17, log $K_{\rm H}^{5}$ =3.47; log $K_{\rm ML}(\rm Co^{2+})$ =18.00, log $K_{\rm ML}(\rm Ni^{2+})$ =21.31, log $K_{\rm ML}(\rm Cu^{2+})$ =23.62, log $K_{\rm ML}(\rm Zn^{2+})$ =15.60. The X-ray structure of its nickel(II) complex [Ni(aptatd)](ClO₄)₂ are reported: orthorhombic space group Pbca, a=15.715(1) Å, b=14.280(2) Å, c=19.443(2) Å, V=4363.4 (9) Å³ with Z=8. The geometry around nickel is a distorted octahedron with the pyridine nitrogen atom being *cis* to the nitrogen atom of the terminal primary amine.

Introduction

Recent investigations in this laboratory have focused on the interaction of open-chain saturated polyamines containing pyridyl or imidazoyl groups with metal ions.^{1,2} Martell *et al.* studied the interaction of pyridyl-containing polyamine 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 in spite of the weak σ -donating ability of the pyridyl group.³⁻⁶ The saturated polyamines, which are soluble and stable in water, have been synthesized by hydrogenation of aldimino groups in Schiff bases.¹² It is to be expected that the hydrogenation will yield ligands which are much more flexible than the parent compounds and which thus can present their donor atoms to a metal from either a planar or a nonplanar arrangement.

In order to get further insight into the chemistry of the polyamines we have synthesized a new unsymmetric N_6 ligand 1-amino-13-(2-pyridy1)-3,6,9,12-tetraazatridecane (aptatd) as its pentahydrochloride salt. This potentially hexadentate ligand contains one pyridyl moiety and five aliphatic amines. Proton association constants and stability constants of the ligand with Co(II), Ni(II), Cu(II), and Zn(II) ions are determined by potentiometry and compared with those of analogous N_4 to N_6 ligands. And X-ray crystal structure of [Ni(aptatd)](ClO₄)₂ is reported.



Experimental

Materials. 1-amino-13-(2-pyridyl)-3.6,9.12-tetraazatridecane(aptatd 5HCl) Pyridine-2-carboxaldehyde 2.14 g, 0.02 mol) and tetraethylenepentamine (1.89 g, 0.01 mol) were dissolved in 50 mL of absolute methanol and refluxed for 3 h under dinitrogen atmosphere. The solution was then hydrogenated at room temperature over 1 g of 10%-platinum on activated carbon for 15 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, 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 H₂O, followed by addition of methanol until the white crystal reprecipitated. Yield: 3.10 g (67%). Anal. Cald for C₁₄H₃₃N₆Cl₅: C, 36.33; H, 7.20; N, 18.16. Found: C, 36.40; H, 7.62; N, 17.94. ¹H NMR (D₂O-DMSOd₆): δ 8.57 (d, 1H, pyridine H), 7.86 (t, 1H, pyridine H), 7.43 (m, 2H, pyridine H), 4.34 (s, 2H, pyridylmethyl), 3.41-3.14 (m, 16H, ethylene). ¹³C NMR (D₂O-DMSO-d₆): δ 151.9, 149.1,144.5, 128.1, 127.8, 52.7, 47.1, 46.8, 46.0, 45.9, 45.8, 37.8.

[Ni(aptatd)](ClO₄)₂·H₂O. Sodium acetate trihydrate (0.680 g, 5 mmol) was added to a solution of aptatd 5HCl (0.463 g, 1 mmol) in absolute methanol (20 mL). The mixture was stirred for 30 min and filtered. Nickel acetate tetrahydrate (0.249 g, 1 mmol) was added to the filtrate, and the resulting violet solution was stirred in air briefly. Excess sodium perchlorate dissolved in methanol was added to the solution and then the mixture was stored in a refrigerator. The red crystals formed were filtered off, washed with a small quantity of cold methanol, and air-dried. Yield: 0.135 g (25%). Anal. Cald for $C_{14}H_{28}Cl_2NiN_6O_8$: C, 31.25; H, 5.21; N, 15.62. Found: C, 31.38; H, 5.35; N, 15.57.

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

Equilibrium Constant Measurement. Protonation and stability constants for Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ of the ligand(L) in aqueous solution were determined by the method described in the previous paper.^{1,2} The protonation constants (K_{H^n}) and stability constants (K_{ML}) for M ion are defined by $[H_nL]/[H^+][H_{n-1}L]$ and [ML]/[M][L], respectively.

Crystal Structure Determination. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK α radiation at room temperature. Lattice parameters and the orientation matrix were obtained from the setting angle values of 25 automatically centered reflections. Standard reflections were periodically monitored for intensity and orientation control. Intensities were corrected for Lorentz and polarization effects and only those with $(F_0)^2 > 3\sigma(F_0)^2$ were used in subsequent Fourier syntheses. Neutral-atom scattering factors were used with anomalous dispersion correction applied. Empirical absorption corrections were made using DIFABS.⁷ They were refined with an overall isotropic thermal parameter and then included as fixed contributions in the final refinements. Final least-squares refinements were carried out either in full-matrix or large-block approximation.

