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Thermodynamic and Kinetic Studies of Zinc(II)–Triamine Complexes as Models of CA and AP

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The formation constant (K_{ZnL}), enthalpy and entropy changes (ΔH and ΔS), and deprotonation constant (K_a) of coordinated water for hydrated zinc(II)–triamine (1 : 1) complexes (N_3–Zn-$(OH_2)_n$ (N_3 = diethylenetriamine (dien), *N*-(2-aminoethyl)-1,3-propanediamine (epd), dipropylenetriamine (dpt), *cis,cis*-1,3,5-triaminocyclohexane (tach), and 1,5,9-triazacyclododecane ([12]aneN_3)) were determined by potentiometry. The pK_a linearly increased along with an increase in $-\Delta H$, and was explained in terms of a ligand–ligand interaction through the N_3–Zn-O bond on the bases of a thermodynamic analysis and strain-energy calculation (MM2). The zinc(II) complex-promoted hydrolysis of 2,4-dinitrophenyl diethyl phosphate was investigated in 1% (v/v) methanol–water; the rate constants linearly increased along with decreases of pK_a and $-\Delta H$. This fact indicates that the hydrolysis proceeds via a concerted direct nucleophilic attacking mechanism of the coordinated hydroxide ion, in which the phosphate ester coordinates to the zinc(II) ion. X-ray structure analyses for synthesized model complexes, $[Zn(OAc)(dien)](ClO_4)$, $[\{Zn(dpt)\}_3(CO_3)](ClO_4)_4 \cdot NaClO_4$, and $[Zn(OAc)(tach)](ClO_4)$, are also reported.

Carbonic anhydrase (CA) and alkaline phosphatase (AP) are monomeric and dimeric zinc(II)-containing enzymes which catalyze the hydration of carbon dioxide and the hydrolysis of phosphate monoesters, respectively.[1—7] The zinc(II) ion at an active center of CA is surrounded in a tetrahedral fashion by three amino acid side chains (three imidazoles) and one water molecule.[8] In the case of AP, one zinc(II) ion (A) is attached by two imidazoles, one carboxylate group, and two water molecules, and another zinc(II) ion (B) by one imidazole, two carboxylate groups, and one water molecule.[7] These zinc enzymes use coordinated water or serine residue as a nucleophile to react with electrophilic substrates, wherein the prior activation of the nucleophiles (and/or the electrophiles) is essential. In the case of CA, the coordinated water deprotonates to produce a nucleophile L–Zn-OH, which attacks the electrophilic center of carbon dioxide.[1—4] In the case of AP, L–Zn(B)-OR (OR=deprotonated form of serine residue) attacks the substrate in the first step to yield phosphoseryl intermediate, followed by an attack of L–Zn(A)-OH on the intermediate.[6,7] In both cases, the L–Zn-OH species play an important role as the nucleophile; however, little is known about the chemical properties of the L–Zn-OH species, except that the counterpart L–Zn-OH_2 has a high deprotonation constant (pK_a of coordinated water is ca. 7 for CA,[5] ca. 5 for AP[6]). More essentially, it is also uncertain why the zinc(II) ion in the enzyme is so acidic compared with a common zinc(II) ion, such as $[Zn(OH_2)_6]^{2+}$ (pK_a is ca. 9[9]).

Recently, many model studies have been conducted to elucidate the role of the zinc(II) ion and the detailed reaction mechanism in these zinc enzymes.[10—22] In the model studies, zinc(II)–triamine or –tetramine complexes have been used to follow an enzyme-like reaction, and the activation of the substrate has been emphasized; however, little is known concerning the thermodynamic and kinetic properties of the active species, L–Zn-OH.[10,11,23,24]

In order to clarify the origin of the strong Lewis acidity of the zinc(II) ion in CA and AP and to explain the reactivity of the coordinated OH^- group on the zinc(II) ion, we investigated the thermodynamic and kinetic properties of model zinc(II) complexes with the triamine ligand in detail. We found that the acidity of the zinc(II) ion is proportional to the enthalpy change ($-\Delta H$) for the formation of zinc(II)–triamine complexes, which corresponds to the total binding energy between zinc(II) and all coordinated ligands; we also found that the hydrolysis rate of 2,4-dinitrophenyl diethyl phosphate (NEP), which was used as a substrate, is reversely proportional to the total binding energy, which suggests the concerned substrate-coordination mechanism. The crystal structures of some 1 : 1 zinc(II)–triamine complexes are also reported.

Experimental

Materials. All of the reagents and solvents used were of analytical grade. *cis,cis*-1,3,5-Triaminocyclohexane (tach) was synthesized by literature methods.[25)] Diethylenetriamine (dien), *N*-(2-aminoethyl)-1,3-propanediamine (epd), dipropylenetriamine (dpt), 1, 5, 9- triazacyclododecane ([12]aneN_3), triethylenetetramine (trien), *N,N,N*- tris(2- aminoethyl)amine (tren), and 1, 4, 8, 11-tetraazacyclotetradecane (cyclam) were purchased from commercial sources. The hydrochloride or hydrobromide salts of triamine and tetramine ligands were purified by literature methods.[26)] Dojin Chemical buffers HEPES (*N*-(2-hydroxyethyl)piperazine-*N′*-3-propanesulfonic acid) and TAPS (3-[[tris(hydroxymethyl)methyl]amino]propanesulfonic acid) were purchased from commercial sources and used without purification. 2,4-Dinitrophenyl diethyl phosphate (NEP) was synthesized by modifying a literature method,[27)] using diethyl ether as the solvent. The ether solution was washed with a saturated NaCl solution and dried over $MgSO_4$.

Synthesis of [Zn(OAc)(dien)](ClO_4) (1). To a methanol solution (50 cm^3) of $Zn(OAc)_2 \cdot 2H_2O$ (2.19 g, 0.01 mol), diethylenetriamine (1.03 g, 0.01 mol) was slowly added. After filtration, a methanol solution (100 cm^3) of $NaClO_4$ (2.44 g, 0.02 mol) was slowly added to the filtrate. After one day, a colorless crystal was obtained (2.41 g, 73.7%). ^{1}H NMR (D_2O, DSS) $\delta = 1.9$ (s, 3 H), 2.5—3.0 (m, 8 H). Found: C, 21.78; H, 4.63; N, 12.83; Zn, 20.07%. Calcd for $C_6H_{16}N_3O_6ClZn$: C, 22.04; H, 4.93; N, 12.85; Zn, 19.99%.

