Mono- and Dinuclear Zinc Complexes Derived from Unsymmetric Binucleating Ligands: Synthesis, Characterization, and Formation of Tetranuclear Arrays

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Zinc complexes of the unsymmetric, binucleating Schiff base ligands 3-{N-[2-(dimethylamino)ethyl]iminomethyl}-salicylic acid (H$_2$L1) and 3-[N-(2-pyridylmethyl)iminomethyl]-salicylic acid (H$_2$L2) have been studied in the solid state as well as in solution. Reaction of ZnX$_2$ (X = NO$_3^-$, CH$_3$CO$_2^-$) with 3-formylsalicylic acid and N,N-dimethylethylenediamine at neutral or slightly acidic pH afforded the dinuclear complexes [Zn$_2$(HL1)$_2$(H$_2$O)$_2$]-(NO$_3$)$_2$·2H$_2$O (**1a**) and [Zn$_2$(HL1)$_2$(CH$_3$CO$_2$)$_2$]·6H$_2$O (**1b**). The Zn ions, which are 3.126(1) Å (**1a**) and 3.2665(7) Å (**1b**) apart, are bridged by two phenolate oxygens. Further coordination sites of the ligand are the imine nitrogen and carboxylate oxygen, while the amino nitrogen is protonated. On dissolution in DMSO or DMF, **1a** and **1b** are converted into the mononuclear species [Zn(HL1)]$^+$. Cleavage of the dinuclear complexes is accompanied by migration of the ammonium proton to the carboxylate group and coordination of the amino nitrogen to Zn. Reaction of **1b** with base yielded the novel tetranuclear Zn complex [Zn$_4$(L1)$_4$]·6.5H$_2$O (**2**) that exhibits coordination number asymmetry. The four Zn ions having N$_2$O$_3$ and N$_2$O$_4$ coordination environments are located at the corners of a nearly square-planar rectangle. H$_2$L2 binds Zn via the phenolate oxygen and, imine and pyridine nitrogens in acidic solution. Deprotonation of the carboxyl group in alkaline solution gave the tetranuclear compound [Zn$_4$-(L2)$_4$]·4.5H$_2$O (**4**) with a cubane-like Zn$_4$O$_4$ core.

Introduction

Since the concept of binucleating ligands has been developed three decades ago,[1-3] various ligands of this type have been designed with the aim to stabilize dinuclear metal complexes.[4-12] The class of binucleating ligands comprises compounds providing bridging atoms such as alkoxo or phenoxo oxygens that held the metal ions in close proximity and compounds having isolated donor sets. In some cases, however, binucleating ligands afforded metal complexes with higher nuclearity. When the denticity of the ligand leaves vacant coordination sites at the metal ions, these are saturated under certain circumstances by self-assembly to polynuclear arrays—often in the presence of additional bridging groups such as hydroxide or carboxylate.[13-16] Frequently, such polynuclear compounds have interesting

magnetic and electronic properties or display unusual structural features. In particular, the coordinatively flexible Zn(II) permits a wide variety of structural arrangements. Krebs and co-workers reported a hexanuclear Zn complex derived from a phenol-based binucleating ligand with the metal ions being arranged in form of a trigonal prism.[17] The same authors obtained a trinuclear Zn complex with the Schiff base ligand 1,3-bis(salicylidenami-no)propan-2-ol,[17] while Mikuriya et al. utilized the corresponding amine to isolate an octanuclear Zn complex.[18] Recently, a triangular Zn complex derived from a pyrazine derivative has been published,[19] and the tetranuclear complex [Mg(H$_2$O)$_6$]-[{Zn$_2$L(CH$_3$CO$_2$)}$_2$(μ_3-OH)$_2$]·6H$_2$O (H$_3$L = Schiff base prepared from 2,6-diformyl-4-methylphenol and glycine) containing a Zn$_4$(μ_2-OAr)$_2$(μ_3-OH)$_2$ core resulted from our own work.[20]

In the present report, Zn complexes of the unsymmetric bridging ligands 3-{N-[2-(dimethylamino)ethyl]iminomethyl}-salicylic acid (H$_2$L1) and 3-[N-(2-pyridylmethyl)iminomethyl]-salicylic acid (H$_2$L2) are described (Chart 1). The ligands having one N$_2$O and one O$_2$ coordination site do not saturate the coordination sphere of Zn and are thus potentially suitable to create polynuclear compounds. Furthermore the number of donor sites available depends on the protonation state of the ligands and can be tuned by the pH. Here the solid-state structures and solution behavior of the mono- and dinuclear Zn

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Chart 1

H₂L1   H₂L2
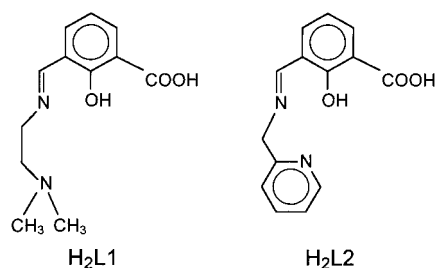
complexes [Zn₂(HL1)₂(H₂O)₂](NO₃)₂·2H₂O (**1a**), [Zn₂(HL1)₂-(CH₃CO₂)₂]·6H₂O (**1b**), and [Zn(HL2)(H₂O)(NO₃)] (**3**) as well as the assembly or conversion of these species to the novel tetranuclear compounds [Zn₄(L1)₄]·6.5H₂O (**2**) and [Zn₄(L2)₄]·4.5H₂O (**4**) are described.