Results and Discussion

Syntheses and Characterization. The ligand, 1amino-13-(2-pyridyl)-3,6,9,12-tetraazatridecane (aptatd) was synthesized as its pentahydrochloride salt by the hydrogen reduction of the Schiff base obtained from the condensation of tetraethylenepentamine and pyridine-2-carboxylaldehyde in methanol. If there is no trace of water in the reaction medium, the main product is 1,15-bis(2-pyridyl)-2,5,8,11,14pentaazapentadecane.² The ligand was characterized by elemental analysis and IR and NMR spectroscopy. The elemental analysis showed that the ligand was isolated as pentahydrochloride salt. Five aliphatic amino groups are likely to be protonated because the nitrogen atoms on the aliphatic amines are more basic than that on the pyridyl moiety. The ligand was also well characterized by ¹H and ¹³C NMR spectra. Five ¹³C signals at >127 ppm and seven ¹³C signals at the higher field correspond to carbons on a pyridyl



Figure 1. Potentiometric equilibrium curves for 1:1 molar ratios of aptatd with Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ ions at 298.1 K. T_L= $T_{M}=1.00 \times 10^{-3}$ mol dm⁻³; ionic strength=0.100 mol dm⁻³ (KNO₃). q is the number of equivalents of KOH added.

Ligand	$\log K_{\rm H}^{1}$	$\log K_{\rm H}^2$	$\log K_{\rm H}^3$	$\log K_{\rm H}^{4}$	$\log K_{\rm H}^{3}$	$\log K_{\rm H}^{*}$	Ref
trien	9.92	9.20	6.67	3.32			3
pytrien	9.08	8.78	7.51	5.42	2.99		1
tetren	9.85	9.27	8.19	5.08	3.43		4
aptatd	8.80	8.49	6.84	4.17	3.47		This work
Me ₂ linpena	10.28	9.52	8.84	6.54	3.80	2.51	9

Table 1. Ligand Protonation Constants for trien, pytrien, tetren, aptatd, and Me₂linpen at 298.1 K in 0.100 mol dm⁻³ KNO₃

⁴ In 0.15 mol dm ⁻³ NaClO₄.

moiety and aliphatic branches, respectively. The ligand is very soluble and stable in concentrated nitric acid solution.

The complex $[Ni(aptatd)](ClO_4)_2 \cdot H_2O$ was synthesized by the reaction of methanolic solution of 1 equiv of aptatd with 5 equiv of sodium acetate and 1 equiv of nickel acetate, followed by the addition of sodium perchlorate. The perchlorate anion in the complex was identified by IR spectroscopy.

Equilibrium Constants. Protonation and stability constants of aptatd have been studied in 0.100 mol dm⁻³ KNO₃ in aqueous solution at 298.1 K. The potentiometric equilibrium curve for the free ligand is shown in Figure 1, along with those for 1:1 molar ratios of aptatd with Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ ions. The ligand protonation constants $(K_{\rm H})$ calculated from the curve are listed in Table 1, along with the values for 1,4,7,10-tetraazadecane(trien), 1,4,7,10, 13-pentaazatridecane(tetren), 1,12-bis(2-pyridyl)-2,5,8,11tetraazadodecane(pytrien), and N,N'-dimethyl-3,6,9,12tetraazatetradecane-1,14-diamine(Me₂linpen). Since all these ligands have the ethylenic spacers between the aliphatic nitrogen atoms (N_4 to N_6), the electrostatic repulsions between protonated nitrogen atoms have the marked effect on the values of $K_{\rm H}^{n}$. The first two protonations of these ligands are expected to occur mainly at the terminal aliphatic nitrogens⁸ and consequently the difference between $K_{\rm H}^{-1}$ and $K_{\rm H}^{2}$ is not so large (ca. 0.5 in log scale). The difference between $K_{\rm H}^{n-1}$ and $K_{\rm H}^{n}$ tends to increase as n increases because of the strong electrostatic repulsions between protonated nitrogen atoms. For trien and pytrien with four aliphatic nitrogens, the first three protonation occurs at the nitrogen atom adjacent to one of the protonated nitrogens, while for the ligand such as tetren, aptatd, and Mealinpen the first four protonation does.

It seems to be reasonable that the magnitude of $\log K_{\rm H}^{1}$ or $\log K_{\rm H}^{2}$ decreases in the order Me₂ linpen>trien~tetren> pytrien~aptatd, in view of the fact that the first two protonations of these ligands mainly occur at the terminal aliphatic nitrogens and pyridyl and methyl groups are electron-withdrawing and -donating ones, respectively.