Synthesis of [Zn(OAc)(epd)](ClO_4) (2). Using the same method as for **1**, **2** was obtained as a colorless crystal (2.42 g, 70.9%). ^{1}H NMR (DMSO, DSS) $\delta = 1.6$ (s, 2 H), 1.9 (s, 3 H), 2.6—2.9 (m, 8 H), 3.5—3.6 (m, 4 H), 3.8 (s, 1 H). Found: C, 24.49; H, 5.04; N, 12.41; Zn, 18.93%. Calcd for $C_7H_{18}N_3O_6$ ClZn: C, 24.65; H, 5.32; N, 12.32; Zn, 19.17%.

Synthesis of [{Zn(dpt)}$_3$(CO_3)](ClO_4)$_4$·$NaClO_4$ (3). To a methanol solution (50 cm^3) of $Zn(OAc)_2 \cdot 2H_2O$ (2.19 g, 0.01 mol), dipropylenetriamine (1.31 g, 0.01 mol) and a methanol solution (50 cm^3) of $NaClO_4$ (2.45 g, 0.02 mol) were slowly added. After filtration, the filtrate was slowly concentrated for two days. A colorless crystal was obtained (0.20 g, 5.1%). ^{1}H NMR (DMSO, DSS) $\delta = 1.7$ (s, 4 H), 2.7 (s, 4 H), 2.9 (s, 4 H), 3.4 (s, 5 H). Found: C, 19.40; H, 4.13; N, 10.27; Zn, 16.45%. Calcd for $C_{19}H_{51}N_9O_{23}Cl_5NaZn_3$: C, 19.50; H, 4.39; N, 10.77; Zn, 16.76%.

Synthesis of [Zn(OAc)(tach)](ClO_4) (4). [Zn(tach)$_2$](NO_3)$_2$[25c)] (0.45 g, 1 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g, 1 mmol) were dissolved in 150 cm^3 of methanol at 50 °C. After cooling, the precipitate was filtered, and the filtrate was concentrated to about 50 cm^3. To the solution, a methanol solution (20 cm^3) of sodium perchlorate (2.45 g, 0.02 mol) was added. After one day, a colorless crystal was obtained (0.21 g, 56.6%). ^{1}H NMR (DMSO, DSS) $\delta = 1.7$ (q, 3 H), 1.9 (s, 3 H), 2.0 (d, 3 H), 2.4 (t, 3 H), 3.9 (s, 3 H). Found: C, 26.63; H, 4.86; N, 11.72; Zn, 20.49%. Calcd for $C_8H_{18}N_3O_6ClZn$: C, 27.21; H, 5.14; N, 11.90; Zn, 20.64%.

Crystallographic Study. Colorless crystals of **1**, **3**, and **4** were used for data collections. The lattice parameters and intensity data were measured on a Rigaku diffractometer (AFC-5R and AFC-7R) with graphite-monochromated Mo $K\alpha$ or Cu $K\alpha$ radiation and a 12-kW rotating-anode generator. The structures were solved by heavy-atom Patterson methods, or direct methods, and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. The final cycle of a full-matrix least-squares refinement was based on 3252 (**1**), 1645 (**3**), and 1290 (**4**) observed reflections ($I > 3.00\sigma(I)$). All of the calculations were performed using the TEXSAN crystallographic software package developed by Molecular Structure Corporation (1985).

Potentiometric pH Titrations. A typical pH-metric determination was performed as follows: an aqueous solution (50 cm^3) of the hydrochloride or hydrobromide salts of triamine and tetramine ligands L (1.00 mM) ($M = mol\,dm^{-3}$) in the absence of zinc(II) ion for determination of the ligand protonation constants, or in the presence of equivalent zinc(II) ion ($ZnSO_4$) for the determination of the zinc(II) complexation constants (K_{ZnL}) and the deprotonation constants of coordinated water in Zn(II)–L complexes, was titrated with a 0.1 M NaOH aqueous solution. All of the samples were kept under a nitrogen gas atmosphere, and the solution temperature was maintained at 15.0, 25.0, and 35.0±0.1 °C. The ionic strength was adjusted to 0.1 M with $NaClO_4$. For the determination of these constants, at least two independent titrations were always made. For the analysis of the deprotonation constants (ligands and coordinated water) and metal complexation constants, literature methods were used.[28)] The used values of K_w (=[H^+][OH^-]) and f_{H^+} were $10^{-14.15}$ and 0.827 at 15 °C, $10^{-13.79}$ and 0.825 at 25 °C, $10^{-13.48}$ and 0.823 at 35 °C, respectively.[29)]

Hydrolysis Kinetics of 2,4-Dinitrophenyl Diethyl Phosphate. The hydrolysis rate of 2,4-dinitrophenyl diethyl phosphate (NEP) was measured by following the increase in 400-nm absorption of the 2,4-dinitrophenolate ion in a 1% (v/v) CH_3OH aqueous solution. The reaction solution contained 0.1 mM NEP and 0.2—0.5 mM zinc(II)-complexes and 50 mM buffer (HEPES (pH 7—8), TAPS (pH 8—9)). The ionic strength was maintained at 0.1 with $NaClO_4$. The absorption increase was recorded until 90% hydrolysis was completed; the end point was determined after $>5t_{1/2}$. This hydrolysis showed a good first-order behavior. The pseudo first-order rate constants (k_{app} (s^{-1})) were obtained by a log-plot method. From the slopes of all the linear plots of k_{app} against concentration of the zinc(II) complexes, the second-order rate constants (k_{obs} ($M^{-1}\ s^{-1}$)) were obtained.

Molecular Mechanics Calculation. The calculations were performed using the molecular-mechanics force-field minimization program MM2 (Molecular Mechanics Version 2).[30)] For the torsional, stretching, van der Waals, and bending parameters, modified literature values was used.[31)] The Zn–N bond-stretch force constant used was 0.89 dyn Å^{-1}. The energy-minimization structures were chosen for some possible isomers. The starting structures were prepared by a computer program (CAChe system) provided by Sony Tektronix. It was used for editing and manipulating the initial structures and viewing the final output.

HPLC Analysis. A product analysis was performed on a JASCO PU-980S pump with a Tosoh ODS-80TM column and a JASCO DG-980-51 degasor. Samples eluted with a 1% (v/v) methanol–water solution, pH 7.0, and a flow rate of 0.250 $dm^3\ min^{-1}$. The eluent was monitored with a Tosoh RI-8010, and the peaks were recorded on a sic Chromatocorder12 integrator (dinitrophenolate ion (time = 12.0 min), diethyl phosphate (time = 5.5 min)).

Peak quantification was accomplished by the external-standard method. Sample peaks could be quantified based on the peak area. The calibration solutions were always prepared using a solvent system identical to that of the reaction solution to be analyzed (including zinc(II) complexes, when appropriate).