Experimental Section

Materials. 3-Formylsalicylic acid was prepared according to ref 21; H₂L1 was prepared via reaction of 3-formylsalicylic acid and *N,N*-dimethylethylenediamine in CHCl₃ and subsequent evaporation of the solvent. All chemicals and solvents were reagent grade and used without further purification.

Complex 1a. Complex 1a was obtained as pale yellow precipitate by reaction of 3-formylsalicylic acid (320 mg, 1.92 mmol) with *N,N*-dimethylethylenediamine (169 mg, 1.92 mmol) and Zn(NO₃)₂·6H₂O (572 mg, 1.92 mmol) in ethanol−water (5:1, 30 mL) at room-temperature overnight: yield 425 mg (56%). Recrystallization from water at 4 °C afforded X-ray suitable crystals of **1a**. Selected IR data (cm⁻¹): 3342 (br), 3055 (br), 2744 (br), 1633 (s), 1597 (s), 1557 (s), 1443 (s), 1414 (s), 1384 (vs), 1319 (s), 1286 (s), 1233 (m), 962 (m), 876 (m), 828 (m). ¹H NMR (D₂O, pD 7.4): δ = 8.49 (s, 2H, azomethine), 8.18 (d, 2H, aryl), 7.58 (d, 2H, aryl), 6.90 (t, 2H, aryl), 4.15 (s, br, 4H, =N−CH₂), 3.60 (s, br, 4H, −N−CH₂), 2.98 (s, 12H, CH₃). ¹³C NMR (D₂O, pD 7.4): δ = 174.8 (carboxyl), 174.5 (azomethine), 166.3 (aryl), 142.4 (aryl), 139.4 (aryl), 122.8 (aryl), 120.9 (aryl), 116.3 (aryl), 57.2 (−N−CH₂), 55.4 (=N−CH₂), 43.2 (N−CH₃).

Anal. Calcd for C₂₄H₃₈N₆O₁₆Zn₂ (M_r = 797.3): C, 36.2; H, 4.8; N, 10.5. Found: C, 36.0; H, 5.0; N, 10.6.

Complex 1b. 3-Formylsalicylic acid (332 mg, 2.00 mmol), *N,N*-dimethylethylenediamine (176 mg, 2.00 mmol), and Zn(CH₃CO₂)₂·2H₂O (878 mg, 4.00 mmol) were stirred in ethanol−water (5:1, 36 mL) at room-temperature overnight. Slow evaporation of the solvent at 4 °C yielded colorless needles of **1b** (530 mg, 64%). Selected IR data (cm⁻¹): 3376 (br), 2998 (br), 2656 (br), 1638 (s), 1602 (s), 1560 (s), 1418 (s), 1343 (m), 1282 (m), 1235 (m), 869 (m), 768 (m).

Anal. Calcd for C₂₈H₄₈N₄O₁₆Zn₂ (M_r = 827.4): C, 40.7; H, 5.9; N, 6.8. Found: C, 40.6; H, 5.6; N, 6.7.

Complex 2. Complex 1b (104 mg, 0.13 mmol) was dissolved in water (10 mL) and brought to pH 9.9 with 1 N NaOH. Slow evaporation of the solvent at room temperature gave yellow cubes (15 mg, 18%). Selected IR data (cm⁻¹): 3380 (br), 2869 (m), 2836 (m), 2792 (m), 1640 (s), 1603 (s), 1561 (s), 1456 (m), 1438 (s), 1409 (s), 1341 (m), 1234 (m), 941 (m), 873 (m), 765 (m). ¹H NMR (CDCl₃): δ = 8.10 (s, 4H, azomethine), 8.06 (d, 4H, aryl), 6.95 (d, 4H, aryl), 6.42 (t, 4H, aryl), 3.80 (m, 8H, =N−CH₂), 3.35 (m, 8H, −N−CH₂), 2.04 (s, 24H, CH₃).

Anal. Calcd for C₄₈H₆₉N₈O₁₈.₅Zn₄ (M_r = 1315.6): C, 43.8; H, 5.3; N, 8.5. Found: C, 43.9; H, 5.2; N, 8.6.

Complex 3. 3-Formylsalicylic acid (102 mg, 0.61 mmol), 2-picolylamine (66 mg, 0.61 mmol), and Zn(NO₃)₂·6H₂O (458 mg, 1.54 mmol) were allowed to react in ethanol−water (5:1, 12 mL) at room-temperature overnight. Yellow cubes of **3** crystallized at 4 °C (123 mg, 49%). Selected IR data (cm⁻¹): 3412 (br), 3073 (m), 2884 (m), 1682 (s), 1657 (s), 1608 (s), 1578 (s), 1474 (m), 1435 (m), 1391 (s), 1356 (s), 1299 (m), 1275 (m), 1192 (s), 1083 (w), 1047 (w), 926 (w),

767 (m). ¹H NMR (DMSO-d_6): δ = 14.80 (s, 1H, COOH), 8.76 (s, 1H, azomethine), 8.55 (d, 1H, aryl), 8.09 (t, 2H, aryl), 7.74−7.59 (m, 3H, aryl), 6.87 (t, 1H, aryl), 5.15 (s, 2H, Ar−CH₂).

