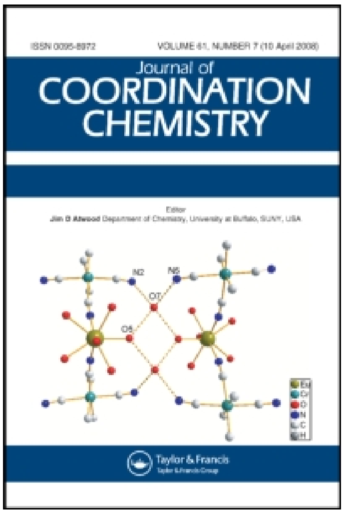

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SOLUTION STUDY AND CRYSTAL STRUCTURE OF A PENTACOORDINATE ZINC(II) COMPLEX WITH *N,N''*-bis-(2-HYDROXYBENZYL)-DIETHYLENETRIAMINE

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SOLUTION STUDY AND CRYSTAL STRUCTURE OF A PENTACOORDINATE ZINC(II) COMPLEX WITH *N,N''*-bis-(2-HYDROXYBENZYL)-DIETHYLENETRIAMINE

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The stability constants of Zn(II) complexes with *N,N''*-bis-(2-hydroxybenzyl)-diethylenetriamine(H_2L) were determined by potentiometric pH titration at 25°C and at 0.1 M KNO_3 ionic strength. A neutral complex ZnL was synthesized. In addition to IR, and ^1H NMR spectra, its structure was established by single crystal X-ray diffraction. The crystal is orthorhombic, of space group Pbca, with cell constants $a = 17.865(4)$, $b = 20.079(4)$, $c = 9.598(2)$ Å, $z = 8$ and $D_c = 1.461\,\mathrm{g\cdot cm^{-3}}$. The structure was solved and refined to $R = 0.049$ ($R_\omega = 0.054$). The coordination geometry around the zinc ion is trigonal-bipyramidal with a large distortion, exhibiting two nonequivalent phenolates.

Keywords: Crystal structures; Zinc complexes; Amine-phenol complexes; Solution study

INTRODUCTION

Zinc ion plays an essential role in the active center of many hydrolases, such as alkaline phosphotase, a nonspecific phosphomonoesterase. Investigations on its coordination chemistry are beneficial to further understand its role in these enzymes. It was reported that zinc coordinated to phenolate in a

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Schiff-base ligand [1], as well as in other ligands [2], can act as a nucleophile to catalyze ester hydrolysis. These results promoted us to investigate linear amine-phenol ligands obtained by reducing Schiff bases, which have greater flexibility, better water solubility and more inertness to hydrolytic decomposition than corresponding Schiff bases. While a number of their complexes with transition metals and main group metals [3–8], such as ^{99m}Tc, Sn, Al and Ga have been reported, the corresponding complexation with zinc remains relatively unexplored [9, 10].

Zinc ion has considerable flexibility of coordination numbers and strongly distorted coordination polyhedra due to its d^{10} configuration [11]. In the crystal structure of an alkaline phosphotase complex with an inorganic phosphate [12], one zinc ion is five-coordinate and another is tetrahedral. The importance of five-coordinate trigonal bipyramidal zinc-ligand bonding in reaction intermediates during the catalysis of zinc enzymes has been stressed. Herein we report the synthesis and crystal structure of a neutral five-coordinate zinc complex with a pentadentate amine-phenol ligand H_2L, and potentiometrically obtained complexation constants, which are useful for further kinetic studies on the catalytic hydrolysis of esters.

EXPERIMENTAL

Reagents, Apparatus and Procedures

Zinc nitrates, diethylenetriamine, and sodium borohydride were commercial reagents of analytical grade, used without further purification. Standardization of KOH, HNO_3 and $Zn(NO_3)_2$ solutions, ^1H NMR, IR spectra, microanalysis of C, H, N, and procedures of potentiometric pH-titration together with the program used to calculate the protonation and Zn(II) complexation equilibria constants were the same as reported [13, 14]. The electrode was calibrated by standard buffer solutions as described in the literature [13]. Protonation equilibria were studied at an ionic strength of 0.10 M KNO_3 and ligand concentration of 1.0×10^{-3} M at 25°C. The formation equilibria were studied by titrating 1.0×10^{-3} M acidified (HNO_3) ligand with equimolar $Zn(NO_3)_2$. The titration was conducted in duplicate, with 75 data points recorded per experiment.