Instruments. ^{1}H NMR spectra were recorded on a JEOL GSX-400 spectrometer (400 MHz). A CHN elemental analysis was performed on a Yanako CHN corder (MT-8). A zinc analysis was performed on a Hitachi 170-30 Atomic Absorption Spectrometer. A kinetic study was carried out by a UV-visible spectral method using a Shimadzu UV-vis recording spectrophotometer (UV-2200).

Results and Discussion

X-Ray Crystal Structures of Model Complexes 1, 3, and 4. Some zinc(II)–triamine complexes (Zn : L = 1 : 1) were synthesized in order to confirm the 1 : 1 composition, and to obtain structural information. The synthesis was carried out in methanol because of the high solubility and/or less stability of the complexes in water. The perchlorates of zinc(II) complexes with dien, epd, dpt, and tach (**1**—**4**) were isolated as colorless crystals. Elemental analyses (C, H, N, Zn) suggested the formulas $[ZnL(OAc)](ClO_4)$ for **1**, **2**, and **4**, and $[(ZnL)_3(CO_3)](ClO_4)_4 \cdot NaClO_4$ for **3**. The $CO_3{}^{2-}$ comes from CO_2 in air. The crystals of **1**, **3**, and **4** were subjected to an X-ray structure analysis. Figures 1, 2, and 3 show ORTEP drawings of the cationic parts of complexes **1**, **3**, and **4**with 50% probability thermal ellipsoids. Selected crystal data and collection parameters are displayed in Table 1. The atomic parameters are listed in Tables 2, 3, and 4. Selected bond distances and bond angles around the zinc(II) ion are given in Table 5. Lists of hydrogen atom coordinates, anisotropic thermal parameter, and bond distances and angles are deposited as Document No. 69017 at the Office of the Editor of Bull. Chem. Soc. Jpn.

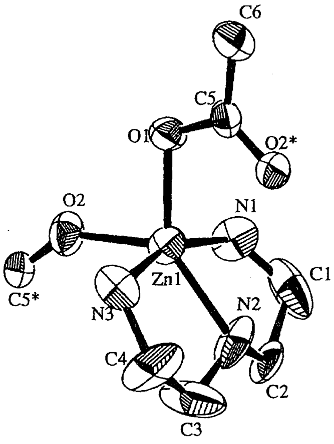


Fig. 1. ORTEP drawing of cationic part of [Zn(dien)(OAc)]-(ClO_4) (**1**) with 50% probability thermal ellipsolids.

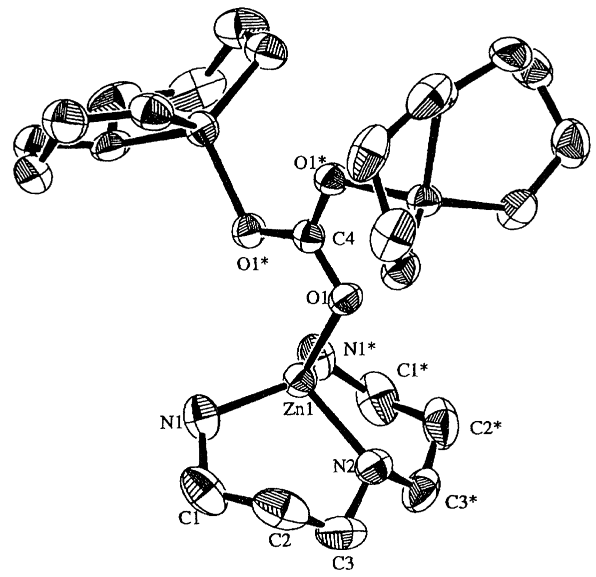


Fig. 2. ORTEP drawing of cationic part of [{Zn-(dpt)}$_3$(CO_3)](ClO_4)$_4$·$NaClO_4$ (**3**) with 50% probability thermal ellipsolids.

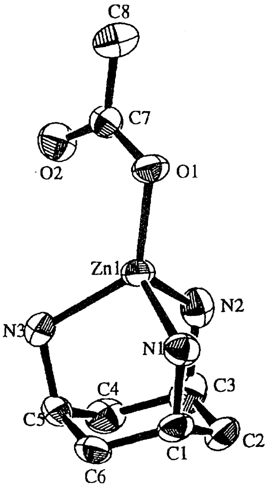


Fig. 3. ORTEP drawing of cationic part of [Zn(tach)(OAc)]-(ClO_4) (**4**) with 50% probability thermal ellipsolids.

In complexes **3** and **4**, the zinc(II) ion is surrounded in a tetrahedral coordination environment by three N atoms of the triamine ligand and one oxygen atom of the carbonato ligand in complex **3**, or of the acetato ligand in **4**. The averaged angles of O–Zn–N and N–Zn–N are 107° and 110° for **3**, and 120° and 97° for **4**, respectively; the distortion is slightly larger in the latter. The averaged angles of O–Zn–N and N–Zn–N for $[Zn([12]aneN_3)(OH)]^+$ are reported to be 114° and 105°, respectively,[10a] which are close to those of **3**. On the other hand, in the case of complex **1**, the zinc(II) ion is surrounded in a distorted trigonal-bipyramidal structure by the three N atoms of diethylenetriamine and two oxygen atoms of two acetato ligands. The averaged angles of O–Zn–N and N–Zn–N are 107.4° and 110.4°, respectively, and the zinc atom lies almost in the basal plane defined by three nitrogen atoms (the total angle is 360.7°).

The averaged Zn–N bond distances for complexes **3** and **4** are 2.010 and 2.036 Å, respectively, which are close to those for the Zn–[12]aneN_3 complex (2.018 Å)[10a] and the tetrahedral zinc(II) complexes (2.034 Å for primary N and 2.039 Å for secondary N).[32] The averaged Zn–N bond distance for complex **1** is 2.115 Å, which lies at the high end of the averaged Zn–N distance (2.064 Å) for five-coordinated zinc(II) complexes.[32] The Zn–O bond distances for complexes **3** and **4** are 1.971 and 1.897 Å, respectively, which are close to those for the Zn–[12]aneN_3 complex (1.944 Å)[10a] and the 4-coordinated zinc(II) complexes (2.006 Å).[32] The averaged Zn–O bond distance for complex **1** is 2.024 Å, which lies at the low end of the 5-coordinated zinc complexes (2.078 Å).[32] In the case of the 6-coordinated 1,4,7-trimethyl-1,4,7-triazacyclononane complex, the averaged Zn–O bond distance is reported to be 2.117 Å.[24]

Table 1. Crystal Data and Data Collection Details of Complexes **1**, **3**, and **4**