Anal. Calcd for C₁₄H₁₄N₃O₇.₅Zn (**3**·0.5H₂O) (M_r = 409.7): C, 41.0; H, 3.4; N, 10.3. Found: C, 41.2; H, 3.3; N, 10.3.

Complex 4. The pH of a solution of **3** (82 mg, 0.21 mmol) in methanol−water (1:1, 24 mL) was adjusted to 8.9 with 0.5 N NaOH. After a few days yellow cubes of **4** formed at 4 °C (17 mg, 24%). Selected IR data (cm⁻¹): 3418 (br), 1639 (s), 1599 (s), 1558 (s), 1435 (s), 1290 (m), 1233 (m), 1201 (w), 1157 (w), 1048 (m), 763 (m). ¹H NMR (DMSO-d_6): δ = 8.69 (s, 4H, azomethine), 8.13 (m, br, 8H, aryl), 7.86 (d, 4H, aryl), 7.65 (m, br, 8H, aryl), 7.48 (d, 4H, aryl), 6.73 (m, 4H, aryl), 5.13 (s, 8H, Ar−CH₂).

Anal. Calcd for C₄₈H₆₉N₈O₁₈.₅Zn₄ (M_r = 1315.6): C, 43.8; H, 5.3; N, 8.5. Found: C, 43.9; H, 5.2; N, 8.6.

Instrumentation. ¹H NMR, ¹³C NMR, and ¹H−¹³C 2D correlation spectra of D₂O, DMSO-d_6, MeOD-d_4, DMF-d_7, or CDCl₃ solutions were recorded on Bruker AC200, DRX 400, and DRX 500 spectrometers. The pD values of D₂O solutions were obtained by use of a glass electrode and addition of 0.4 to the pH meter reading. Infrared spectra of KBr pellets were taken on a Bruker IFS 28 FT-spectrometer. ESI mass spectra were measured on a Finnigan MAT 90 spectrometer.

Crystal Structure Analyses. Crystal data for compounds **1a−4** (see Table 1) were collected at room temperature on an Enraf-Nonius-Kappa CCD diffractometer[22] using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). For data reduction and cell refinement the programs DENZO and SCALEPACK were used.[23] The structures were solved by conventional Patterson (**1a**, **3**, and **4**) or direct (**1b** and **2**) methods and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 using the SHELXTL PLUS and SHELXL-93 programs.[24] All non-hydrogen atoms were refined anisotropically (with the exception of some of the carbon atoms and the oxygen atoms of the disordered water molecules in **2**). The hydrogen atoms of **1a**, **1b**, **3**, and **4** were located in the final Fourier-difference maps (except for those of the acetate groups in **1b**, some of the aryl protons in **4** as well as the majority of those of the water molecules of crystallization) and refined isotropically. In **2** carbon-bound hydrogen atoms were placed at calculated positions and given fixed isotropic temperature factors.

Results and Discussion

Metal complexes of Schiff bases are generally prepared in a one-step synthesis by condensation of an aldehyde with an amine in the presence of the metal ion.[25] Treating 3-formylsalicylic acid with *N,N*-dimethylethylenediamine and Zn(CH₃CO₂)₂ or Zn(NO₃)₂ in neutral or slightly acidic solution affords the zinc complexes **1a** and **1b**. Determination of the solid-state structures by X-ray analyses revealed the dinuclear compounds [Zn₂-(HL1)₂(H₂O)₂](NO₃)₂·2H₂O (**1a**) and [Zn₂(HL1)₂(CH₃CO₂)₂]·6H₂O (**1b**).

Solid-State Structure of 1a and 1b. A view of the cation of **1a** is depicted in Figure 1 and selected bond lengths are listed in Table 2. The centrosymmetric cation is built up of two Schiff base ligands that bridge a pair of Zn atoms at a distance of 3.126(1) Å through the deprotonated phenolic oxygens. Further coordination sites of the ligands are the imine nitrogens and carboxylate oxygens, while the amino groups of the ligand sidearms are protonated. The ammonium protons were located in the final Fourier-difference map. The donor atoms of the ligands span the basal plane of a square pyramid, the apical position of which is occupied by a water molecule.

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Table 1. Crystallographic Data

	1a	**1b**	**2**	**3**	**4**
formula	$C_{24}H_{38}N_6O_{16}Zn_2$	$C_{28}H_{48}N_4O_{16}Zn_2$	$C_{48}H_{69}N_8O_{18.5}Zn_4$	$C_{14}H_{13}N_3O_7Zn$	$C_{56}H_{49}N_8O_{16.5}Zn_4$
fw	797.34	827.44	1315.59	400.64	1359.51
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
a, Å	6.696(1)	7.002(2)	44.954(2)	8.125(1)	13.669(2)
b, Å	12.867(3)	9.200(1)	11.656(3)	8.498(1)	28.704(5)
c, Å	18.482(4)	14.309(1)	22.943(2)	12.051(1)	15.024(3)
α, deg		92.27(1)		96.23(1)	
β, deg	92.05(3)	98.56(1)	93.14(2)	97.22(1)	115.72(1)
γ, deg		97.79(1)		106.69(1)	
V, Å^3	1591.3(6)	901.4(3)	12004(3)	781.5(2)	5311(2)
Z	2	1	8	2	4
d(calc), g cm^{-3}	1.664	1.524	1.456	1.703	1.700
μ(Mo Kα), mm^{-1}	1.591	1.406	1.652	1.616	1.868
T, K	293	293	293	293	293
R1, wR2 [$I > 2\sigma(I)$]^a	0.033, 0.085	0.037, 0.083	0.083, 0.219	0.034, 0.085	0.041, 0.077
R1, wR2 (all data)^a	0.055, 0.131	0.053, 0.088	0.169, 0.252	0.046, 0.093	0.125, 0.095

