

Zinc Complexes of the Ligand Dipicolylglycine

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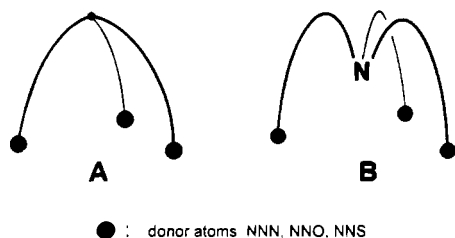
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N,N-bis(2-picolyl)glycine (**L-H**) which was not obtained in the free state was introduced into zinc complexes via its ethyl ester (**L-Et**) which yielded the intermediate complexes (**L-Et**)ZnBr₂ (**1**), (**L-Et**)Zn(NO₃)₂ (**2**), and (**L-Et**)₂Zn(ClO₄)₂·H₂O (**3**). Autocatalytic hydrolysis in the presence of water turned **2** into [L·Zn(H₂O)₂]NO₃·H₂O (**4**) with an octahedral and **3** into trimeric [L·Zn]ClO₄·H₂O (**5**) with a trigonal-bipyramidal coordination of zinc in the solid state. **5** was found to be a good starting material for the introduction of coligands forming complexes that mimic the coordination of zinc in enzymes with a N,N,O donor set: With imidazole the octahedral complex [L·Zn(Im)(H₂O)]ClO₄ (**6**) was obtained, with 2-methylimidazole the trigonal-bipyramidal complex [L·Zn(MeIm)]ClO₄ (**7**), and with diphenyl phosphate the trigonal-bipyramidal complex [L·Zn(Phos)]·2H₂O (**8**). The coordination in the solid state was confirmed for **1** and **4–8** by X-ray work. NMR studies (solid state and solution) and conductivity measurements have revealed various states of dissociation and solvation in solution, with the trigonal-bipyramidal cation [L·Zn(H₂O)]⁺ probably being a common and major constituent of all aqueous equilibria.

Introduction

As zinc complexes are generally labile and of low stability, controlling their structure and functionality requires the use of multiply chelating ligands.¹ In biological systems these are provided by the protein environment; synthetic studies have mostly used the tripod ligand types **A** and **B**.^{1–3} The classical

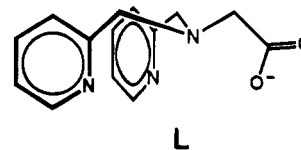


prototypes for **A** and **B** are tris(aminomethyl)methane and tris(aminoethyl)amine. Applications to the bioinorganic chemistry of zinc could be achieved with tris(pyrazolyl)borates (type **A**)⁴ and with type **B** ligands containing heterocyclic nitrogen donors.⁵

Both ligand types have been used almost exclusively with three identical (i.e. mostly nitrogen) donor atoms. Modeling the structure and function of zinc enzymes containing a protein N₂O, N₂O₂, or N₃O donor set by ligands of this type therefore remains a challenge. Such enzymes are for instance the well-known carboxypeptidase,⁶ superoxide dismutase,⁷ or alkaline

phosphatase,⁸ as well as L-fucose 1-phosphate aldolase⁹ or the peptidase astacin.¹⁰ The ligands of type **A** or **B** required to model them should contain two neutral nitrogen donors and one anionic oxygen donor (carboxylate or phenolate).

To our knowledge such a modification of type **A** has not been realized yet. A phenolate variant of **B** has been used to model structural features of alkaline phosphatase.¹¹ The only carboxylate derivative of **B** which has been described in full but not used for a zinc complex is *N,N*-bis(2-picolyl)-β-alanine.¹² The simplest carboxylate derivative of **A**, *N,N*-bis(2-aminoethyl)glycine, was first used by Collman et al.¹³ for a cobalt complex and recently by Mao et al.¹⁴ for zinc complexes in attempts to model superoxide dismutase. Both authors did not describe the isolation of the ligand. Similarly, Que et al.,¹⁵ who first described the ligand *N,N*-bis(2-picolyl)glycine (**L-H**) and used it for an iron complex, did not obtain the ligand in a pure form.



We have been interested in N,N,O ligands as part of our approach to localizing the functionality of zinc complexes on one ligand position by use of encapsulating ligands. In this context the title ligand **L-H** seemed favorable for (i) imposing

- [⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1995.
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a fixed geometry upon the zinc ion and (ii) possessing (as L) a negative charge which, like in the pyrazolyl borate complexes, should greatly enhance complex stability and inertness. Our access to the complexes described below became possible due to the observation that it is not necessary to try to isolate the ligand. Instead, zinc salts can be used to extract its ester L-Et from a crude reaction mixture and to saponify it autocatalytically, resulting in L-Zn complexes.

Experimental Section

General Methods. All experimental techniques and the standard IR and NMR equipment were described previously,¹⁶ starting materials were purchased from Aldrich. Whenever required, solvents were dried according to standard laboratory procedures, and 99.99% nitrogen was used as an inert atmosphere.

Solid state ¹³C-NMR measurements were performed on a Varian Unity 300 spectrometer (¹³C: 75 MHz) fitted with a solid state probe. Spectra were recorded at room temperature using the "magic angle" spinning technique (CP-MAS) and spinning rates between 3 and 5 KHz. Chemical shifts were referenced to hexamethylbenzene ($\delta(-\text{CH}_3) = 17.21$ ppm).¹⁷ Chemical shift anisotropies were not determined. Peaks appearing in the chemical shift region between 120 and 160 ppm could not be assigned reliably because of (i) the large number of heteroaromatic carbon atoms in the compounds described here, (ii) typical line widths of 1–2 Hz, and (iii) the appearance of spinning side bands. It was possible, however, to unambiguously assign peaks within the shift range of 60–70 ppm to methylene groups as well as signals located beyond 170 ppm to carboxylate groups.

Conductivity Measurements. Electric conductivities were determined using a L 201 conductometer (manufactured by Ludwig Pusch, München, Germany) fitted with a platinum electrode. Complex samples were dissolved in doubly distilled water at 21 °C at an initial concentration between 2×10^{-3} and 3×10^{-3} mol·L⁻¹. Accurate concentration and conductivity data are available as supplementary material. After every series of measurements, each solution was diluted with doubly distilled water to 60% of the initial concentration. This procedure was repeated until each compound had been measured at four different concentrations. Molar conductivities (λ_c) were plotted versus the square root of the concentration ($c^{0.5}$) displaying a linear dependence for the compounds **1**, **5**, **6**, and **7** and significant deviations from such a behavior for compounds **4** and **8**. A standard least-square-fit routine was used to perform a linear extrapolation to $c^{0.5} = 0$. Three causes of inaccuracy were taken into account to evaluate the error range: (i) The pure solvent's conductivity was deemed to be the only significant source of amperometric error. (ii) An error range of 1.5% was allowed for volumetric and weighing errors. (iii) The temperature was assumed to vary from 19 to 23 °C. Temperature dependent deviations of conductivity were evaluated using known temperature dependences of the conductivities of Zn²⁺, Br⁻, NO₃⁻, and ClO₄⁻.¹⁸ The relative temperature dependence of the conductivity of LZn⁺_{aq} was approximated by that of aquated Zn²⁺ in the absence of chelating ligands. The obtained error ranges represent only rough estimations for compound **4** and compound **8** since both did not behave as strong electrolytes in terms of Kohlrausch's law. The resulting molar conductivities at infinite dilution in cm² mol⁻¹ Ω⁻¹ [error range] were as follows: **1**, 250 [230–270]; **4**, 74 [66–81/poor linear fit]; **5**, 106 [98–114]; **6**, 98 [91–105]; **7**, 110 [102–118]; **8**, 47 [40–45/poor linear fit].

Preparations. N,N-Dipicolylglycine Ethyl Ester (L-Et). The reaction was carried out under a nitrogen atmosphere. A suspension of 2-(chloromethyl)pyridine hydrochloride (12.25 g, 74.7 mmol) and glycine ethyl ester hydrochloride (5.21 g, 37.5 mmol) in 1,4-dioxane/triethyl amine (85 mL, 10:7 v/v) was refluxed for 20 min. The initially colorless liquid phase turned deeply red. A white bulky precipitate of triethylamine hydrochloride formed. The solution was allowed to cool to 30 °C. The solid bulk was crushed with a spatula. After being

refluxed for 5 d, the suspension was again allowed to cool down to 30 °C. All volatile components were removed *in vacuo* before the remaining brown solid was again coarsely ground. The solids were refluxed in absolute diethyl ether (100 mL) for 40 min. The following workup was carried out under an ambient atmosphere. The brown ether phase was filtered off the white insolubles. Removal of the filtrate's solvent by rotary evaporation and drying *in vacuo* for 2 h yielded 8.58 g of a light brown oil containing L-Et (69 mol %, 76 wt %) and the byproduct N-picolylglycine ethyl ester (31 mol %, 24 wt %), amounting to a yield of 6.52 g (61%) of L-Et. The percentages of L-Et and of the byproduct were calculated for each run from the intensity ratio of the ¹H-NMR signals of the pyridine H_a-protons at 8.54 ppm and of the ester group's methyl protons at 1.27 ppm. The content of L-Et varied between 30 and 80% upon repetition of the above described reaction. ¹H-NMR (CDCl₃): 1.27 ppm, t, 7.1 Hz, (–CH₃); 2.45 ppm, s (NH byproduct); 3.47 ppm, s (NCH₂COO both species); 3.95, s (NHCH₂ pyridine byproduct); 4.01, s (NCH₂ pyridine L-Et); 4.18, m (two overlapping quartets of both species OCH₂⁻); 7.14–7.65, m (pyridine H_β, H_γ, H_δ of both species); 8.54, m (pyridine H_a of both species).