Complex	**1**	**3**	**4**
Formula	$C_6H_{16}N_3O_2ClZn$	$C_{19}H_{51}N_9O_{23}Cl_5Zn_3Na$	$C_8H_{18}N_3O_6ClZn$
Formula weight	263.04	1170.05	353.08
Crystal system	Orthorhombic	Hexagonal	Triclinic
Space group	$Pna2_1$	$P6_3/m$	$P\bar{1}$
a/Å	8.336(2)	12.938(2)	9.579(2)
b/Å	17.702(2)	12.938(3)	10.578(2)
c/Å	8.638(7)	14.883(3)	7.562(2)
α/deg			110.75(2)
β/deg			110.45(2)
γ/deg			90.44(2)
V/Å^3	1274(1)	2157.7(5)	663.8(3)
Z	4	2	2
d(calcd)/g cm^{-3}	1.371	1.801	1.766
Crystal size/mm^3	$0.25 \times 0.15 \times 0.10$	$0.40 \times 0.33 \times 0.17$	$0.15 \times 0.15 \times 0.35$
t/°C	23 ± 1	23 ± 1	20 ± 1
Radiation	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
	$\lambda = 1.54178$ Å	$\lambda = 0.71069$ Å	$\lambda = 0.71069$ Å
μ/cm^{-1}	44.58	20.63	20.77
Scan mode	ω–2θ	ω–2θ	ω–2θ
Scan width/deg	$1.78 + 0.30 \tan \theta$	$1.57 + 0.30 \tan \theta$	$1.47 + 0.30 \tan \theta$
Scan speed/deg min^{-1}	4.0	16.0	8.0
2θ range	40.7—51.6°	28.2—29.9°	20.4—24.7°
No. of measured reflections	1290	1949	3252
No. of observed reflections	1004	1269	1951
R/%	4.4	4.3	4.3
R_w/%	6.3	4.4	4.4

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Complex **1**

Atom	x	y	z	B_{eq}[a)]
Zn(1)	0.33391(9)	0.20543(4)	0.9809	3.59(2)
Cl(1)	0.6808(2)	0.13356(8)	0.4812(8)	3.85(3)
O(1)	0.3350(5)	0.3198(2)	0.981(3)	3.9(1)
O(2)	0.5773(5)	0.2005(2)	0.980(3)	4.0(1)
O(3)	0.623(1)	0.2062(4)	0.511(3)	11.9(5)
O(4)	0.565(1)	0.0821(5)	0.507(5)	17.2(7)
O(5)	0.827(1)	0.1174(8)	0.554(2)	12.2(5)
O(6)	0.700(2)	0.1279(8)	0.332(1)	14.1(5)
N(1)	0.311(3)	0.185(1)	1.228(2)	4.7(4)
N(2)	0.1640(8)	0.1174(4)	0.973(2)	4.9(2)
N(3)	0.312(3)	0.192(2)	0.742(3)	5.4(6)
C(1)	0.197(3)	0.132(2)	1.260(2)	5.8(5)
C(2)	0.178(2)	0.077(1)	1.126(3)	4.8(5)
C(3)	0.185(3)	0.076(1)	0.841(3)	7.1(6)
C(4)	0.198(3)	0.123(2)	0.714(2)	9.6(6)
C(5)	0.1938(8)	0.3443(4)	0.979(3)	3.5(1)
C(6)	0.168(2)	0.4278(5)	0.973(5)	5.7(3)

a) $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Complex **3**

Atom	x	y	z	B_{eq}[a)]
Zn(1)	0.32844(4)	0.45274(4)	0.2500	2.99(1)
Cl(1)	0.39855(8)	0.11928(8)	0.2500	3.22(2)
Cl(2)	0.6667	0.3333	0.0214(1)	4.250(8)
Na(1)	0.6667	0.3333	0.2500	3.38(2)
O(1)	0.2557(2)	0.5551(2)	0.2500	3.07(6)
O(2)	0.4206(3)	0.2387(3)	0.2500	4.66(8)
O(3)	0.3325(2)	0.0575(2)	0.1720(2)	6.08(6)
O(4)	0.5113(3)	0.1242(3)	0.2500	6.4(1)
O(5)	0.629(1)	0.364(2)	0.1011(5)	8.0(4)
O(6)	0.786(3)	0.419(3)	0.012(3)	9.4(7)
O(7)	0.589(1)	0.326(1)	−0.0476(6)	7.4(3)
O(8)	0.676(3)	0.234(3)	0.017(3)	12(1)
N(1)	0.4029(3)	0.4585(3)	0.1311(2)	4.03(7)
N(2)	0.1780(3)	0.2891(3)	0.2500	3.76(8)
C(1)	0.3351(4)	0.3575(4)	0.0692(3)	5.3(1)
C(2)	0.2027(4)	0.2951(4)	0.0837(3)	5.5(1)
C(3)	0.1579(3)	0.2182(3)	0.1669(3)	5.1(1)
C(4)	0.3333	0.6667	0.2500	2.65(4)

a) $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

It is well known that the bond distance between the zinc(II) and the coordinated atom becomes longer as the coordination number increases from 4 to 5 and 5 to 6.[32,33)] This inclination was also observed for the zinc(II)–triamine complexes treated here, suggesting that the acidity of coordinated water for hydrated zinc(II)–triamine complexes becomes lower along with an increase in the coordination number. Further, the X-ray data show that the 1 : 1 zinc(II)–triamine complexes with dien and 1,4,7-trimethyl-1,4,7-triazacyclononane, which form five-membered chelates, take coordination numbers 5 and 6, respectively, and those with dpt, tach, and [12]aneN_3, which form 6-membered chelates, take coordination number 4. Thus, on the basis of this fact, we adopted coordination number 4 in the MM2 calculation for hydrated zinc(II)–triamine complexes of dpt, tach, and [12]aneN_3 (as mentioned

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Complex **4**

Atom	x	y	z	B_{eq}[a]
Zn(1)	0.25498(7)	−0.06908(7)	0.0937(1)	2.62(1)
Cl(1)	0.1705(2)	0.1802(2)	0.7502(2)	3.51(4)
O(1)	0.2454(4)	0.1193(3)	0.2174(5)	3.07(8)
O(2)	0.4919(4)	0.1463(4)	0.3619(6)	3.8(1)
O(3)	0.0648(5)	0.1051(5)	0.7818(7)	6.4(1)
O(4)	0.2587(5)	0.2894(4)	0.9383(7)	5.6(1)
O(5)	0.0869(7)	0.2350(6)	0.6094(8)	9.3(2)
O(6)	0.2632(6)	0.0954(7)	0.682(1)	10.9(2)
N(1)	0.0689(6)	−0.1717(5)	−0.1588(8)	3.0(1)
N(2)	0.2485(6)	−0.1894(5)	0.2481(8)	3.3(1)
N(3)	0.4090(5)	−0.1538(5)	−0.0195(9)	3.0(1)
C(1)	0.0801(6)	−0.3189(5)	−0.233(1)	3.1(1)
C(2)	0.0848(7)	−0.3774(6)	−0.074(1)	3.5(1)
C(3)	0.2312(7)	−0.3370(6)	0.107(1)	3.7(2)
C(4)	0.3655(7)	−0.3614(7)	0.043(1)	3.6(2)
C(5)	0.3654(6)	−0.3057(5)	−0.114(1)	3.1(1)
C(6)	0.2155(6)	−0.3445(6)	−0.293(1)	3.2(1)
C(7)	0.3719(6)	0.1930(5)	0.3362(8)	2.7(1)
C(8)	0.3672(9)	0.3396(6)	0.437(1)	4.1(2)

a) $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 5. Selected Bond Distances and Bond Angles for Complexes **1**, **3**, and **4**[a]