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; w^{-1} = $\sigma^2(F_o^2) + (aP)^2$; P = $(F_o^2 + 2F_c^2)/3$; a = 0.0605 for **1a**, 0.0492 for **1b**, 0.1319 for **2**, 0.0626 for **3**, and 0.0439 for **4**.
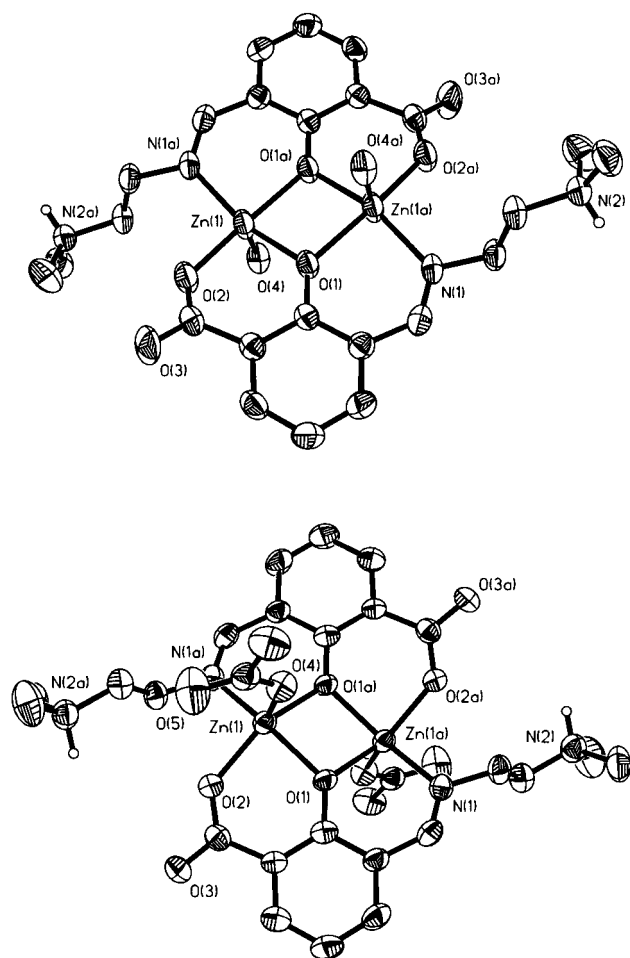

Figure 1. View of the cations of **1a** (top) and **1b** (bottom). Hydrogen atoms were located in the Fourier-difference maps, but for clarity only the hydrogen atoms bound to the amino nitrogens are shown.

In the crystal lattice, the cations are connected through a strong hydrogen bond between carboxylate oxygens and coordinating water molecules [O(3)···O(4) 2.643(4) Å, $-x + 1$, $-y$, $-z$] leading to a stairlike arrangement of the cations (see the Supporting Information). A short contact is observed between Zn and the carboxylate oxygen O(3) at $-x + 1$, $-y$, $-z$; however, the distance of 2.987(3) Å clearly rules out significant bonding interactions. The ammonium groups form hydrogen

Table 2. Selected Bond Lengths (Å) for **1a** and **1b**

	1a	**1b**
Zn(1)−N(1a)	2.034(2)	2.071(3)
Zn(1)−O(1)	2.018(2)	2.048(2)
Zn(1)−O(1a)	2.036(2)	2.077(2)
Zn(1)−O(2)	1.979(2)	2.010(2)
Zn(1)−O(4)	2.060(3)	1.966(2)

bonds to the nitrate anions. Other hydrogen-bonding interactions occur between the coordinating water molecules, nitrate anions, and water molecules of crystallization.

The basic structure of **1b** (Figure 1, Table 2) is identical to that of **1a**. Again, the metal centers are five-coordinate, with the water ligands being replaced by acetate groups. Compared with **1a** the Zn atoms, which lie 0.597(1) Å above the least-squares planes defined by the ligand donor atoms [0.276(1) Å in **1a**], assume a more distorted square-pyramidal coordination geometry. The bond angles between the axial and equatorial coordination sites are 6.5 to 22.8° larger than the ideal 90° values in a regular pyramid, the structural index τ indicating the relative amount of trigonality (square pyramid $\tau = 0$, trigonal bipyramid $\tau = 1$)[26] is 0.12 (0.03 in **1a**). The unit cell contains six water molecules of crystallization that form hydrogen bonds among each other, with the carboxylate oxygen as well as with the ammonium groups. In the crystal packing (see the Supporting Information), the neutral molecules built layers parallel to the *bc* plane. Within these layers the molecules are connected through a water molecule of crystallization that hydrogen bonds to the carboxylate and acetate oxygen of neighboring molecules.