(Dipicolylglycine ethyl ester)zinc Dibromide (1). L-Et as a 39 wt % mixture (2.00 g, 2.7 mmol) was dissolved in ethanol (10 mL). To this solution was added diethyl ether (22 mL). Zinc bromide (0.66 g, 2.9 mmol) was dissolved in ethanol (10 mL). Diethyl ether (25 mL) was added to the zinc salt solution. The zinc salt solution was added dropwise to the vigorously stirred solution of L-Et until an initially formed light yellow precipitate did not dissolve any more upon stirring. Stirring was discontinued, and the rest of the zinc bromide solution was added very slowly within 2 h. The suspension was stored overnight at 4 °C. The crystalline precipitate was filtered off, washed with ethanol (20 mL) and diethyl ether (10 mL), respectively, and dried *in vacuo* to yield **1** (1.28 g, 92%) as a bright white crystal powder melting at 212 °C. Single crystals suitable for X-ray structure determination were obtained by recrystallization from ethanol. ¹H-NMR (D₂O): 1.10 ppm, t, 7.1 Hz (3H, CH₃); 3.51 ppm, s (2H, NCH₂COO); 3.86 ppm, q, 7.1 Hz (2H ethyl CH₂); 4.19 ppm, d, ²J = 16.3 Hz (2H, CH₂ pyridine axial); 4.37 ppm, d, ²J = 16.3 Hz (2H, CH₂ pyridine equatorial); 7.37 ppm, m (4H, pyridine H_β, H_δ); 7.85 ppm, twinned triplet, ³J = 7.8 Hz, ⁴J = 1.6 Hz (1H, pyridine H_γ); 8.46 ppm, d, ³J = 5.1 Hz (2H, pyridine H_a). ¹³C-NMR (D₂O): 12.94, methyl; 56.10, NCH₂COO; 59.88, OCH₂; 63.53, CH₂ pyridine; 124.80, pyridine NCHC_β; 125.09, pyridine NC(CH₂)C_δ; 141.08, pyridine NCCC_γ; 147.35, pyridine NC_αH; 153.46, pyridine NC_{quat} (–CH₂); 174.09, –COO– ester. ¹³C-NMR (solid): 12.4, 56.9, 122.1, 124.8, 138.9, 142.5, 151.5, 171.5, 169.4 ppm. Anal. Calc for C₁₆H₁₉Br₂N₃O₂Zn: C, 37.64; H, 3.72; N, 8.22. Found: C, 37.94; H, 3.67; N, 8.14.

(Dipicolylglycine ethyl ester)zinc Dinitrate (2). L-Et as a 39 wt % mixture (4.32 g, 5.92 mmol) was dissolved in ethanol/diethyl ether (60 mL, 2:1 v/v). Zinc nitrate hexahydrate (1.54 g, 5.92 mmol) was dissolved in the same solvent mixture (50 mL). The zinc nitrate solution was added dropwise within 45 min to the stirred precursor ligand solution. A yellowish-white precipitate formed immediately. The solution was stored at 4 °C for 2 h before the amorphous precipitate was filtered off. Washing with diethyl ether (10 mL) and drying *in vacuo* afforded **2** (2.60 g, 93%) as a yellowish-white amorphous powder melting at 182 °C. ¹H-NMR (D₂O): 1.10 ppm, t, 7.1 Hz (3H, CH₃); 3.51 ppm, s (2H, NCH₂COO); 3.86 ppm, q, 7.1 Hz (2H ethyl CH₂); 4.19 ppm, d, ²J = 16.3 Hz (2H, CH₂ pyridine axial); 4.37 ppm, d, ²J = 16.3 Hz (2H, CH₂ pyridine equatorial); 7.37 ppm, m (4H, pyridine H_β, H_δ); 7.85 ppm, twinned triplet, ³J = 7.8 Hz, ⁴J = 1.6 Hz (1H, pyridine H_γ); 8.46, d, ³J = 5.1 Hz (2H, pyridine H_a). Anal. Calc for C₁₆H₁₉N₃O₈Zn: C, 40.48; H, 4.03; N, 14.75. Found: C, 40.49; H, 3.95; N, 14.53.

Bis(dipicolylglycine ethyl ester)zinc Diperchlorate Monohydrate (3). **Warning:** Perchlorate salts of metal complexes are potentially explosive!¹⁹ They must be handled with great caution and in small quantities. Laboratories not equipped with appropriate safety gear are advised to perform the preparations of **3** and **5** with quantities of 1 g or less of zinc perchlorate.

L-Et as a 39 wt % mixture (7.00 g, 9.58 mmol) was dissolved in ethanol (80 mL). To this solution was added diethyl ether (100 mL).

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Zinc perchlorate hexahydrate (3.57 g, 9.57 mmol) was dissolved in ethanol (30 mL). Diethyl ether (30 mL) was added to the zinc salt solution, which was then added dropwise without stirring within 4 h to the solution of **L-Et**. A yellow precipitate formed immediately, which turned into a brown oily layer on the flask's wall after being stored at 4 °C for 16 h. The supernatant liquid was decanted. The oily residue was washed with ethanol/diethyl ether (40 mL, 1:1 v/v) and dried *in vacuo* for 4 h to yield 6.82 g (83%) of yellow amorphous **3** melting at 98 °C. ¹H-NMR (D₂O): 1.18 ppm, t, ³J = 7.1 Hz (3H, ethyl CH₃); 1.25 ppm, m, (3H, ethyl CH₃); 3.51 ppm, s, (NCH₂); 3.65 ppm, q, ³J = 7.1 Hz, (ethyl CH₂); 3.75, 3.75, 4.14, 4.18, 4.21, 4.39, 4.47 ppm (various NCH₂); 7.64, m, (8H pyridine H_β, H_δ); 8.08, m (4H pyridine H_γ); 8.50, d, ³J = 4.8 Hz (1H, pyridine H_γ, uncoordinated); 8.65, d, ³J = 4.8 Hz (1H, pyridine H_γ, coordinated). Anal. Calc for C₃₂H₄₀Cl₂N₆O₁₃Zn: C, 45.06; H, 4.73; N, 9.85. Found: C, 45.27; H, 4.48; N, 9.83.

Diaqua(bis(2-picolyl)glycinato)zinc Nitrate Monohydrate (4). The precursor complex **2** (2.60 g; 5.48 mmol) was refluxed in water (20 mL) for 24 h. The resulting clear solution was filtered hot and cooled to 0 °C. After 2 h, the mother liquor was filtered off a first fraction of white crystals (0.4 g). The filtrate's volume was reduced *in vacuo* to 10 mL. Cooling to 0 °C for 24 h and subsequent filtration yielded 0.74 g of a second crystal fraction. Washing the combined crystal fractions with a small amount of chilled water and careful drying on a paper filter and in a stream of dry nitrogen for not longer than 2 min gave **4** (1.14 g, 44%) as colorless shiny cuboids melting at 168 °C. ¹H-NMR (D₂O): 3.41 ppm, s (2H, NCH₂COO); 4.29 ppm, s (4H, CH₂ pyridine); 7.50, m, (4H pyridine H_β, H_δ); 7.98 ppm, twinned triplet, ³J = 7.8 Hz, ⁴J = 1.6 Hz (1H, pyridine H_γ); 8.55, d, ³J = 5.1 Hz (2H, pyridine H_α). ¹³C-NMR (D₂O): 59.46, NCH₂COO; 60.09, CH₂ pyridine; 124.45, pyridine NCHC_β; 124.87, pyridine NC(CH₂)C_δ; 140.90, pyridine NCCC_γ; 147.38, pyridine NC_αH; 154.08, pyridine NC_{quat} (-CH₂); 177.56 ppm, -COO⁻. ¹³C-NMR (solid): 66.4, 68.3, 130.6, 132.4, 142.5, 143.3, 151.8, 153.14, 157.5, 182.3 ppm. Anal. Calc for C₁₄H₂₀N₄O₈Zn: C, 38.41; H, 4.61; N, 12.80. Found: C, 38.33; H, 4.53; N, 12.64.