	$[Zn(dien)(OAc)](ClO_4)$ (**1**)		
	Bond distances (Å)		
Zn–N(1)	2.19(2)	Zn–N(2)	2.094(7)
Zn–O(1)	2.019(5)	Zn–O(2)	2.029(5)
		Zn–N(3)	2.06(2)
	Bond angles (°)		
N(1)–Zn–N(2)	80.6(7)	N(2)–Zn–N(3)	80.9(7)
N(1)–Zn–O(1)	100.0(8)	N(2)–Zn–O(1)	138.1(2)
N(1)–Zn–O(2)	93.5(8)	N(2)–Zn–O(2)	129.7(3)
O(1)–Zn–O(2)	92.2(2)	N(3)–Zn–N(1)	160.8(3)
		N(3)–Zn–O(1)	97.1(8)
		N(3)–Zn–O(2)	94.4(8)
	$[Zn(dpt)_3(CO_3)](ClO_4)_4\cdot NaClO_4$ (**3**)		
	Bond distances (Å)		
Zn–N(1)	2.000(4)	Zn–N(2)	2.035(6)
		Zn–O(1)	1.973(4)
	Bond angles (°)		
N(1)–Zn–N(2)	103.3(1)	N(1)–Zn–N(1)	124.9(3)
N(2)–Zn–O(1)	100.1(2)	N(1)–Zn–O(1)	110.7(1)
	$[Zn(tach)(OAc)](ClO_4)$ (**4**)		
	Bond distances (Å)		
Zn–N(1)	2.034(5)	Zn–N(2)	2.023(5)
Zn–O(1)	1.897(3)	Zn–N(3)	2.020(5)
	Bond angles (°)		
N(1)–Zn–N(2)	96.9(2)	N(2)–Zn–N(3)	98.0(2)
N(1)–Zn–O(1)	113.4(2)	N(2)–Zn–O(1)	117.7(2)
		N(3)–Zn–N(1)	97.1(2)
		N(3)–Zn–O(1)	127.9(2)

a) Estimated standard deviation are given in parentheses.

later).

Acidity of Coordinated Water in Zinc(II)–Triamine Complexes. For a wide variety of zinc(II)–polyamine complexes, the 1 : 1 complex formation constant (K_{ZnL}) has been reported; however, quite a few data have been reported concerning the deprotonation constant of coordinated water (K_a). This may be due to the less stability of the zinc(II)–triamine (1 : 1) complexes, which often induces a precipitation of zinc(II)-hydroxide in pH titration.[34] We thus selected several triamines whose formation constants of 1 : 1 zinc(II) complexes are higher than ca. 10^7, and determined the K_a values by potentiometry. Further, the enthalpy (ΔH) and entropy (ΔS) changes for the formation of the 1 : 1 complexes were obtained from the temperature dependence of K_{ZnL}. The results are summarized in Table 6, along with some reference values.[35,36] For a comparison, the data for some tetramine complexes are also listed in Table 6.[10a,28,37,38] The complexes treated here are shown in Chart 1.

Regarding the acidity of coordinated water of zinc(II) complexes, it has been pointed out from limited experimental data that the acidity increases along with a decrease in coordination number, due to an increase in polarity of the Zn–OH$_2$ bond.[16,23,24,39] Since the polarity of the Zn–OH$_2$ bond is induced by the zinc(II) ion, the acidity of coordinated water has been regarded as being a measure of the Lewis acidity of the zinc(II) ion.[40] The Lewis acidity of the zinc(II) ion decreases due to the coordination of strong Lewis bases; it is thus expected from simple acid-base theory that the Lewis acidity of the zinc(II) ion depends on the total binding energy between the zinc(II) ion and all of the coordinated ligands (see Appendix). We thus investigated the relation between the pK_a of coordinated water and the $-\Delta H$ value.

As shown in Fig. 4, the plots of pK_a vs. $-\Delta H$ for the triamine complexes exhibit a linear relation with a positive slope. Further, the relation is also consistent with that for the tetramine complexes. Since the linearity is good, it is clear that pK_a of coordinated water is proportional to $-\Delta H$; the relation can be written as

$$\mathrm{p}K_a = \alpha\Delta H + \beta, \qquad (1)$$

where α and β are proportional constants. This fact implies that the acidity of coordinated water (K_a) increases along with a decrease in the total binding energy ($-\Delta H$); that is, the Zn–OH$_2$ binding energy increases along with a decrease in the total binding energy ($-\Delta H$). This fact is consistent with the increase in polarity of the Zn–OH$_2$ bond along with a decrease in the coordination number.[24]

In order to confirm the relation in Eq. 1 from another point of view, we examined the MM2 calculation for tetrahedral zinc(II)–triamine complexes. This is because the calculated MM2 energy corresponds to the strain energy for the complexes, which reduces the total binding energy ($-\Delta H$) of the complexes, so that it is expected that the pK_a of coordinated water is reversely proportional to the MM2 energy. Indeed, as shown in Fig. 5, the plot of pK_a vs. the strain energy exhibits a linear relation with a negative slope, indi-

Table 6. Thermodynamic and Kinetic Data for Zinc(II)–Triamine and –Tetramine Complexes