Solution-State Structure of 1a and 1b. When **1a** or **1b** is dissolved in D$_2$O or MeOD-d_4, the ^{1}H NMR resonance of the *N*-methyl protons appears at 2.97 (D$_2$O, pD 7.4) and 3.01 ppm (MeOD-d_4), in accordance with the adjacent nitrogen being protonated. In both solvents, the signals of the methylene, methyl, and aromatic protons are considerably broadened at room temperature, suggesting fluxional processes or interconversion of different species on the NMR time scale. This may involve release of metal ion, binding and release of the amino nitrogen, or an equilibrium between dinuclear and mononuclear species. When mononuclear species are formed in solution, an exchange between the two coordination sites of the ligand is

(26) The structural index τ is defined as $\tau = (\beta - \alpha)/60°$, where α and β are the two largest angles around the metal. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
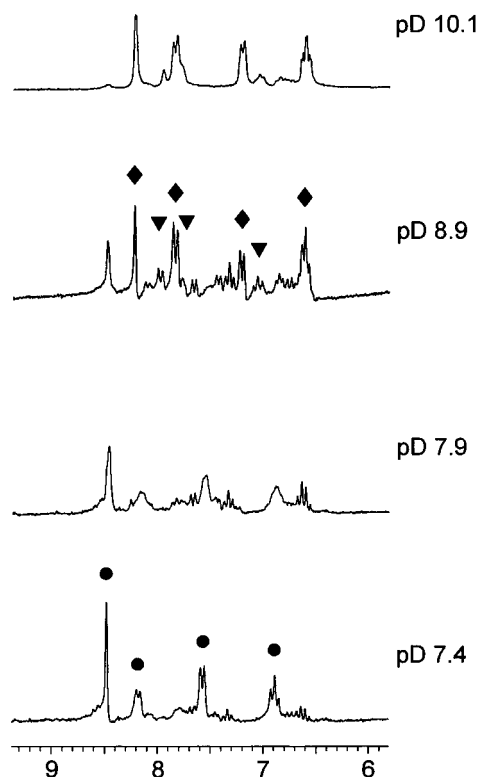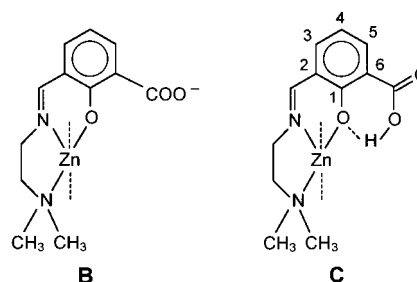
Figure 2. pH-dependent changes in the ^{1}H NMR spectrum of **1a**. Spectra were taken immediately after dissolving pure **1a** in D$_2$O and adjusting the pD. Resonances are assigned as follows: (●) **A**, (◆) **B** and (▼) 3-formylsalicylic acid.

Chart 2

protons appear at 2.33 ppm, indicative of the ammonium proton having migrated to the carboxyl group. Unambiguous evidence for the location of the proton in DMSO was obtained by a ^{1}H$-$^{13}C 2D correlation experiment (see the Supporting Information). The contour plot displays correlation peaks at 16.48 ppm to the ring carbon C6 as well as to the carboxyl carbon and/or the ring carbon C1, confirming the solution-state structure **C**. Considering the fact that the DMSO solution of **1a** contains two water molecules per Zn/ligand (Zn-bound water and water of crystallization) that offer exchangeable protons, the resonance of the carboxyl proton is remarkably sharp suggesting a strong intramolecular hydrogen bond to the deprotonated phenolic oxygen as found in the solid-state structure of **3** (see below). Since the chemical shift of the carboxyl proton is not affected by the concentration, intermolecular hydrogen-bonding interactions can be excluded. The complex is remarkably stable in solution, probably owing to the proposed tridentate coordination by the chelating sidearm of the ligand. Except for the position and line width of the carboxyl resonance, the proton NMR spectrum remains unchanged at elevated temperature (heating to 75 °C results in a 0.33 ppm upfield shift and line-broadening of the carboxyl signal).

The solution behavior of **1a** in DMF is similar to that observed in DMSO. As evident from a sharp resonance at 15.96 ppm in the ^{1}H NMR spectrum, the carboxyl group is protonated and noncoordinating.

We attribute the different solution-state structures in neutral aqueous solution, DMSO, and DMF to the fact that carboxylic acids show higher ionization constants in aprotic, organic solvents than in water. For example, the pK_a value of benzoic acid, which is ca. 4 in water, rises to ca. 11 in DMSO.[27] On the other hand, lower pK_a values are reported for amines in organic solvents than in water (e.g., pK_a of trimethylammonium 9.8 in water and 8.4 in DMSO[27]). Furthermore, deprotonation of the amino group is facilitated by the chelate effect.

Solid-State Structure of 2. From the alkaline solution of **1b** yellow cubes crystallized after 1 week. The crystals contain neutral molecules of composition [Zn$_4$(L1)$_4$] (**2**), whose structure is displayed in Figure 3. The four Zn ions are located at the corners of a nearly planar rectangle. Each ligand binds one Zn through the phenolate oxygen, the imine nitrogen, and the amine nitrogen. Neighboring Zn ions are connected through phenolate bridges. The carboxylate group of the ligand bound to Zn(2) forms an asymmetric, single-atom bridge between Zn(3) and Zn(4) [O(2B)$-$Zn(3) 2.038(8) Å and O(2B)$-$Zn(4) 2.310(8) Å (Table 3)]. Likewise, Zn(1) and Zn(2) are linked through a