Syntheses of Compounds

$H_2L \cdot 3HCl$

The ligand was prepared by Pillai's method[3] with the exception that the final product was taken up in ethanol and saturated with HCl gas resulting

$H_2L{\cdot}3HCl{\cdot}0.5H_2O$. Yield 80%. Anal. Calc. for $C_{18}Cl_3H_{29}N_3O_{2.5}$(%): C, 49.84; H, 6.74; N, 9.69%. Found: C, 49.68; H, 6.54; N, 9.76. IR. (KBr, cm^{-1}): 3433(*b*, *s*, OH), 2944, 2770, 2679, 2426(*s*, NH_2^+), 1585(*m*), 1492(*m*), 1460(*m*), 1212 (*m*, C—O), 1167(*m*), 757.9(*s*). ^{1}H NMR, $\delta(D_2O)$: 6.96–7.35 (*m*, 8H, aryl), 4.29(*s*, 4H, benzylic), 3.46(*m*, 8H, CH_2CH_2).

ZnL

0.01 mol ligand was added to 100 mL 0.1 M $Zn(NO_3)_2$, the pH of the solution was adjusted to 9.5 with 0.5 M KOH solution, and the resulting mixture was stirred for 2 hours. The precipitated zinc complex was recrystallized from DMF yielding 2.3 g single crystals suitable for X-ray diffraction. Yield 60%. Anal. Calc. for $C_{18}H_{23}N_3O_2Zn$: C, 57.08; H, 6.12; N, 11.09. Found: C, 56.94; H, 6.29; N, 11.20. IR(KBr, cm^{-1}): 3416(*b*, *w*), 3284(*s*, υ_{NH}), 3167(*s*), 3125(*m*), 2915(*s*), 2855(*s*), 1591(*s*), 1558(*w*, δ_{NH}), 1475(*s*), 1448(*s*), 1189(*w*), 1085(*m*), 760(*s*), 729(*m*), 582(*w*), 530(*w*), 463(*w*). ^{1}H NMR, $\delta(CDCl_3)$: 7.09(*m*, 4H, aryl), 6.62(*m*, 4H, aryl), 2.1–4.4(complex, 15H).

Crystal Structure Determination

A crystal with dimensions 0.20 × 0.20 × 0.30 mm was mounted on a glass fiber and scanned on a Rigaku AFC7R diffractometer equipped with graphite-monochromated MoKα ($\lambda = 0.71069$ Å) radiation. Intensity data were obtained by using an $\omega - 2\theta$ scan mode with a scan speed of 16°/min to a maximum 2θ of 50.0°. The cell parameters were obtained from a least-squares fit of 19 reflections ($18.49 < 2\theta < 20.96°$).

A total of 3264 reflections was collected and 1718 observed reflections with $I > 2.00\sigma(I)$ used in the structure determination. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques with the teXan [15] software package. Neutral atom scattering factors were taken from Cromer and Waber [16]. Anomalous dispersion effects were included in Fcalc [17]. The structure was refined by full-matrix least-squares techniques based on F^2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms are included but not refined. The final cycle of full-matrix least-squares refinement converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$ and $R_\omega = [[\sum\omega(|F_o| - |F_c|)^2]/\sum\omega F_o^2]^{1/2} = 0.054$, $w = 1/[\sigma^2(Fo)] + 4Fo^2/[\sigma^2(Fo^2)]$, where $\sigma^2(Fo)^2 = [\sigma^2(C + R^2B) + (pFo^2)^2]/(Lp^2)$ with S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz-polarization factor, p = p-factor.