Tris(μ₂-bis(2-picolyl)glycinato)trizinc Triperchlorate Trihydrate (5). The precursor ligand perchlorate complex **3** (6.82 g, 8.00 mmol) was dissolved in water (75 mL). Zinc perchlorate hexahydrate (2.99 g, 8.00 mmol) and 70% perchloric acid (0.5 mL) were added. The resulting yellow solution was refluxed under a nitrogen atmosphere for 24 h and then filtered hot. Cooling the filtrate slowly to room temperature within 8 h led to the deposition of **5** as yellowish-brown square-shaped crystals suitable for X-ray structure determination. Decanting the mother liquor, washing the solids with chilled water, ethanol, and diethyl ether, respectively, and drying *in vacuo* for 10 min afforded crystalline **5** (3.12 g, 40% of Zn²⁺) melting at 290 °C (dec). ¹H-NMR (D₂O): 3.51 ppm, s, (2H, NCH₂); 4.38 ppm, s, (4H, CH₂ pyridine); 7.60, m, (4H pyridine H_β, H_δ); 8.07, td, ³J = 7.8 Hz, ⁴J = 1.6 Hz, (2H, pyridine H_γ); 8.64, d, ³J = 5.1 Hz (2H, pyridine H_α). ¹³C-NMR (D₂O): 59.54, CH₂COO; 60.18, CH₂ pyridine; 124.48, pyridine NCHC_β; 124.89, pyridine NCCH₂C_δ; 140.92, pyridine NCCC_γ; 147.41, pyridine NC_αH; 154.10, pyridine NC_{quat}C; 177.65 ppm, COO⁻. ¹³C-NMR (solid): 63.3, 67.5, 67.6, -CH₂; 130.0, 132.8, 148.5, 149.8, 153.2, 154.5, 163.7 pyridine; 186.7, 187.7, 188.2 ppm, COO⁻. Anal. Calc for C₄₂H₄₈Cl₃N₉O₂₁Zn₃: C, 38.29; H, 3.67; N, 9.57; Zn, 14.89. Found: C, 37.97; H, 3.35; N, 9.43; Zn, 15.60.

Aqua(imidazole)(bis(2-picolyl)glycinato)zinc Perchlorate (6). **5** (0.153 g, 0.348 mmol) and imidazole (0.028 g, 0.34 mmol) were dissolved in water (5.7 mL) at 60 °C. The resulting yellow solution was filtered hot and placed in a flask inside a Dewar vessel filled with hot water. After 28 h, the solution had cooled down to room temperature and a first fraction of yellowish-brown crystalline **6** had been formed. The solution was removed and concentrated *in vacuo* until about 40% of the initial solvent volume had been removed. A second crystal fraction precipitated and was filtered off. The combined crystal fractions were washed with ethanol and diethyl ether and dried in a stream of dry nitrogen for 2 min to give **6** (0.138 g, 76%) as yellowish-brown crystal clusters suitable for X-ray structure determination and melting at 166 °C. ¹H-NMR (D₂O): 3.49 ppm, s, (2H, NCH₂); 4.41 ppm, s, (4H, CH₂ pyridine); 7.38 ppm, s, broad, 2H, imidazole H₄, H₅; 7.50–7.61, m (4H, pyridine H_β, H_δ); 8.07, twinned doublet, ³J = 7.8 Hz; ⁴J = 1.7 Hz (2H, pyridine H_γ); 8.14, s, br, (1H,

imidazole H₂); 8.29, d, 4.8 Hz (2H, pyridine H_α). ¹³C-NMR (D₂O): 59.33, CH₂COO; 60.04, CH₂ pyridine; 122.10, imidazole C₄C₅; 124.47, pyridine NCHC_β; 124.76, pyridine NCCH₂C_δ; 137.07, imidazole C₂; 140.83, pyridine NCCC_γ; 147.38, pyridine NC_αH; 154.15, pyridine NC_{quat}C; 177.83 ppm, COO⁻. ¹³C-NMR (solid): 65.9, 68.5, CH₂; 123.7, 128.1, 129.2, 132.6, 142.3, 144.1, 150.6, 153.0, 157.3, 156.0; 180.8 ppm, COO⁻. Anal. Calc for C₁₇H₂₀ClN₅O₇Zn: C, 40.25; H, 3.97; N, 13.81. Found: C, 40.08; H, 4.04; N, 13.52.

(2-Methylimidazole)(bis(2-picolyl)glycinato)zinc Perchlorate (7). **5** (0.833 g, 1.90 mmol) and 2-methylimidazole (0.157 g, 1.91 mmol) were dissolved in boiling water (15 mL). After 4 h of refluxing, the resulting yellow solution was filtered hot and allowed to cool down slowly to room temperature. After standing for 16 h, the solution was cooled to 0 °C and decanted from the crystalline precipitate. Repeated washing with ethanol and diethyl ether followed by drying *in vacuo* afforded **7** (0.745 g, 78%) as light brown crystal blades melting at 253 °C. Single crystals suitable for X-ray structure determination were obtained by recrystallization from water. ¹H-NMR (D₂O): 2.49 ppm, s (3H, methyl); 3.49 ppm, s, (2H, NCH₂); 4.35 ppm, s, (4H, CH₂ pyridine); 7.19 ppm, s, broad, 2H, imidazole H₄, H₅; 7.53–7.61, m (4H, pyridine H_β, H_δ); 8.08, twinned doublet, ³J = 7.8 Hz; ⁴J = 1.5 Hz (2H, pyridine H_γ); 8.29, d, 4.8 Hz (2H, pyridine H_α). ¹³C-NMR (D₂O): 12.33, CH₃; 58.75, CH₂COO; 59.24, CH₂ pyridine; 121.15, imidazole C₄C₅; 124.54, pyridine NCHC_β; 124.88, pyridine NCCH₂C_δ; 141.03, pyridine NCCC_γ; 146.26, imidazole C₂; 147.76, pyridine NC_αH; 154.44, pyridine NC_{quat}C; 177.88 ppm, COO⁻. ¹³C-NMR (solid): 14.8, methyl; 60.3, CH₂; 124.1, 125.9, 130.7, 139.1, 144.1, 146.3, 157.4, 155.6; 176.7 ppm, COO⁻. Anal. Calc for C₁₈H₂₀N₅O₇Zn: C, 42.86; H, 4.01; N, 13.92. Found: C, 42.85; H, 3.93; N, 13.91.

(Bis(2-picolyl)glycinato)(diphenyl phosphato)zinc (8). **5** (0.445 g, 1.06 mmol) was dissolved in water (14.9 mL) at 40 °C. Ethanol (16.7 mL) was added. Phosphoric acid diphenyl ester (0.264 g, 1.06 mmol) was dissolved in ethanol/water (14 mL, 5:2 v/v). The solutions were combined. A solution of KOH (0.059 g, 1.04 mmol) in water (0.5 mL) was added dropwise. An initially formed precipitate redissolved upon completion of the addition of KOH. The solution was slowly cooled to -30 °C and stored at this temperature overnight. Then all volatile components were removed *in vacuo* and the brownish solid remainder was treated with boiling ethanol (10 mL). The resulting suspension was filtered hot and allowed to cool slowly to room temperature. After 24 h, unreacted **5** (0.082 g, 18%) had deposited as a fine crystalline layer on the flask's walls. The yellow mother liquor was decanted, and its volume was reduced *in vacuo* to 2 mL. The solution was carefully layered with diethyl ether (2 mL). After 10 d, a yellowish-white crystal layer had formed on the flask's walls. The mother liquor was poured off, and the solid was washed with ethanol/diethyl ether (1:4 v/v) and dried *in vacuo* to give **8** (0.233 g, 37%) as yellowish-white crystals suitable for X-ray crystallography and melting at 141 °C. ¹H-NMR (D₂O): 3.50 ppm, s, (2H, NCH₂); 4.37 ppm, s, (4H, CH₂ pyridine); 7.18–7.29 ppm, m (6H, phenyl H_β, H_γ); 7.39–7.47 ppm, m (4H, phenyl H_α), 7.57–7.67, m (4H, pyridine H_β, H_δ); 8.07, twinned doublet, ³J = 7.8 Hz; ⁴J = 1.6 Hz, (2H, pyridine H_γ); 8.65, d, 4.8 Hz, (2H, pyridine H_α). ³¹P-NMR (D₂O): -8.97, phosphate [vs H₃PO₄ external]. ¹³C-NMR (D₂O): 59.44, CH₂COO; 60.04, CH₂ pyridine; 120.14, d, ³J_{CP} = 4.7 Hz, phenyl C_{ortho}; 124.41, phenyl C_{para}; 124.46, pyridine NCHC_β; 124.89, pyridine NCCH₂C_δ; 129.73, phenyl C_{meta}; 140.92, pyridine NCCC_γ; 147.44, pyridine NC_αH; 151.63, phenyl CO; 154.11, pyridine NC_{quat}C; 177.64 ppm, COO⁻. ¹³C-NMR (solid): 60.1, -CH₂; 119.6, phenyl C_{ortho}; 123.9, 126.6, 130.1, 131.8, 139.8, 145.1, 147.1, 152.3, 155.6, 157.6; 175.6, COO⁻. Anal. Calc for C₂₆H₂₆N₃O₇PZn: C, 51.46; H, 4.65; N, 6.93. Found: C, 52.04; H, 4.58; N, 6.99.