likely to occur, since Zn shows no pronounced preference for N or O donors. The signals of the methyl and methylene protons display upfield shifts with increasing pD due to deprotonation of the ammonium group. At the same time, the resolution of the spectrum is further decreased and a new set of signals emerges at 8.23 (s), 7.85 (d), 7.22 (d), and 6.63 (t) ppm around pD 8 (Figure 2), indicating formation of a new species **B** in alkaline solution. The concentration of **B** increases with increasing pD, while no significant changes are observed with time. Around pD 9 the signals become sharp, and at pD 10 conversion of **A** into **B** is almost complete. The formation of **B** is reversible, since the original spectrum is obtained after lowering the pD. As evident from the minor peaks at 7.89 (d), 7.67 (d), and 7.06 (t) ppm corresponding to 3-formylsalicylic acid a small amount of the imine ligand is hydrolyzed in basic solution. Further signals of low intensity observed in the spectra at pD 7.9 and 8.9 have not been identified. As **B** is formed at alkaline pH, chelating coordination through the amino nitrogen of the ligand sidearm can be assumed. However, it seems unlikely that binding of the amino group is the only difference between the two species observed in alkaline solution. Interaction of the amino nitrogen with Zn does not explain the pronounced upfield shift of the aromatic protons of **B** [δ(**B**) $-$ δ(**A**) = 0.26$-$0.36 ppm at pD 9]. Furthermore, averaged signals would be expected for the open and the chelate species rather than two distinct signal sets due to the lability of Zn complexes. Our preferred interpretation of the NMR data is cleavage of **1** in alkaline solution and formation of the mononuclear species **B** outlined in Chart 2.

In contrast to the spectra run in D$_2$O, sharp resonances are observed, when **1a** is dissolved in DMSO-d_6, which can be ascribed to a rigid solution structure. Furthermore the DMSO-d_6 spectrum features a signal at 16.48 ppm, while the methyl

(27) (a) Izutsu, K. *IUPAC Chemical Data Series No. 35, Acid$-$Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific Publications: Oxford, 1990. (b) Serjeant, E. P.; Dempsey, B. *IUPAC Chemical Data Series No. 23, Ionisation Constants of Organic Acids in Aqueous Solution*; Boca Raton, FL, Pergamon Press: 1979. (c) *CRC, Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: 1999$-$2000.
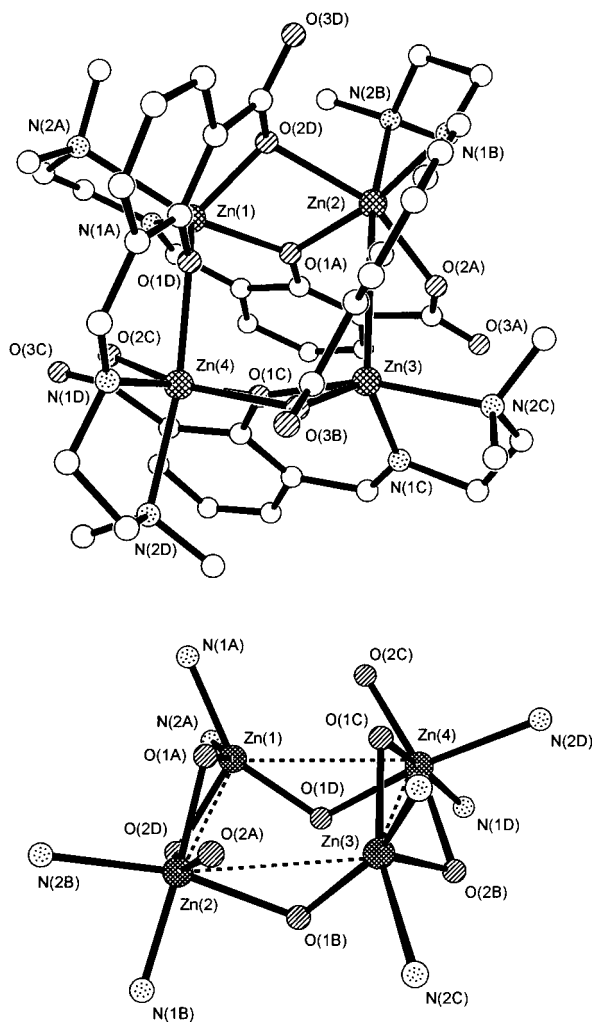
Figure 3. Molecular structure and tetranuclear core of **2**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) for **2**

Zn(1)−N(1A)	2.04(1)	Zn(2)−N(1B)	2.051(9)
Zn(1)−N(2A)	2.39(1)	Zn(2)−N(2B)	2.235(9)
Zn(1)−O(1A)	2.145(7)	Zn(2)−O(1A)	2.021(6)
Zn(1)−O(1D)	1.985(8)	Zn(2)−O(1B)	2.157(7)
Zn(1)−O(2D)	1.999(7)	Zn(2)−O(2A)	2.034(8)
Zn(3)−N(1C)	2.01(1)	Zn(4)−N(1D)	2.05(1)
Zn(3)−N(2C)	2.33(1)	Zn(4)−N(2D)	2.28(1)
Zn(3)−O(1B)	1.992(7)	Zn(4)−O(1C)	2.032(7)
Zn(3)−O(1C)	2.139(8)	Zn(4)−O(1D)	2.149(8)
Zn(3)−O(2B)	2.038(8)	Zn(4)−O(2C)	2.039(8)
Zn(2)−O(2D)	2.270(8)	Zn(4)−O(2B)	2.310(8)
Zn(1)···Zn(2)	3.261(2)	Zn(2)···Zn(3)	3.376(2)
Zn(1)···Zn(3)	4.401(2)	Zn(2)···Zn(4)	4.955(2)
Zn(1)···Zn(4)	3.389(2)	Zn(3)···Zn(4)	3.277(2)

tempting to speculate that intramolecular stacking is the driving force for the formation of the tetranuclear complex in the solid state.