TABLE I Crystal and experimental data for ZnL

Formula	$C_{18}H_{23}N_3O_2Zn$
Formular weight	378.78
Crystal Size (mm)	0.20 × 0.20 × 0.30
System	Orthorhombic
Space group	Pbca(#61)
a(Å)	17.865(4)
b(Å)	20.079(4)
c(Å)	9.598(2)
Z(molecules/cell)	8
Density(calculated)	1.461 g·cm^{-3}
Absorption Correction	Empirical
Transmission factors	0.9697–1.0000
Radiation(λ, Å)	MoKα(0.71069)
Temperature(K)	293(1)
Unit reflections	3264
Observed reflections	1718
R	0.049
R_ω	0.054

The largest and smallest peak in the final difference Fourier map had a height of 0.45 and $-0.54\,\mathrm{e}\cdot\text{Å}^{-3}$. Crystal data together with some experimental details are listed in Table I.

RESULTS AND DISCUSSION

Protonation and Complexation Equilibria of Zn(II) with the Ligand

The protonation of the ligand has been studied potentiometrically by titrating acidified aqueous solution (HNO_3) of the ligand ($C_L = 1.0 \times 10^{-3}$ M, 25°C, and ionic strength 0.10 M KNO_3) with 0.1522 M KOH. The protonation constants $\beta_{011}-\beta_{015}$ are defined as follows (a_{H^+} is the activity of H^+):

$$L^{2-} + nH^+ = H_nL^{n-2}, \quad \beta_{01n} = [H_nL^{n-2}]/[L^{2-}](a_{H^+})^n \quad (n = 1, 2, 3, 4 \text{ and } 5) \tag{1}$$

Where the equilibria constants are symbolized as $\log\beta_{mln}$, and m, l and n represent the number of the metal ion, the ligand and hydrogen atom in the complex, respectively. $\beta_{01n}(m = 0)$ expresses only the protonation constants, without metal ion. The $\log\beta_{01n}(n = 1, 2, 3, 4$ and 5) values obtained are 11.14(3), 21.57(4), 30.55(6), 38.45(8) and 42.45(9), where the first two correspond to the protonation of the phenolates, and the successive three correspond to those of amine nitrogens.

Zinc(II) complexation constants were determined by titrating $H_2L \cdot 3HNO_3$ with equimolar $Zn(NO_3)_2$ and the data were treated for monoprotonated complex $ZnHL^+$(Eq. (2)) and complex ZnL(Eq. (3))(a_{H^+} is the activity of H^+):

$$Zn^{2+} + L^{2-} + H^+ = ZnHL^+ \quad \beta_{111} = [ZnHL^+]/[Zn^{2+}][L^{2-}]a_{H^+} \tag{2}$$

$$Zn^{2+} + L^{2-} = ZnL \quad \beta_{110} = [ZnL]/[Zn^{2+}][L^{2-}] \tag{3}$$

The values of $\lg\beta_{111}$ and $\lg\beta_{110}$ obtained are 22.65(3) and 16.47(6), respectively; $\log\beta_{110}$ for an analogous tetradentate ligand *N,N′*-bis-(2-hydroxybenzyl)-ethylenediamine is 11.97 [9], and the value for a H_2L derived potentially octadentate ligand, *N,N″*-bis-(2-hydroxybenzyl) diethylenetriamine-*N,N′,N″*-triacetic acid [18], is 16.04(6). It can be seen that $\log\beta_{110}$ for the pentadentate H_2L is larger than both tetradentate and octadentate analogues. These results indicate a tendency of zinc ion to preferably form pentacoordinate complexes.

The following equation can be obtained from Eqs. (2) and (3).

$$ZnHL^+ = ZnL + H^+ \quad Ka = [ZnL]a_{H^+}/[ZnHL^+] = K_{110}/K_{111} \tag{4}$$

Ka is the deprotonation constant of the second coordinated phenol group. $pKa = \log\beta_{111} - \log\beta_{110} = 6.18$. Upon coordination, the phenol group is activated and can yield nucleophile Zn(II)—$^-$OAr at neutral pH, which may result in catalysis of ester hydrolysis [19].