Complexes	Formation constants of Zn–L			pK_a Values of coordinated water	Hydrolysis rate constants
	log K_{ZnL}	$-\Delta H$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}		k_{OH}/10^{-2}M^{-1} s^{-1}
5	8.92±0.01 (8.80$^{a)}$)	28.9±0.1 (27.2$^{a)}$)	73.9±0.1 (79.5$^{a)}$)	8.93±0.01	13.4±1.1
6	8.41±0.01 (8.77$^{a)}$)	27.9±2.6 (35.2$^{b)}$)	67.8±8.9 (50.6$^{b)}$)	8.90±0.01 (8.86$^{a)}$)	13.7±2.3
7	7.94±0.05 (7.92$^{a)}$)	22.0±1.8 (22.6$^{a)}$)	77.8±0.1 (75.3$^{a)}$)	8.58±0.03 (8.56$^{a)}$)	15.6±1.7
8	6.95±0.01 (6.90$^{a)}$)	3.4±0.1 (0.2$^{a)}$)	121.7±0.1 (129.7$^{a)}$)	7.95±0.01 (8.00$^{a)}$)	19.7±1.5
9	8.25±0.01 (8.41$^{a)}$)	−14.6±0.1	207.1±0.5	7.44±0.01 (7.30$^{a)}$)	22.5±1.6
10	(12.1$^{c)}$)	(37.2$^{c)}$)	(104.6$^{c)}$)	8.79±0.05	3.9±0.1
11	(14.5$^{d)}$)	(57.5$^{d)}$)	(83.7$^{d)}$)	9.87±0.03	3.7±0.2
12	(15.5$^{c)}$)	(61.9$^{e)}$)	(175.7$^{e)}$)	(9.8$^{f)}$)	4.9±0.1

References values are given in parentheses. a) References are in Ref. 35. b) Ref. 36. c) Ref. 28. d) Ref. 37. e) Ref. 38. f) Ref. 10a.

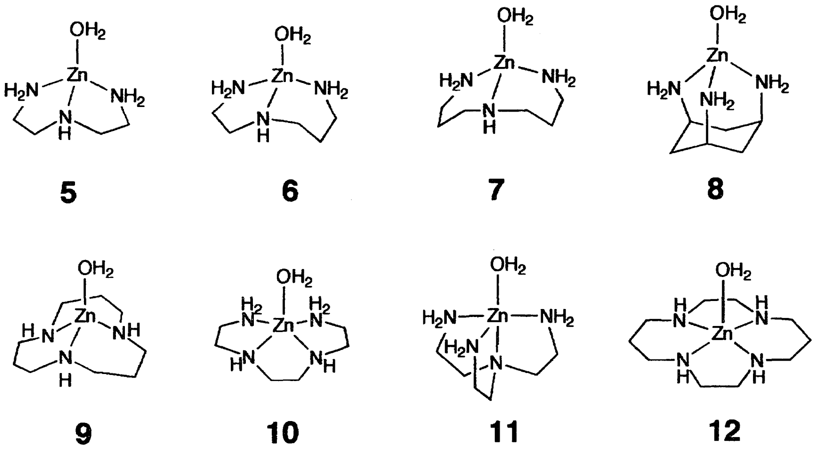


Chart 1.

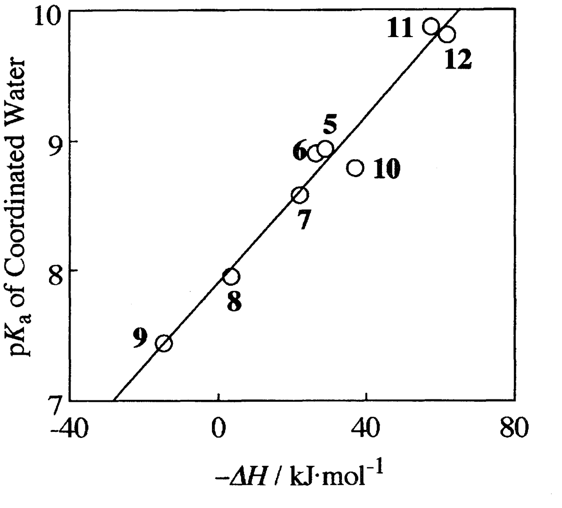


Fig. 4. Relation between pK_a of coordinated water and $-\Delta H$ for formation of zinc(II)–polyamine (1 : 1) complexes (**5**—**12**).

cating that the acidity of coordinated water linearly increases along with an increase in the strain energy of the complexes. Since the strain energy comes mainly from the triamine ligand, it is seen that the Zn–OH$_2$ bond becomes strong as the zinc(II)–triamine bond becomes weak.

On the basis of the above results and discussion, the following can be concluded for hydrated zinc(II)–triamine complexes: (i) the acidity of coordinated water linearly increases along with a decrease in the total binding energy ($-\Delta H$); (ii) the acidity linearly increases along with a decrease in the zinc(II)–triamine binding energy. In the case of CA and AP, the zinc(II) ion is surrounded by four or five ligands having weak basicity, such as imidazole and carboxylate. Therefore, on the basis of our model study, it is suggested that CA and AP have a low total zinc(II)–ligand binding energy ($-\Delta H$) so that the coordinated water exhibits high acidity. As shown in Table 6, the ΔS values for zinc(II)–triamine complexes increase along with a decrease in the $-\Delta H$ values. This fact indicates that the entropy effect works as the driving force for complex formation.

Hydrolysis of Phosphate Ester (NEP) with Zinc(II)

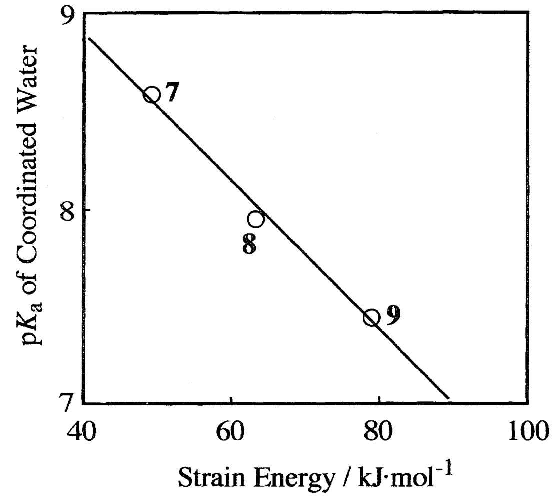


Fig. 5. Relation between pK_a of coordinated water and strain energies calculated from MM2 for tetrahedral zinc(II)–triamine complexes (**7**—**9**).