X-ray Crystallography. The crystals of **1** and **4–8** were obtained as described above. Diffraction data were recorded with the ω/2θ scan mode in the 2θ range 2–48° on a Nonius CAD4-diffractometer fitted with a molybdenum tube (λ_{Kα} = 0.710 73 Å) and a graphite monochromator at 294 K. Data were corrected for Lorentz and polarization effects.²⁰ Absorption corrections based on ψ scans were applied.²¹ Scattering factors were obtained from common sources.²² The structures were solved employing standard Patterson and difference-

Table 1. Crystallographic Details

	1	4	5	6	7	8
color	yellow	colorless	yellow-brown	pale yellow	colorless	colorless
formula	C ₁₆ H ₁₉ Br ₂ N ₃ O ₂ Zn	C ₁₄ H ₂₀ N ₄ O ₈ Zn	C ₄₂ H ₄₈ Cl ₃ N ₉ O ₂₁ Zn ₃	C ₁₇ H ₂₀ ClN ₅ O ₇ Zn	C ₁₈ H ₂₀ N ₅ O ₆ Zn	C ₂₆ H ₂₅ N ₃ O ₇ PZn
fw	510.5	437.7	1317.4	507.2	503.2	588.8
cryst size, mm	0.6 × 0.3 × 0.4	0.5 × 0.4 × 0.3	0.6 × 0.3 × 0.3	0.6 × 0.5 × 0.2	0.4 × 0.4 × 0.4	0.6 × 0.15 × 0.1
space group	Cc	P2 ₁ 2 ₁ 2 ₁	P1	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	P1
a, Å	9.682(2)	8.938(2)	13.026(3)	7.443(1)	10.139(2)	9.778(2)
b, Å	13.616(3)	12.024(2)	15.240(3)	13.159(3)	13.510(3)	10.081(2)
c, Å	14.821(3)	16.516(3)	16.228(3)	21.606(4)	15.031(3)	13.715(3)
α, deg	90	90	65.06(3)	90	90	85.16(3)
β, deg	99.02(3)	90	75.00(3)	93.26(3)	90	85.33(3)
γ, deg	90	90	66.18(3)	90	90	88.02(3)
V, Å ³	1929.7(7)	1774.9(6)	2657.0(9)	2112.7(7)	2058.9(7)	1342.1(5)
Z	4	4	2	4	4	2
ρ _{calc} , g/cm ³	1.765	1.638	1.639	1.595	1.623	1.474
μ, mm ⁻¹	5.419	1.465	1.611	1.339	1.369	1.044
F(000)	1004	904	1332	1040	1032	614
hkl range	+h,+k,±l	-h,+k,-l	-h,±k,±l	-h,±k,±l	±h,±k,±l	±h,-k,±l
data/param	2228/221	1942/244	8556/628	3779/303	2733/260	2681/347
refinement	F	F	F	F ²	F	F
goodness-of-fit	2.24	2.18	3.23	1.287	2.75	2.29
R(unweighted)	0.037	0.027	0.064	0.037	0.065	0.063
R(weighted)	0.040	0.041	0.104	0.137	0.073	0.063

Table 2. Fractional Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for Compound 1

	x	y	z	U(eq) ^a
Zn(1)	-889(1)	121(1)	-120(1)	35(1)
Br(11)	-387(1)	1168(1)	1199(1)	54(1)
Br(12)	-2198(1)	-1340(1)	153(1)	65(1)
N(11)	7(1)	729(1)	-1362(1)	39(1)
N(12)	1089(1)	-552(1)	-44(1)	43(1)
N(13)	-2526(1)	941(1)	-868(1)	45(1)
C(11)	1075(1)	2291(1)	-1829(1)	57(1)
C(12)	612(1)	1716(1)	-1061(1)	43(1)
C(121)	1662(1)	-1008(1)	715(1)	54(1)
C(122)	2985(1)	-1390(1)	845(1)	63(1)
C(123)	3777(1)	-1256(1)	150(1)	62(1)
C(124)	3214(1)	-777(1)	-631(1)	55(1)
C(125)	1812(1)	-422(1)	-719(1)	41(1)
C(126)	1103(1)	34(1)	-1554(1)	55(1)
C(131)	-3631(1)	1245(1)	-491(1)	60(1)
C(132)	-4649(1)	1838(1)	-958(1)	62(1)
C(133)	-4566(1)	2136(1)	-1822(1)	60(1)
C(134)	-3412(1)	1823(1)	-2218(1)	54(1)
C(135)	-2442(1)	1224(1)	-1717(1)	42(1)
C(136)	-1191(1)	825(1)	-2095(1)	46(1)
O(11)	223(1)	3046(1)	-2063(1)	85(1)
C(116)	645(1)	3911(1)	-2603(1)	60(1)
C(117)	-801(1)	3888(1)	-3408(1)	109(1)
C(118)	602(1)	3537(1)	-2931(1)	170(1)
C(119)	-178(1)	4410(1)	-3010(1)	165(1)
O(12)	2019(1)	2077(1)	-2217(1)	92(1)

^a Equivalent isotropic *U* values are defined as one-third of the trace of the orthogonal *U*_{ij} tensors.

Fourier techniques implemented in the programs SHELX86 and SHELX93,²³ which were run on a PC. The following molecule parts could not be located precisely due to crystallographic disorder: the ethyl group in **1**, the oxygen atoms belonging to the perchlorate counterions and crystal water molecules in **5**, the oxygen atoms of the perchlorate counterion in **6** and in **7**, and two sites of crystal water molecules in **8**. Elemental analysis of **8** indicates the presence of one molecule of crystal water whereas structure refinement gave the best agreement with crystallographic data when an occupancy of 2/3 for two sites of disordered crystal water was assumed, thus amounting to 1.5 molecules of crystal water. Crystallographic data did allow, however, one to ascertain that in none of the structures described here disordered

Table 3. Fractional Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for Compound 4

	x	y	z	U(eq) ^a
Zn(1)	6148(1)	3487(1)	7335(1)	29(1)
O(1)	6217(3)	5258(2)	7410(2)	34(1)
O(2)	7785(3)	6684(2)	7497(2)	46(1)
O(3)	3911(3)	3433(2)	7217(2)	51(1)
O(4)	6225(3)	1622(2)	7323(2)	40(1)
O(5)	8022(5)	152(4)	6391(2)	93(2)
O(6)	8192(5)	-642(3)	5239(3)	77(1)
O(7)	7360(6)	991(4)	5331(4)	123(3)
O(8)	12403(4)	5143(3)	6449(2)	60(1)
N(1)	6853(3)	3502(3)	6112(2)	32(1)
N(2)	6411(3)	3396(2)	8612(2)	35(1)
N(3)	8578(3)	3714(2)	7458(2)	30(1)
N(4)	7859(4)	164(3)	5665(2)	46(1)
C(1)	7504(4)	5676(3)	7459(2)	29(1)
C(2)	8873(3)	4922(3)	7461(2)	32(1)
C(3)	9252(4)	3171(3)	6743(2)	35(1)
C(4)	9010(4)	3172(3)	8221(2)	37(1)
C(11)	5984(5)	3650(3)	5459(2)	42(1)
C(12)	6535(6)	3708(3)	4682(3)	50(1)
C(13)	8059(6)	3640(4)	4572(3)	51(1)
C(14)	8970(5)	3516(3)	5241(2)	41(1)
C(15)	8342(4)	3431(3)	6001(2)	31(1)
C(21)	5315(4)	3523(3)	9154(2)	45(1)
C(22)	5589(6)	3623(4)	9969(3)	52(1)
C(23)	7059(6)	3588(4)	10238(3)	55(1)
C(24)	8189(5)	3470(3)	9678(2)	44(1)
C(25)	7844(4)	3364(3)	8863(2)	34(1)

^a Equivalent isotropic *U* values are defined as one-third of the trace of the orthogonal *U*_{ij} tensors.

components are involved in metal binding. Table 1 gives a summary of crystallographic data of **1** and **4–8**. The *R* values are defined as follows: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The atomic parameters for the six structures are presented in Tables 2–7.

Results

L-Et and Its Zinc Complexes. Que et al. had reported the synthesis of **L-H** from bromoacetic acid and dipicolylamine.¹⁵ We found a different approach more efficient although it looks more cumbersome on paper. We started with the alkylation of glycine ethyl ester with 2-(chloromethyl)pyridine in ether solvents. This produced a mixture of the *N*-mono- and *N,N*-dipicolyl derivatives of glycine ethyl ester. NMR was used to determine the amount of **L-Et** in this mixture which varied irregularly between 30 and 80%, with a total yield of **L-Et**

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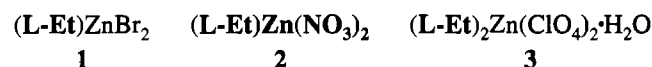
(23) Sheldrick, G. M. SHELX-86 and SHELXL93, Programs for Crystal Structure Determination, Göttingen, 1986 and 1993.