IR Spectrum

In the infrared spectrum for the ligand, the strong broad band in the region 3650–3300 cm^{-1} (centered at ~3433 cm^{-1}) was assigned to the OH stretching mode of the water of crystallization, or lattice water, which was found in the elemental analysis. Strong bands appeared at 2770, 2679 and 2426 cm^{-1}, corresponding to stretching mode of the protonated amines NH_2^+, which disappeared upon coordination. New medium to strong bands at 3284, 3167, 3125 and a weak band at 1558 cm^{-1} were assigned to stretching and bending modes of the coordinated NH groups, respectively. Additional bands that were probably due to Zn–O and Zn–N stretches were observed below 750 cm^{-1}; however, assignments of these bands were not conclusive because of their low energies.

^{1}H NMR Spectrum

The ^{1}H NMR spectrum of the complex recorded in D_2O was extremely complicated. Coordination of the amine phenol to zinc caused greater complexity of aromatic resonances. The multiplet from the aromatic hydrogens split into two sets of multiplets at 7.09 and 6.62. This was attributed to the two hydroxybenzyl groups becoming nonequivalent upon coordination, which was indicated by the crystal structure. In addition, the singlet from the benzylic hydrogens and the multiplet from the amines became a complicated series of overlapping signals from 2.1 to 4.4 ppm. Detailed assignments of the individual resonances were not carried out.

Crystal Structure of ZnL

Selected bond distances and angles for the crystal are reported in Table II. Figure 1 shows the crystal structure of ZnL with molecular labeling.

As is seen from Table II and Figure 1, the coordination geometry of the zinc ion can be described as trigonal-bipyramidal with large distortion of O(1), O(2) and N(3) in the equatorial plane, and Zn-0.099, N(1)-2.128 and N(2) 2.000 Å out of the plane. The N(1)—Zn—N(2) angle is only 153.1°. The Zn—N distances of 2.125 and 2.130 Å for N1 and N2 are in the normal range for Zn coordinated with secondary amines [20]. There are two different Zn—O distances of 1.941 and 2.001 Å representing the two nonequivalent phenolates. The Zn—N(3) bond with a distance of 2.221 Å is the longest bond within the zinc coordination sphere, and the distance is significantly longer than normal Zn—N distances [1], which may be related to the stress derived from the presence of two five-membered rings.

Supplementary Material

A full list of crystallographic data is available from the authors upon request.

TABLE II Selected bond distances (Å) and angles (°) for complex ZnL

Zn—O(1)	2.001(4)	Zn—O(2)	1.941(4)
Zn—N(1)	2.125(5)	Zn—N(2)	2.130(5)
Zn—N(3)	2.221(5)		
O(1)—Zn—O(2)	115.6(2)	O(1)—Zn—N(1)	90.3(2)
O(1)—Zn—N(2)	89.5(2)	O(1)—Zn—N(3)	128.7(2)
O(2)—Zn—N(1)	109.3(2)	O(2)—Zn—N(2)	94.9(2)
O(2)—Zn—N(3)	115.1(2)	N(1)—Zn—N(2)	153.1(2)
N(1)—Zn—N(3)	80.7(2)	N(2)—Zn—N(3)	78.5(2)

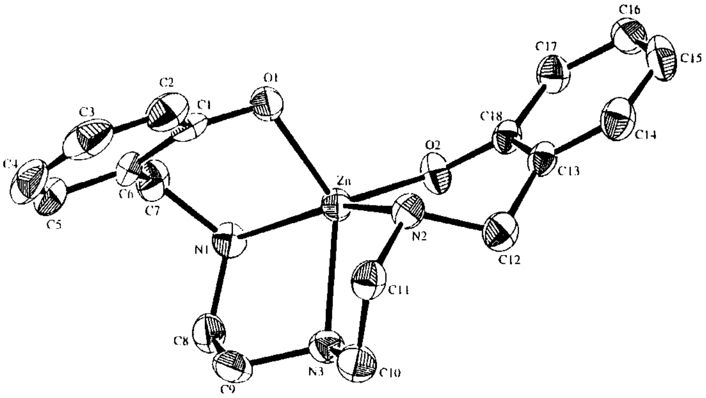

FIGURE 1 The molecular structure of ZnL, with the atom numbering scheme.

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