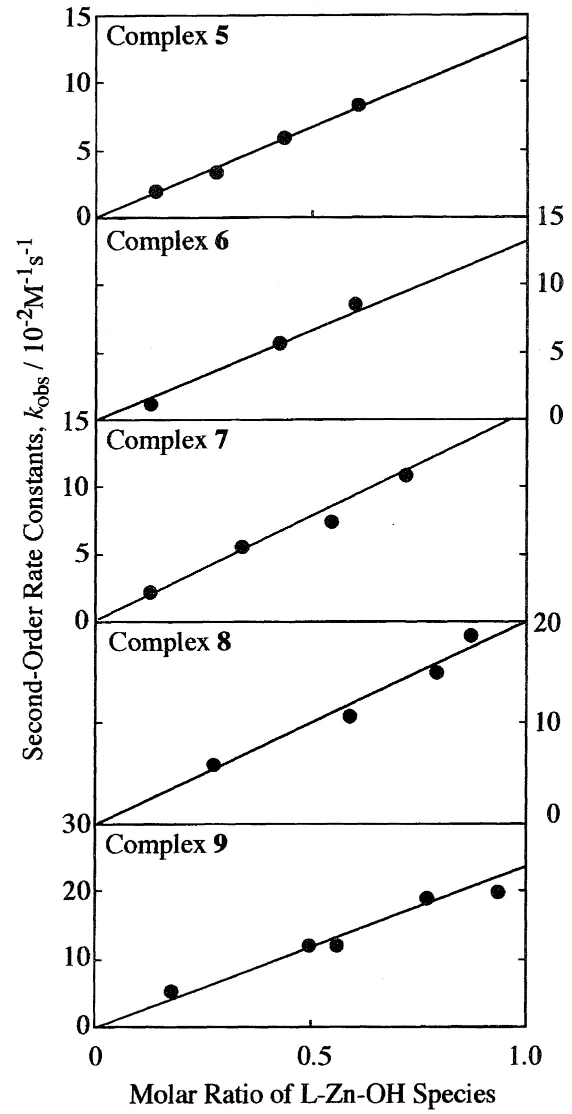


Fig. 6. Relation between observed second-order rate constants (k_{obs}) of NEP hydrolysis promoted by zinc(II)–triamine complexes (**5**—**9**) and molar ratio of L–Zn-OH species in the zinc(II) complexes.

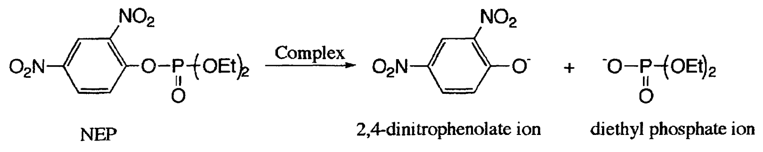
–Triamine Complexes. In a previous paper, we reported on the hydrolysis rate constants of diphenyl 4-nitrophenyl phosphate (NPP) with zinc(II)–triamine complexes in 20% (v/v) acetonitrile–water.[35] In the present work, we investigated the hydrolysis of 2,4-dinitrophenyl diethyl phosphate (NEP) promoted by the model zinc(II)–polyamine complexes by the use of 1% (v/v) methanol–water as a solvent, and neglected the effect of methanol on the solution pH.[41] We confirmed that only the diethyl phosphate ion and the 2,4-dinitrophenolate ion were formed from the ^{1}H NMR spectra and an HPLC analysis for the hydrolysis products. Generally, the hydrolysis of dinitrophenyl phosphate ester proceeds through two types of bond fission: P–O bond fission and C–O bond fission.[42,43] However, when using water as a solvent, P–O bond fission occurs predominantly.[43] We thus assumed that the hydrolysis of NEP mainly proceeded through P–O bond fission in our experiment using 99% water as the solvent (Scheme 1).

The ester hydrolysis promoted by zinc(II) complexes obeyed a second-order rate law for all of the zinc(II)–triamine complexes treated here (Eq. 2), where (rate) and $[Zn]_t$ are the hydrolysis rate promoted by the complex and total concentration of the zinc(II) ion, respectively. The observed rate constant (k_{obs}) shows a pH dependency, and plots of the k_{obs} values vs. the concentrations of the L–Zn-OH species (which was calculated from the deprotonation constants of the triamine ligands, the formation constants, the pK_a of coordinated water of complexes, and the solution pH) exhibit a linear relation through the origin for all triamine complexes (Fig. 6). Hence, the L–Zn-OH species can be ascribed to the active species in the reaction, and the rate is given by Eq. 3. The thus-obtained hydrolysis rate constants are summarized in Table 6, together with those for some zinc(II)–tetramine complexes for a comparison.

$$(\text{rate}) = k_{obs}[\text{Zn}]_t[\text{NEP}], \qquad (2)$$

$$= k_{OH}[\text{L–Zn-OH}][\text{NEP}]. \qquad (3)$$

As shown in Fig. 7, the logarithm of the hydrolysis rate constant for the zinc(II)–triamine complexes exhibits a linear



Scheme 1.

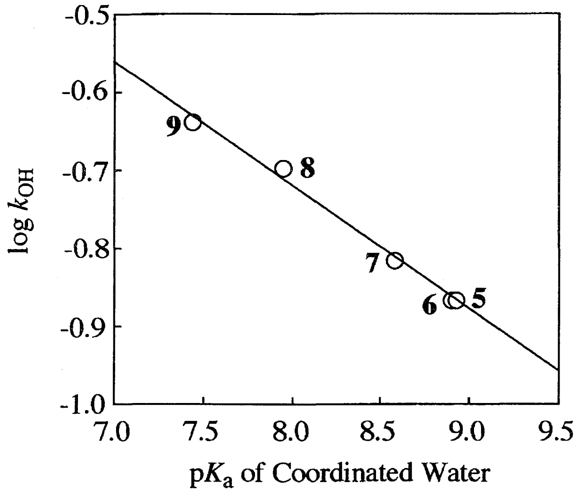
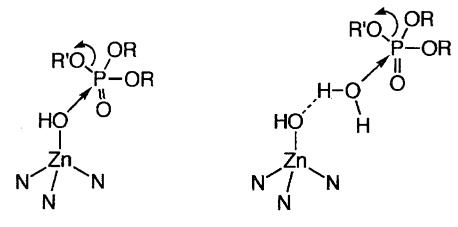


Fig. 7. Relation between logarithm of NEP-hydrolysis rate constant with L–Zn-OH (log k_{OH}) and pK_a of coordinated water in zinc(II)–triamine complexes (**5**—**9**).

relation with the pK_a of coordinated water. This fact indicates that the hydroxo complex becomes less active for the hydrolysis of NEP along with a increase in the Lewis basicity of the coordinated OH^- group, and clearly disagrees with general base catalysis.[22b)] A similar inclination to NEP has also been observed for NPP.[35)] Therefore, a nucleophilic displacement, which includes a direct attack of the coordinated OH^- group on phosphate ester, is plausible (Chart 2).



Nucleophilic Displacement General Base Catalysis

Chart 2.

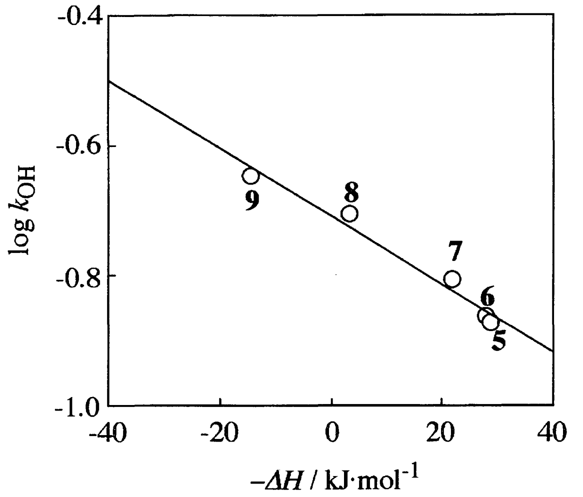


Fig. 8. Relation between logarithm of NEP-hydrolysis rate constant with L–Zn-OH (log k_{OH}) and $-\Delta H$ for formation of zinc(II)–triamine complexes (**5**—**9**).