Titrations of aptatd 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 Figure 1. The chelate stability constants (K_{MI}) obtained are listed in Table 2, along with those of other N₆ ligands. The constants for all ligands given follow the order Co²⁺<Ni²⁺<Cu²⁺>Zn²⁺ in accord with the general Irving-Williams order. The stabilities of the complexes of aptatd are not so different from those of pytrien carrying two pyridyl moieties but higher than those of the aliphatic N₆-containing ligands such as Me₂linpen and taoda (4,8,11,15-tetraazaoctaadecane-1,18-diamine). This is in

Table 2. Logarithms of Stability Constants for Co^{24} , Ni^{24} , Cu^{24} , and Zn^{24} Complexes of N₆-Containing Ligands at 298.1 K in 0.100 mol dm⁻³ KNO₃

Ligand	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Ref
pytrien	17.02	23.03	24.15	16.03	1
pyrrotrien	12.28	13.46	20.77	11.08	1
taoda""	10.30	12.23	19.35	10.53	8
Me ₂ linpen ^o	14.8	18.2	21.6	14.0	9,10,11
aptatd	18.00	21.31	23.62	15.60	This work

^e In 0.15 mol dm⁻³ NaClO₄. ^b4,8,11,15-tetraazaoctadecane-1,18diamine.



Figure 2. X-ray crystal structure of $[Ni(aptatd)]^{2*}$ cation. All hydrogen atoms are omitted for clarity.

agreement with the general trend that the stability constants for first-row transition metal ions of pyridyl-containing ligands are higher than those of the analogous polyamines.³⁻⁶ This enhanced stability is partially attributed to π bonding between the pyridyl π or π^* orbitals and the d orbitals of Co(II), Ni(II), and Cu(II) ions.⁵ But the enhanced stability of Zn(II) ion with the d¹⁰ 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.

X-ray Structure of $[Ni(aptatd)](CIO_4)_2 \cdot H_2O$. OR-TEP drawing of $[Ni(aptatd)]^{2+}$ cation is presented in Figure 2. Selected bond distances and bond angles are given in Table 3. The $[Ni(aptatd)]^{2+}$ ion has distorted octahedral geometry. All the nitrogen atoms are coordinated to nickel, atom with the pyridine nitrogen atom(N1) being *cis* to the nitrogen atom (N3) of the terminal primary amine. Although several isomers are possible for linear hexamine li**Table 3.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[Ni(aptatd)]^{2+}$

Bo	nd Lengths			
Ni(1)-N(1) 2.107(4)	Ni(1)-N(2) 2.156(5)			
Ni(1)-N(3) 2.089(5)	Ni(1)-N(4) 2.121(5)			
Ni(1)-N(5) 2.133(5)	Ni(1)-N(6) 2.079(5)			
Во	nd Angles			
N(1)-Ni(1)-N(2) 79.6(2)	N(1)-Ni(1)-N(3) 89.5(2)			
N(2)-Ni(1)-N(3) 97.5(2)	N(1)-Ni(1)-N(4) 171.4(2)			
N(2)-Ni(1)-N(4) 100.9(2)	N(3)-Ni(1)-N(4) 81.9(2)			
N(1)-Ni(1)-N(5) 99.1(2)	N(2)-Ni(1)-N(5) 163.5(2)			
N(3)-Ni(1)-N(5) 99.0(2)	N(4)-Ni(1)-N(5) 82.9(2)			
N(1)-Ni(1)-N(6) 91.9(2)	N(2)-Ni(1)-N(6) 82.5(2)			
N(3)-Ni(1)-N(6) 178.5(2)	N(4)-Ni(1)-N(6) 96.7(2)			
N(5)-Ni(1)-N(6) 81.1(2)				

gands, the one observed here being of the ffmf type,¹² as for Ni(pytrien)]^{2+,13} The distances Ni-N(3) and Ni-N(6) are a little shorter than other Ni-N distances. Each Ni-N distance in the [Ni(aptatd)]²⁺ is very similar to the corresponding distance in the [Ni(pytrien)]²⁺ except for the distance Ni-N(2). And the average value of five chelate bond angles subtended by the ligand at the nickel atom is nearly the same as that of [Ni(pytrien)]²⁺.

The UV-vis electronic absorption spectra of $[M(aptatd)]^{2*}$ (M=Co and Cu) in aqueous solution were measured and their absorption maxima in the visible region were determined to be 471 nm for the Co complex and 630 nm for the Cu complex. This indicates that both complexes have distorted octahehral geometry.¹⁴

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Supplementary Material Available. Crystal data (Table S1), atomic positional parameters (Table S2), com-

plete bond distances (Table S3), and bond angles (Table S4) are available from one of authors (SDK).

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