A macrocyclic ligand that accommodates four Zn ions in a distorted square-planar arrangement has been reported by Robson and co-workers.[29] However, **2** appears to be the first example for a tetranuclear Zn complex with a binucleating ligand, in which the four Zn ions are arranged in form of a rectangle.

NMR Spectroscopic Characterization of 2. Complex **2** readily dissolves in chloroform. The two negative charges per ligand lead to 0.14−0.41 ppm upfield shifts of the ^{1}H NMR resonances of the azomethine and aromatic ring protons relative to those of the uncoordinated, neutral ligand. The signals of the methylene protons that are sharp triplets in the spectrum of the free ligand (3.74 and 2.71 ppm), appear as broadened multiplets with maxima at 3.80 and 3.35 ppm due to chelate formation. Binding of Zn to the amino nitrogen induces a drastic downfield shift of the $-N-CH_2-$ protons ($\Delta\delta = 0.64$ ppm). The proton NMR spectrum is consistent with coordination of Zn to the ligand donor atoms, but it does not allow any conclusions whether the tetranuclear arrangement is preserved in solution. However, the ESI mass spectrum of a CHCl$_3$ solution of **2** shows no signals corresponding to a Zn$_4$ species. The most intense signal centered at m/z 333.0 displays an isotope splitting pattern assignable to a mononuclear Zn species of composition [Zn(C$_{12}$H$_{14}$N$_2$O$_3$)Cl]$^-$. Obviously, the Zn$_4$ complex is not sufficiently stable to survive ESIMS conditions.

Zinc Complexes of H$_2$L2. Since pyridine nitrogens have lower pK_a values than amino nitrogens, a different coordination behavior is expected, when the amino group in H$_2$L1 is replaced by a pyridine ring. In contrast to H$_2$L1, H$_2$L2 forms the mononuclear complex [Zn(HL2)(H$_2$O)(NO$_3$)] (**3**) in acidic solution, with the ligand binding Zn through the deprotonated phenolic oxygen, the imine nitrogen, and the pyridine nitrogen, while the carboxyl group is protonated (Figure 4). The carboxyl proton which could be located in the Fourier-difference map forms an intramolecular hydrogen bond to the phenolate oxygen. The coordination sphere of Zn is completed by a water molecule and a bidentate nitrate. The oxygen atoms of the nitrate are symmetrically bound, the Zn−O bond lengths differ only slightly (Table 4). In the crystal lattice the neutral molecules are arranged in layers (see the Supporting Information). The structure is stabilized by stacking interactions of the aromatic rings (mean distance ca. 3.7 Å) as well as by hydrogen-bonding interactions involving the carbonyl oxygens of the carboxyl groups and the Zn-bound water.

carboxylate oxygen of the ligand of Zn(4) in addition to a phenolate bridge. This type of monodentate bridging by carboxylate groups is relatively rare in metal carboxylate complexes[28] and formation of the monatomic bridges may be supported by the overall geometry of the tetranuclear complex. By contrast, the carboxylate groups of the remaining ligands coordinate only terminally to Zn(2) and Zn(4). The distances of 2.87(1) Å [Zn(1)−O(2C)] and 2.842(9) Å [Zn(3)−O(2A)] clearly rule out additional bonding interactions with Zn(1) and Zn(3). Owing to the different coordination modes of the carboxylate groups, distorted octahedral N$_2$O$_4$ coordination spheres are observed for Zn(2) and Zn(4), with the ligands being mer, while Zn(1) and Zn(3) are five-coordinate. As evident from the structural indices [τ = 0.142 for Zn(1) and 0.177 for Zn-(3)] the N$_2$O$_3$ coordination polyhedra of Zn(1) and Zn(3) are best described as distorted square pyramids with bridging carboxylate oxygens occupying the apical positions. The Zn ions and phenolate oxygens form an eight-membered ring in which the phenolate oxygens lie alternating below and above the plane defined by the four Zn ions (Figure 3). The angles between the aromatic rings and the Zn$_4$ plane range from 75.8 to 88.3°, and the opposite rings form angles of 12.7(7)° (ring A/C) and 20.9-(6)° (ring B/D) with each other. The mean distance of 3.6 Å between opposite rings suggests some π-interactions and it is

(28) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic: New York, 1983.

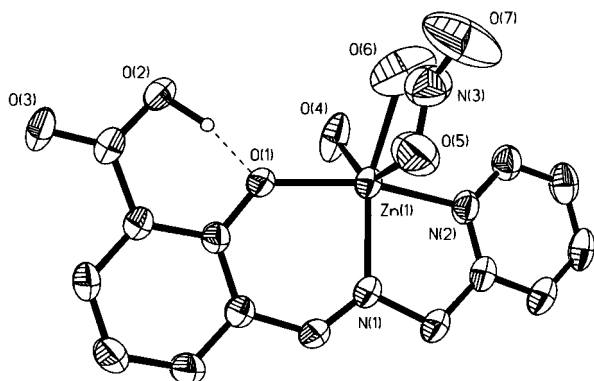(29) Bell, M.; Edwards, A. J.; Hoskin, B. F.; Kachab, E. H.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 3603.