Table 4. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Compound 5

	x	y	z	U(eq) ^a		x	y	z	U(eq) ^a
Zn(1)	2392(1)	4114(1)	1288(1)	39(1)	C(225)	1346(5)	8420(4)	2144(4)	50(3)
Zn(2)	1757(1)	6267(1)	3283(1)	38(1)	C(226)	167(5)	8353(4)	2309(4)	53(3)
Zn(3)	4977(1)	2651(1)	3892(1)	37(1)	C(231)	640(5)	5934(4)	5234(4)	51(3)
O(12)	1377(3)	5519(3)	1291(3)	53(2)	C(232)	-268(7)	6017(5)	5916(4)	70(4)
O(13)	3241(3)	3395(3)	2379(2)	44(2)	C(233)	-1354(6)	6435(5)	5672(5)	68(4)
O(21)	1915(3)	5480(3)	2504(3)	49(2)	C(234)	-1518(5)	6792(5)	4757(5)	61(3)
O(23)	3032(3)	5434(3)	4087(3)	47(2)	C(235)	-577(5)	6704(4)	4115(4)	46(3)
O(31)	4801(3)	2156(3)	2979(3)	45(2)	C(236)	-724(5)	7020(5)	3090(4)	55(3)
O(32)	3928(3)	4124(3)	3595(2)	42(2)	C(311)	4283(5)	3971(4)	5043(4)	52(3)
N(11)	3441(4)	2610(3)	1074(3)	41(2)	C(321)	3835(5)	1094(5)	5118(5)	59(3)
N(12)	1135(4)	3654(4)	1215(3)	47(2)	C(322)	3415(7)	501(5)	5918(6)	79(4)
N(13)	3400(4)	4622(3)	89(3)	43(2)	C(323)	3621(7)	460(6)	6709(6)	87(4)
N(21)	239(4)	7288(3)	2496(3)	43(2)	C(324)	4266(7)	1010(5)	6713(4)	76(4)
N(22)	2169(4)	7581(3)	2556(3)	46(2)	C(325)	4709(5)	1594(4)	5867(4)	53(3)
N(23)	467(4)	6278(3)	4342(3)	44(2)	C(326)	5446(5)	2164(4)	5791(4)	55(3)
N(31)	5293(4)	3081(3)	4961(3)	47(2)	C(331)	7335(5)	1884(5)	3048(4)	55(3)
N(32)	4469(4)	1636(3)	5085(3)	46(2)	C(332)	8501(6)	1648(6)	2915(5)	78(4)
N(33)	6676(4)	2417(3)	3580(3)	45(2)	C(333)	8945(6)	1977(8)	3354(7)	100(6)
C(13)	4074(4)	2588(4)	2415(3)	37(2)	C(334)	8275(6)	2533(6)	3903(5)	73(4)
C(21)	1308(4)	5921(4)	1854(3)	39(2)	C(335)	7135(5)	2729(5)	4006(4)	55(3)
C(32)	3714(4)	4561(4)	4165(3)	38(2)	C(336)	6332(5)	3386(5)	4559(5)	62(4)
C(111)	4290(5)	2085(5)	1721(4)	53(3)	Cl(1)	7097(2)	6125(2)	2470(1)	72(1)
C(121)	48(5)	4276(5)	1196(4)	57(3)	O(111)	7604(10)	6190(10)	1644(8)	204(5)
C(122)	-786(6)	3992(6)	1031(5)	69(4)	O(112)	7782(7)	5525(7)	3185(6)	141(3)
C(123)	-403(7)	3081(6)	860(5)	79(5)	O(113)	6740(11)	7135(11)	2426(9)	222(5)
C(124)	714(6)	2489(5)	874(5)	62(4)	O(114)	6048(10)	5889(9)	2726(7)	183(4)
C(125)	1461(5)	2774(5)	1085(4)	50(3)	Cl(2)	2076(2)	511(2)	3905(2)	80(1)
C(126)	2652(5)	2039(5)	1275(5)	60(3)	O(221)	1537(8)	1553(8)	3793(6)	157(3)
C(131)	3444(5)	5582(5)	-300(4)	54(3)	O(222)	1717(8)	291(8)	3333(7)	163(3)
C(132)	4196(6)	5853(6)	-1075(4)	66(4)	O(223)	3238(9)	386(8)	3539(7)	165(3)
C(133)	4918(7)	5129(7)	-1417(4)	72(4)	O(224)	2102(10)	-137(10)	4718(9)	209(5)
C(134)	4909(6)	4150(6)	-1030(4)	64(4)	Cl(3)	7798(2)	1213(2)	623(1)	72(1)
C(135)	4102(5)	3892(5)	-272(4)	49(3)	O(332)	7317(8)	2014(7)	-163(6)	151(3)
C(136)	3902(6)	2896(5)	107(4)	58(3)	O(333)	7295(10)	1460(9)	1381(8)	202(5)
C(211)	505(5)	7012(4)	1688(4)	52(3)	O(334)	7841(11)	265(11)	738(9)	229(5)
C(221)	3210(6)	7617(5)	2434(4)	58(3)	O(331)	8931(12)	1105(11)	352(9)	224(5)
C(222)	3468(7)	8497(6)	1888(5)	74(5)	O(1)	242(7)	8788(7)	4128(5)	140(3)
C(223)	2590(8)	9380(6)	1473(5)	83(5)	O(2)	5006(15)	137(14)	654(12)	296(8)
C(224)	1530(7)	9355(5)	1579(4)	65(4)	O(3)	7170(12)	8756(11)	703(10)	248(6)

^a Equivalent isotropic U values are defined as one-third of the trace of the orthogonal U_{ij} tensors.

between 30 and 65%. This mixture was treated without further purification in nonaqueous solvents with zinc salts in the amount according to the content of L-Et. This led to the exclusive precipitation of 1–3 as analytically pure compounds in high yields.



Solution NMR data of 1–3 could only be obtained in water where anion dissociation and ester saponification set in which reduced their information to the fact that (L-Et)Zn and LZn units are present. The IR data of 1–3 in KBr show the ester band at ca. 1730 cm^{-1} and the anion bands for NO_3^- (1384 cm^{-1}) and ClO_4^- (1088 cm^{-1}). A strong indication for the dissociation of these complexes in aqueous solution into [(L-Et)Zn]²⁺ or even simple hydrated Zn^{2+} cations and the corresponding anions comes from conductivity measurements. They show 1 to be a strong electrolyte with a conductivity ($250\text{ cm}^2/\Omega\text{mol}$ at infinite dilution) corresponding to that of zinc bromide.¹⁸

Proof for the molecular nature of 1 in the solid state was obtained through its crystal structure determination; see Figure 1. The structure consists of neutral molecules of complex 1. The central atom displays a 5-fold coordination achieved by binding to two bromine atoms and to the tridentate L-Et moiety. The latter chelates the zinc ion exclusively through its nitrogen donor functions; the ester group is not involved in metal coordination. The geometry of the Br_2N_3 coordination sphere

is halfway between that of a square pyramid and that of a trigonal-planar bipyramid, the largest bond angle (149°) being that between the two zinc–pyridyl bonds (N(12)–Zn(1)–N(13)). The heteroaromatic rings are close to coplanarity with an angle of approximately 170° between the ring planes. The bridgehead nitrogen atom, N(11), does not lie in the plane defined by the metal ion and the other nitrogen atoms, N(12) and N(13). It is shifted out of that plane toward the ester group and toward one of the bromide ligands, Br(11). This displacement allows an almost perfectly tetrahedral arrangement of N(11)'s direct neighbors. Bond lengths of the Zn–Br bonds in 1 roughly match those of known complexes of CN 5.^{24,25} Zinc–nitrogen bond lengths are dominated by the amine ligand's constitution. Due to its steric constraints the metal-to-bridgehead (N(11)) bond is considerably elongated compared to the zinc–pyridyl bonds. The same elongation has been observed for related compounds and is more pronounced when ligands contain benzimidazole moieties instead of pyridyl groups.²⁶ On the other hand, similar complexes which contain a secondary amine $\text{NH}^{24,25}$ instead of the tertiary one in 1 display a smaller extent of elongation of the metal–bridgehead bond. Hence the triamine unit of L-Et can be classified as a zinc chelator of intermediate steric constraint.

We assume 2 to have a structure like 1 in the solid state with

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Table 5. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Compound **6**

	x	y	z	$U(\text{eq})^a$
Zn(1)	4910(1)	3023(1)	2131(1)	31(1)
O(11)	2138(2)	2892(1)	2249(1)	41(1)
O(12)	77(2)	2178(2)	2798(1)	47(1)
O(13)	7765(3)	3122(2)	2008(1)	48(1)
N(11)	4958(3)	1902(1)	2914(1)	33(1)
N(12)	4791(3)	1576(2)	1647(1)	40(1)
N(13)	5365(3)	3953(2)	2938(1)	36(1)
N(14)	4405(3)	4070(2)	1446(1)	40(1)
N(15)	2934(4)	4940(2)	724(1)	59(1)
C(11)	1673(3)	2331(2)	2671(1)	33(1)
C(12)	3087(3)	1790(2)	3093(1)	38(1)
C(121)	4279(4)	1440(2)	1048(1)	52(1)
C(122)	3987(5)	496(3)	795(2)	67(1)
C(123)	4210(5)	-342(3)	1167(2)	68(1)
C(124)	4727(4)	-212(2)	1783(2)	54(1)
C(125)	5009(3)	753(2)	2013(1)	40(1)
C(126)	5701(3)	958(2)	2670(1)	42(1)
C(131)	5143(3)	4964(2)	2953(1)	43(1)
C(132)	5371(4)	5531(2)	3486(1)	54(1)
C(133)	5849(4)	5020(2)	4035(2)	61(1)
C(134)	6076(4)	3982(2)	4027(1)	54(1)
C(135)	5824(3)	3470(2)	3469(1)	37(1)
C(136)	6131(3)	2337(2)	3422(1)	39(1)
C(141)	2844(4)	4182(2)	1139(1)	51(1)
C(142)	4600(5)	5326(2)	769(1)	63(1)
C(143)	5508(4)	4793(2)	1214(1)	52(1)
Cl(1)	6044(1)	7907(1)	4775(1)	62(1)
O(111)	4419(6)	7341(4)	4664(2)	116(2)
O(112)	7033(6)	7569(4)	5278(2)	133(2)
O(113)	5317(13)	8650(10)	5129(7)	113(5)
O(114)	6469(41)	7585(7)	4226(6)	168(10)
O(115)	5854(11)	9008(4)	4738(5)	90(4)
O(116)	6907(22)	8002(21)	4265(6)	230(10)