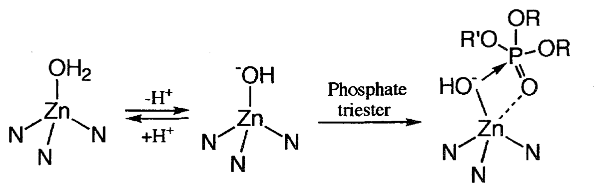


Fig. 9. Proposed "concerted substrate-coordination mechanism" for phosphate ester-hydrolysis promoted by zinc(II)–triamine complexes.

As shown in Fig. 8, the hydrolysis rate constants (k_{OH}) exhibit a linear relation with $-\Delta H$ having a negative slope. This fact indicates that the higher is the Lewis acidity of zinc(II) ion, the faster is the hydrolysis rate. A similar result to that for NEP has also been observed for NPP.[34)] Since the Lewis acidity of the zinc(II) ion is higher, coordination of the substrate is easier. Accordingly, this suggests that hydrolysis proceeds via a concerted mechanism (Fig. 9), in which the substrate coordinates to the zinc(II) ion, followed by an attack of the OH group on the coordinated substrate. In fact, hydrolysis with tetramine complexes, in which the coordinating site for the substrate is occupied by the fourth nitrogen atom of the tetramine ligand, is rather slow compared with that with triamine complexes, supporting the concerned substrate-coordination mechanism.

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Appendix

The ΔH for 1 : 1 complexation between the zinc(II) ion and the polyamine ligand, L in an aqueous solution defined by Eq. A1, corresponds to the enthalpy change in Eq. A2, when only the coordinated water at the first coordination sphere is considered:

$$[\mathrm{Zn(OH_2)_6}]^{2+} + \mathrm{L} \rightleftarrows [\mathrm{ZnL(OH_2)}_m]^{2+} + (6-m)\mathrm{H_2O} \qquad \text{(A1)}$$

$$\begin{aligned}\Delta H = {} & H([\mathrm{ZnL(OH_2)}_m]^{2+}) + (6-m)H(\mathrm{H_2O}) \\ & -H([\mathrm{Zn(OH_2)_6}]^{2+}) - H(\mathrm{L}). \qquad \text{(A2)}\end{aligned}$$

Here, $[\mathrm{ZnL(OH_2)}_m]^{2+}$ denotes the 1 : 1 complex. Since no ligand field stabilization energy is concerned regarding d^{10}-zinc(II) complex, ΔH can be written by Eq. A3 using the binding enthalpy, H_b:

$$\begin{aligned}\Delta H = {} & H_b(\mathrm{Zn\text{–}L}) + mH_b(\mathrm{Zn\text{-}OH_2}^{(c)}) \\ & +(6-m)H(\mathrm{H_2O}) - 6H_b(\mathrm{Zn\text{-}OH_2}) - H(\mathrm{L}) \\ = {} & 6\{H(\mathrm{H_2O}) - H_b(\mathrm{Zn\text{-}OH_2})\} - m\{H(\mathrm{H_2O}) \\ & -H_b(\mathrm{Zn\text{-}OH_2}^{(c)})\} - \{H(\mathrm{L}) - H_b(\mathrm{Zn\text{-}L})\}. \qquad \text{(A3)}\end{aligned}$$

Here, $H_b(\mathrm{Zn\text{-}OH_2}^{(c)})$ indicates the binding enthalpy between the zinc and coordinated water of the 1 : 1 complex. When the enthalpys of naked Zn^{2+} in water and water (solvented water) are taken to be zero, the first term in Eq. A3 corresponds to the binding energy (E) of the Zn–OH$_2$ bond for $[\mathrm{Zn(H_2O)_6}]^{2+}$ in aqueous solution. Similarly, the second and third terms in Eq. A3 correspond to the binding energies of Zn–OH$_2$ and Zn–L for the 1 : 1 complex, respectively. Accordingly, ΔH can be written as follows by using the binding energy:

$$\Delta H = 6E(\text{Zn–OH}_2) - \{mE(\text{Zn-OH}_2{}^{(c)}) + E(\text{Zn–L})\}. \tag{A4}$$

Although the second term in Eq. A4 corresponds to the total binding energy of the zinc(II)–polyamine complex, since the first term is constant for all complexations for the zinc(II) ion in water, one can regard $-\Delta H$ as being the total binding energy of the zinc(II)–polyamine complex in aqueous solution, when the relative energy is treated.

Since the Lewis acidity of the zinc(II) ion is thought to be reversely proportional to the strength of the coordination bond between the zinc(II) ion and all of the ligands, we can express the Lewis acidity of the zinc(II) ion as Eq. A5 using the total binding energy ($-\Delta H$):

$$\text{Lewis acidity} \propto \Delta H. \tag{A5}$$

On the other hand, the pK_a of coordinated water is a parameter for the Lewis acidity of a metal ion, and the Lewis acidity is reversely proportional to pK_a:[40)]

$$\text{Lewis acidity} \propto -\text{p}K_a. \tag{A6}$$

Therefore, from Eqs. A5 and A6, Eq. A7 can be derived;

$$\text{p}K_a = -\alpha \Delta H + \beta, \tag{A7}$$

where α and β are proportional constants.

In the above treatment, we considered only the coordinated water at the first coordination sphere as the effect of water. However, in a more-detailed treatment, the enthalpy changes of hydration or dehydration for each species in Eq. A1 should be considered, because each species is solvated in water. When the hydration enthalpy change is designated as ΔH_{sol}, we obtain

$$\begin{aligned}\Delta H = {} & [6E(\text{Zn-OH}_2) - \{mE(\text{Zn-OH}_2{}^{(c)}) + E(\text{Zn–L})\}] \\ & -\Delta H_{\text{sol}}([\text{Zn(OH}_2)_6]^{2+}) + \{\Delta H_{\text{sol}}([\text{ZnL(OH}_2)_m]^{2+}) \\ & -\Delta H_{\text{sol}}(\text{L})\}.\end{aligned} \tag{A8}$$

Since the second term of Eq. A8 is constant, Eq. A8 shows that Eq. A7 is realized only when the third term of Eq. A8 is constant, or varies with a constant value for each L.

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