Figure 4. Molecular structure of **3**. Hydrogen atoms were located in the Fourier-difference map, but for clarity only the hydrogen atom bound to the carboxyl oxygen is shown.

Table 4. Selected Bond Lengths (Å) for **3**

Zn(1)−N(1)	2.053(2)
Zn(1)−N(2)	2.109(2)
Zn(1)−O(1)	2.044(2)
Zn(1)−O(4)	2.062(2)
Zn(1)−O(5)	2.264(3)
Zn(1)−O(6)	2.218(3)

When a solution of **3** is brought to pH 9, deprotonation of the carboxyl group results in crystallization of the tetranuclear compound $[Zn_4(L2)_4]\cdot4.5H_2O$ (**4**) shown in Figure 5. Bond lengths relevant to the coordination environments of the metals are listed in Table 5. Four Zn(L2) entities with L2 coordinating via the phenolate oxygen and the chelating sidearm assemble to a tetramer containing a cubane-like $Zn_4O(phenolate)_4$ core situated around a crystallographic 2-fold axis of symmetry. The subunits are linked through the carboxylate oxygens that bind in a monodentate mode to the respective neighboring Zn ion and bridging phenolate oxygens that are attached to three Zn ions each resulting in octahedral N_2O_4 coordination polyhedra. Within the Zn_4O_4 cube the phenolate bridges are asymmetric: Each oxygen coordinates to one Zn at a "normal" distance (2.022−2.056 Å), while the distance to the second Zn is significantly longer (2.158−2.172 Å) and the interaction with the third Zn is even weaker (2.453−2.496 Å). The angles between the six planes of the Zn_4O_4 cube are close to the ideal 90° values. Zn−Zn separations are 3.202−3.594 Å.

The ^1H NMR spectrum of **3** in DMSO-d_6 (see Experimental Section) is fully consistent with the solid-state structure. Protonation of the carboxyl group is evident from the sharp singlet at 14.80 ppm. On deprotonation of the carboxyl group in **4** this signal disappears and the other resonances are shifted to higher field ($\Delta\delta$ 0.02−0.42 ppm).

Conclusions

The unsymmetric bridging ligand H_2L1 forms centrosymmetric dinuclear Zn complexes of type $[Zn_2(HL1)_2]^{2+}$ (**1**) in neutral or slightly acidic aqueous solution. Protonation of the amino group at neutral pH prevents chelating coordination by the ligand sidearm. The coordination mode of $HL1^-$ can be varied by use of aprotic solvents such as DMSO and DMF. A mononuclear complex **3** is isolated from acidic solution, when the amino nitrogen of the ligand sidearm is replaced by a pyridine nitrogen. In alkaline solution, Zn(L1) and Zn(L2) units assemble to tetranuclear species. While in $[Zn_4(L1)_4]\cdot6.5H_2O$ (**2**) the four Zn ions having dissimilar coordination environments form a rectangle, $[Zn_4(L2)_4]\cdot4.5H_2O$ (**4**) contains a cubane-like Zn_4O_4 cluster. Future work will focus on the unsymmetric nature
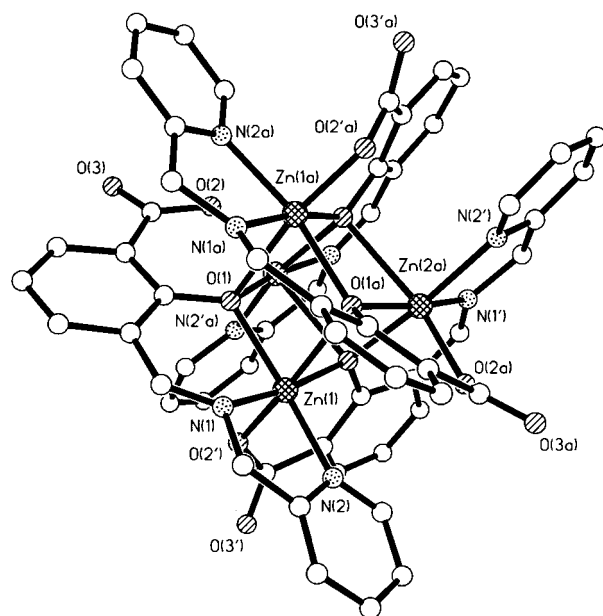

Figure 5. Molecular structure and tetranuclear core of **4**. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) for **4**

Zn(1)−N(1)	2.006(4)	Zn(2)−N(1′)	2.029(5)
Zn(1)−N(2)	2.138(4)	Zn(2)−N(2′)	2.112(5)
Zn(1)−O(1)	2.172(3)	Zn(2)−O(1)	2.056(3)
Zn(1)−O(1a)	2.453(3)	Zn(2)−O(1′a)	2.496(3)
Zn(1)−O(1′)	2.022(3)	Zn(2)−O(1′a)	2.158(3)
Zn(1)−O(2′)	1.978(4)	Zn(2)−O(2)	1.975(4)
Zn(1)···Zn(2)	3.273(1)	Zn(2)···Zn(1a)	3.594(1)
Zn(1)···Zn(2a)	3.2027(9)	Zn(2)···Zn(2a)	3.576(1)

of the ligands which are potentially suitable to prepare heteronuclear complexes.

Supporting Information Available: Packing diagrams of compounds **1a**−**4**; listings of hydrogen-bonding interactions; and ^1H−^{13}C 2D correlation spectrum of **1**. Five crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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