^a Equivalent isotropic U values are defined as one-third of the trace of the orthogonal U_{ij} tensors.

monodentate nitrate ligands on the basis of the experience that nitrate is a reasonably good ligand for zinc,¹ that the nitrate IR band is in the range for monodentate coordination,²⁷ and that the IR spectra of **1** and **2** are almost identical. The structure of **3** is more difficult to assign as there is an oversupply of donor atoms. Assuming that the ester groups are noncoordinating and the water molecule is coordinated to zinc, an octahedral coordination of zinc would require only five of the six nitrogen atoms to be bound. The only spectroscopic evidence to test this is hidden: a medium-intensity IR band at ca. 1590 cm^{-1} which would be indicative of a noncoordinating pyridyl substituent²⁸ cannot be observed due to the presence of the very strong band of the coordinating pyridyls at 1608 cm^{-1} . The alternative description of **3** as a complex with ZnN_6 coordination and a water molecule of crystallization must therefore be considered as well.

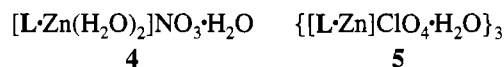
Simple L·Zn Complexes. The autocatalytic hydrolytic conversion of an ester function on a ligand to a zinc-bound carboxylate group was already observed by Weitzel in 1957.²⁹ We used it to convert **2** and **3** into **4** and **5** by heating them in water. For **5** the reaction could be accelerated and the yield improved by adding perchloric acid. Both **4** and **5** crystallized from water as cationic complexes with noncoordinating anions. The NMR (see Experimental Section) and IR data of **4** and **5** give indication only of the presence of the ligands respective anions but not of the constitution of the complexes. **4** shows the typical nitrate band at 1384 cm^{-1} in the IR (KBr) while the

Table 6. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Compound **7**

	x	y	z	$U(\text{eq})^a$
Zn(1)	-2484(1)	166(1)	2858(1)	23(1)
N(3)	-2348(9)	992(5)	4050(5)	30(2)
N(2)	-2223(7)	795(5)	1598(4)	24(2)
N(1)	-4238(7)	1119(5)	2784(5)	28(2)
N(4)	-797(7)	-622(6)	2977(6)	27(3)
C(1)	-5047(10)	-600(7)	3062(6)	25(3)
C(2)	-5287(9)	486(7)	3154(7)	29(3)
C(36)	-3970(10)	2020(7)	3321(7)	33(3)
C(33)	-2462(18)	2005(8)	5641(7)	58(4)
C(25)	-3210(9)	1362(7)	1315(6)	27(3)
C(34)	-3320(12)	2284(10)	4931(8)	52(4)
C(31)	-1565(10)	720(8)	4738(7)	39(4)
C(32)	-1663(11)	1248(9)	5565(7)	41(4)
C(23)	-1998(13)	1770(9)	-13(8)	49(4)
C(35)	-3196(10)	1727(8)	4139(7)	34(3)
C(21)	-1150(9)	667(8)	1083(7)	32(3)
O(2)	-5960(7)	-1180(6)	3198(5)	34(2)
C(24)	-3109(11)	1900(8)	487(7)	39(4)
C(22)	-996(11)	1160(9)	277(7)	42(4)
C(43)	559(11)	-1899(7)	3043(7)	40(4)
C(42)	-716(9)	-1631(7)	2971(7)	34(3)
C(41)	458(9)	-283(8)	3046(6)	30(3)
C(44)	835(10)	765(8)	3114(8)	40(4)
C(26)	-4473(9)	1364(7)	1830(6)	28(3)
O(1)	-3859(6)	-880(5)	2882(5)	31(2)
N(5)	1281(8)	-1034(7)	3096(6)	34(3)
Cl(1)	-2623(3)	5016(3)	4351(2)	56(1)
O(3)	-2207(12)	5921(8)	3943(7)	89(3)
O(6)	-3288(15)	4414(12)	3754(11)	138(5)
O(4)	-1758(16)	4588(13)	4930(12)	152(6)
O(5)	-3702(19)	5391(15)	4915(13)	179(7)

^a Equivalent isotropic U values are defined as one-third of the trace of the orthogonal U_{ij} tensors.

carboxylate and pyridyl bands overlap with maxima at 1609 and 1572 cm^{-1} . **5** shows similar overlapping bands and the perchlorate band at 1090 cm^{-1} .



The extreme differences between **4** and **5** in the constitution and structure of the complex cations could only be resolved through the structure determinations. Compound **4** (see Figure 2) consists of complex cations of $[\text{L}\cdot\text{Zn}(\text{H}_2\text{O})_2]^+$ which are surrounded by one noncoordinating crystal water molecule and one noncoordinating nitrate counterion each. The metal adopts a distorted octahedral coordination in which **L** provides three amine donor atoms as well as a coordinating carboxylate group. The fifth and sixth coordination site are occupied by two water molecules. The nature and extent of the octahedral coordination sphere's distortion can be summarized as follows: the chelate ligand provides a fairly good set of bond lengths to the hexacoordinate zinc ion but requires considerably distorted bond angles. The monodentate ligands, in turn, are located at a perfect right angle with respect to one another, but their bond lengths differ by more than 0.2 \AA . This must be related to the low symmetry and hence varying trans-effects of ligand **L**. Related hexacoordinate zinc complexes which contain more symmetric ligands than **L** like triazacyclononane³⁰ do not display such a variation of bond lengths and angular distortions, but they do show a similar average of Zn-N and Zn-O bond lengths. Like these octahedral complexes, **4** may be considered a structural model of the reactive center of the enzyme glyoxalase I which

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Table 7. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Compound **8**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Zn(1)	725(1)	2451(1)	2856(1)	41(1)
P(1)	-2182(2)	1586(2)	2100(1)	47(1)
O(1)	-319(5)	3984(5)	3320(4)	62(2)
O(2)	-230(6)	5932(5)	3905(4)	80(2)
O(3)	-676(4)	1647(5)	2148(3)	56(2)
O(4)	-3184(5)	2111(5)	2835(4)	64(2)
O(5)	-2376(5)	41(5)	2035(4)	60(2)
O(6)	-2594(5)	2307(5)	1076(4)	65(2)
N(1)	1286(6)	887(6)	3803(4)	48(2)
N(2)	2178(5)	2754(5)	1671(4)	43(2)
N(3)	2383(6)	3372(5)	3565(4)	47(2)
C(1)	312(8)	4886(8)	3653(5)	53(3)
C(2)	1826(8)	4708(8)	3692(6)	72(4)
C(3)	2426(8)	2614(9)	4528(6)	72(4)
C(4)	3651(7)	3241(9)	2964(6)	76(4)
C(11)	2208(8)	1140(8)	4430(6)	56(3)
C(12)	2788(9)	135(10)	5002(6)	76(4)
C(13)	2383(12)	-1140(10)	4974(7)	90(5)
C(14)	1431(10)	-1367(9)	4339(7)	79(4)
C(15)	911(8)	-348(8)	3775(6)	59(3)
C(21)	3374(7)	3260(7)	1884(6)	50(3)
C(22)	4413(8)	3524(7)	1147(7)	63(3)
C(23)	4210(9)	3298(8)	186(7)	68(4)
C(24)	2998(9)	2818(8)	3(6)	63(3)
C(25)	1992(8)	2576(7)	747(5)	51(3)
C(31)	-3658(8)	-574(8)	2113(6)	54(3)
C(32)	-3740(9)	-1784(9)	2643(6)	72(4)
C(33)	-4977(12)	-2426(10)	2675(7)	95(5)
C(34)	-6046(10)	-1920(11)	2211(9)	99(5)
C(35)	-5930(9)	-734(10)	1709(9)	106(5)
C(36)	-4742(8)	-54(8)	1628(8)	85(4)
C(41)	-1717(7)	2388(9)	214(5)	52(3)
C(42)	-1408(8)	3652(9)	-184(7)	68(4)
C(43)	-602(10)	3788(10)	-1064(7)	81(4)
C(44)	-158(9)	2692(12)	-1511(7)	77(4)
C(45)	-491(9)	1469(10)	-1111(7)	74(4)
C(46)	-1276(8)	1338(8)	-234(6)	58(3)
O(100)	6833(6)	4592(7)	3550(6)	141(4)
O(101)	5347(14)	4354(13)	5172(10)	126(5)

^a Equivalent isotropic *U* values are defined as one-third of the trace of the orthogonal U_{ij} tensors.

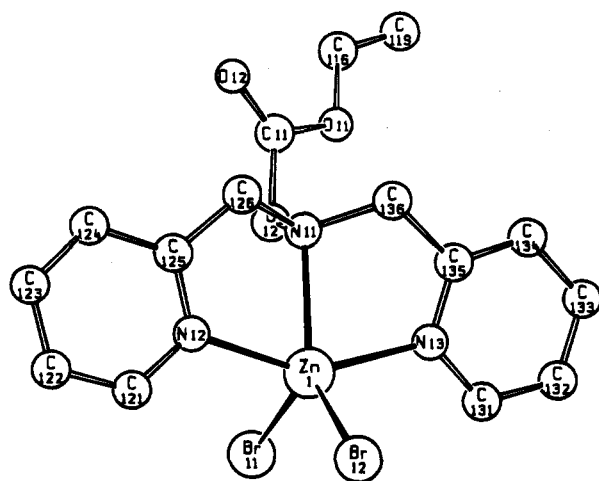


Figure 1. Molecular structure of **1**. Selected bond lengths (\AA) and angles (deg): Zn(1)–Br(11) 2.407(1); Zn(1)–Br(12) 2.427(1); Zn(1)–N(11) 2.308(1); Zn(1)–N(12) 2.110(1); Zn(1)–N(13) 2.107(1); Br(11)–Zn(1)–Br(12) 113.2(1); Br(11)–Zn(1)–N(11) 112.5(1); Br(12)–Zn(1)–N(11) 134.3(1); Br(11)–Zn(1)–N(12) 98.5(1); Br(12)–Zn(1)–N(12) 97.4(1); Br(11)–Zn(1)–N(12) 98.8(1); N(11)–Zn(1)–N(13) 74.7(1); N(12)–Zn(1)–N(13) 149.3(1).

according to spectroscopic data contains a hexacoordinate zinc ion bound to an N,O-donor set.³¹

All components of **4** are connected to one another and to neighboring molecules by a network of hydrogen bonds in which

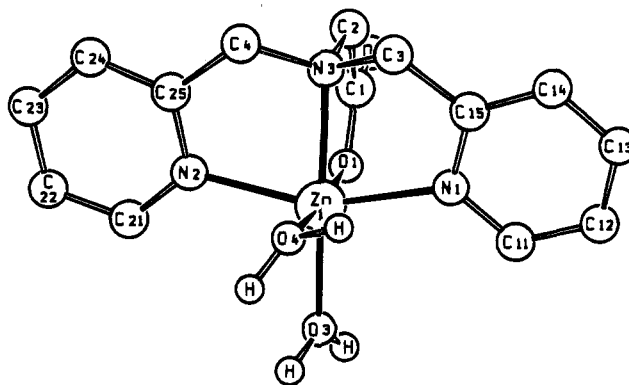


Figure 2. Solid state structure of **4**. Selected bond lengths (\AA) and angles (deg): Zn(1)–O(1) 2.135(2); Zn(1)–O(3) 2.010(2); Zn(1)–O(4) 2.243(2); Zn(1)–N(1) 2.116(3); Zn(1)–N(2) 2.125(3); Zn(1)–N(3) 2.198(3); O(1)–Zn(1)–O(3) 93.8(1); O(1)–Zn(1)–O(4) 175.6(1); O(3)–Zn(1)–O(4) 89.9(1); O(1)–Zn(1)–N(1) 92.2(1); O(3)–Zn(1)–N(1) 101.8(1); O(4)–Zn(1)–N(1) 89.5(1); O(1)–Zn(1)–N(2) 89.5(1); O(3)–Zn(1)–N(2) 101.8(1); O(4)–Zn(1)–N(2) 87.4(1); N(1)–Zn(1)–N(2) 156.2(1); O(1)–Zn(1)–N(3) 80.9(1); O(3)–Zn(1)–N(3) 174.7(1); O(4)–Zn(1)–N(3) 95.4(1); N(1)–Zn(1)–N(3) 78.0(1); N(2)–Zn(1)–N(3) 78.8(1).

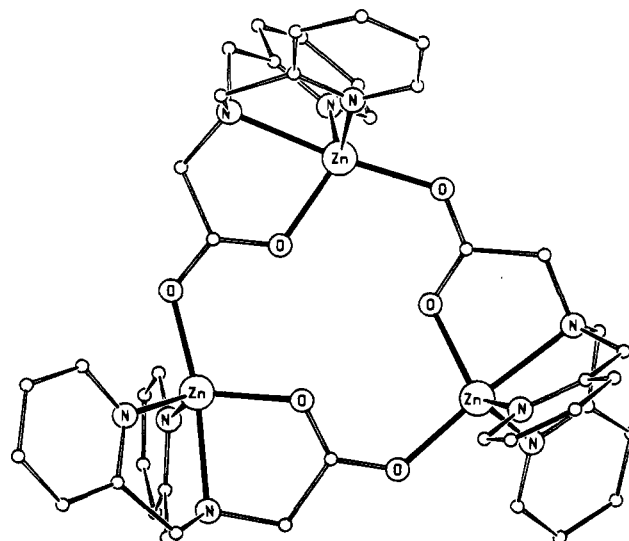


Figure 3. Solid state structure of **5** showing the trimeric arrangement.

the two metal-bound water molecules participate as well as both oxygen atoms of the carboxylate group, the noncoordinating water molecule, and the nitrate counterion.

The structure of **5** bears no resemblance to that of **4**; cf. Figure 3. Complex **5** consists of trimeric trications of $[\text{ZnL}]_3^{3+}$ which are surrounded by three perchlorate counterions and three molecules of crystal water. Counterions and water molecules are not involved in metal binding. The trimeric units are cyclic and contain three crystallographically independent zinc ions which are joined by three μ_2 -bridging carboxylate functions. Each ligand **L** binds to a zinc ion in a tetradentate manner via one carboxylate group, one nitrogen bridgehead, and two pyridyl groups. It acts as a monodentate ligand toward a second, neighboring zinc ion using that oxygen atom of its carboxylate group which is not employed for chelation. The resulting coordination number for each of the zinc ions is 5. The coordination geometry is that of a slightly distorted trigonal bipyramid. One major cause of distortion, like in the structures described above, lies in the chelating angles of **L** which are limited to approximately 80° . The second important deviation of bond angles from those of an ideal trigonal bipyramid

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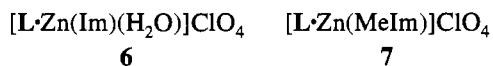
originates from the trimeric nature of the complex. In order to enable the coordination of the bridging carboxylate oxygen in an axial position the main axes of the three trigonal bipyramids are bent by 5–9°, thus allowing each subunit to get closer to its neighbors. Since each carboxylate group binds the two zinc ions in an *anti*-conformation, the intermetallic distances (ca. 5.3 Å) are nevertheless relatively large. The Zn–N bond lengths in **5** vary between ca. 2.3 Å for metal–bridgehead bonds and approximately 2.1 Å for metal–pyridyl bonds as can be expected from the structure of the bromide complex **1**. Trimeric **5** differs from **1**, however, in the angles between two pyridine ring planes belonging to the same **L** moiety. For all subunits of the trimer these angles are slightly smaller than 120°. In this respect **5** bears resemblance to $[(L'Zn)_3-\mu_3-CO_3](ClO_4)_4$ ($L' = \text{tris}(2\text{-picolyl})\text{amine}$).⁵ **5** matches the zinc-containing metalloenzyme phospholipase C with respect to the arrangement of three zinc ions and with respect to the presence of N and O donors.³²

The solid state spectral data of **4** and **5** are in agreement with the crystal structures. Specifically the solid state ¹³C-NMR data (see Experimental Section) confirm that **4** contains terminal carboxylate ligands by a resonance in the typical shift range³³ at 182.3 ppm, while **5** shows the dissymmetry of the trimeric cation and the presence of bridging carboxylate ligands by three resonances in the typical shift range³³ at 186.7, 187.7, and 188.2 ppm.

In aqueous solution **4** and **5** seem to have more similarities than in the solid state. Thus both complexes show just one ¹³C-NMR resonance for the coordinated carboxylate group at 177.6 ppm and their ¹H and ¹³C NMR spectra are very similar. The electrical conductivity of **5** (106 cm²/Ω·mol) is higher than that of **4** (74 cm²/Ω·mol, both at infinite dilution). That of **5** corresponds to roughly 40% of that of Zn(ClO₄)₂,¹⁸ which might be expected taking into account the smaller number of charge carriers and the larger size of the cation. The fact that solutions of **4** are less conductive than those of **5** cannot be related to the partial conductivities of the anions which are virtually equal.¹⁸ As we assume the solutions to contain identical cations (see below) we think that the linking of cations and anions in **4** by ion pairing or by hydrogen bridges (as observed in the solid state) is the reason for its reduced conductivity.

L·Zn-X Complexes. The simple composition, solid state structure, and solution behavior of **5** lead to the interpretation that it contains a hidden coordination site which in the presence of the noncoordinating perchlorate ions is available for occupation by a water molecule or other substrates in solution. In an attempt to approach the bonding situation of zinc in the enzymes superoxide dismutase (N,N,O protein ligation and histidine imidazolidine as a coligand⁷) and alkaline phosphatase (three zinc ions with varying N and O protein ligation and phosphate-containing substrate⁸) we therefore tried to attach the corresponding coligands to the L·Zn⁺ unit starting from **5**.

Treating **5** with imidazole or 2-methylimidazole in water resulted, after cooling, in the ternary complexes **6** and **7**. The



compositions of both complexes could easily be deduced from their NMR spectra (see Experimental Section) and the presence of the perchlorate bands at 1097 and 1087 cm⁻¹, respectively, in the IR (KBr). The unusual observation that in the solid state they vary in their coordination number was, however, left to

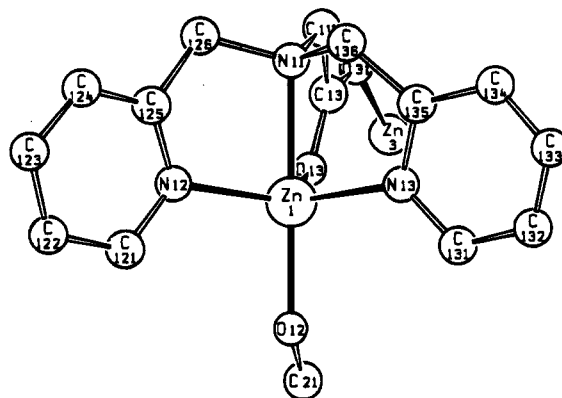


Figure 4. Coordination of one complex unit in **5**. Selected bond lengths (Å) and angles (deg), values for the three equivalent units of the trimer: Zn(1)–N(11) 2.266(5)/2.261(4)/2.270(7); Zn(1)–N(12) 2.069(6)/2.058(5)/2.053(4); Zn(1)–N(13) 2.083(4)/2.070(4)/2.053(5); Zn(1)–O(12) 2.013(4)/2.005(5)/2.019(5); Zn(1)–O(13) 1.991(4)/2.024(4)/2.023(3); N(11)–Zn(1)–N(12) 79.4(2)/79.2(2)/78.2(2); N(11)–Zn(1)–N(13) 79.4(2)/79.1(2)/79.3(2); N(11)–Zn(1)–O(13) 80.4(2)/79.5(2)/78.3(2); N(11)–Zn(1)–O(12) 171.2(2)/173.7(2)/175.2(1); N(12)–Zn(1)–N(13) 118.1(2)/118.9(2)/117.4(2); N(12)–Zn(1)–O(13) 120.6(2)/118.1(2)/116.9(2); N(12)–Zn(1)–O(12) 96.2(2)/96.0(2)/97.8(2); N(13)–Zn(1)–O(13) 112.0(2)/112.9(2)/114.2(2); N(13)–Zn(1)–O(12) 96.2(2)/99.9(2)/97.8(2); O(13)–Zn(1)–O(12) 108.4(2)/106.5(2)/106.4(2).

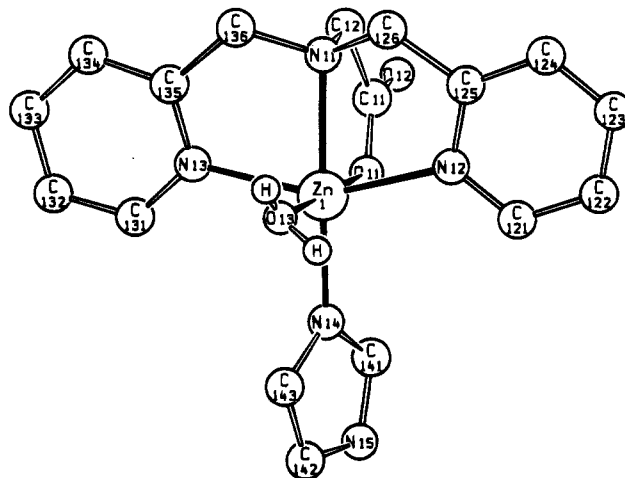


Figure 5. Structure of the cation of **6**. Selected bond lengths (Å) and angles (deg): Zn(1)–N(14) 2.041(2); Zn(1)–O(11) 2.100(2); Zn(1)–N(13) 2.141(2); Zn(1)–O(13) 2.160(2); Zn(1)–N(12) 2.172(2); Zn(1)–N(11) 2.243(2); N(14)–Zn(1)–O(11) 90.07(8); N(14)–Zn(1)–N(13) 102.62(9); O(11)–Zn(1)–N(13) 93.40(8); N(14)–Zn(1)–O(13) 90.68(9); O(11)–Zn(1)–O(13) 178.73(7); N(13)–Zn(1)–O(13) 87.44(8); N(14)–Zn(1)–N(12) 103.96(8); O(11)–Zn(1)–N(12) 88.45(8); N(13)–Zn(1)–N(12) 153.36(8); O(13)–Zn(1)–N(12) 90.38(8); N(14)–Zn(1)–N(11) 170.06(8); O(11)–Zn(1)–N(11) 80.13(7); N(13)–Zn(1)–N(11) 76.52(8); O(13)–Zn(1)–N(11) 99.15(8); N(12)–Zn(1)–N(11) 77.63(7).

their structure determinations. Compound **6** consists of complex cations of $[L \cdot Zn(\text{imidazole})(H_2O)]^+$ and perchlorate counterions which are not bound to the metal atom. The zinc ion adopts the same slightly distorted octahedral coordination (see Figure 4) as is described above for the diaqua complex **4**. In the imidazole complex **6** the ligand **L** adopts a conformation in which the pyridine rings are close to coplanarity. The coordination sphere is completed by an imidazole and a water molecule. The Zn–imidazole bond is surprisingly short compared to those found in octahedral hexakis(imidazole)zinc dichloride³⁴ or bis(glycylhistidine)zinc,³⁵ which like in complex **4** is a reflection of the long Zn–N(11) bond *trans* to it. The crystal structure

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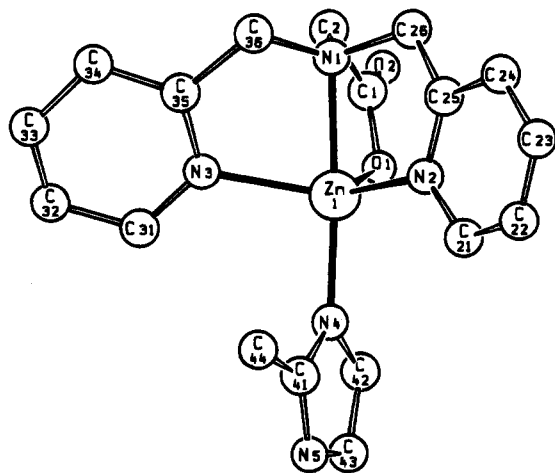


Figure 6. Structure of the cation of **7**. Selected bond lengths (Å) and angles (deg): Zn(1)–N(3) 2.116(7); Zn(1)–N(2) 2.092(7); Zn(1)–N(1) 2.198(7); Zn(1)–N(4) 2.022(7); Zn(1)–O(1) 1.986(6); N(3)–Zn(1)–N(2) 123.0(3); N(3)–Zn(1)–N(1) 77.7(3); N(2)–Zn(1)–N(1) 79.6(3); N(3)–Zn(1)–N(4) 98.5(3); N(2)–Zn(1)–N(4) 100.8(3); N(1)–Zn(1)–N(4) 175.4(3); N(3)–Zn(1)–O(1) 114.0(3); N(2)–Zn(1)–O(1) 113.2(3); N(1)–Zn(1)–O(1) 81.4(3); N(4)–Zn(1)–O(1) 102.6(3).

of **6** is again stabilized through a network of hydrogen bonds involving water molecules, noncoordinating oxygen atoms of carboxylate groups, imidazole N–H groups, and perchlorate counterions.

Compound **7** consists of complex cations in which zinc adopts a trigonal-bipyramidal coordination (see Figure 6) and of noncoordinating perchlorate counterions. Unlike in complex **6** there is only one coligand in addition to the tetradentate **L**. 2-Methylimidazole acts as a monodentate ligand and is bound to zinc in the *trans* position to the nitrogen bridgehead N(1). The methyl group of the imidazole coligand occupies the space between the pyridyl substituents. Consequently, the angle between adjacent pyridyl ring planes is 10° larger in **7** than in related trimeric **5**. The structure is stabilized by hydrogen bonds between the N–H group of the monodentate ligand and the noncoordinating oxygen atom of an adjacent complex cation in such way that one-dimensional, infinite chains are formed.

The bond lengths in **7** do not differ substantially from those found in the zinc complex formed by the [12]ane-N₃ ligand with a pendant imidazole group.³⁶ They also correspond to those found in dinuclear, imidazolide-bridged species of the ligand bis(aminoethyl)glycine which is similar to **L**.¹⁴ This is somewhat surprising since **7** does not contain an anionic imidazolide but a neutral imidazole ligand and therefore should display a longer Zn–imidazole bond.

The solid state ¹³C-NMR data reflect the difference between **6** and **7** in coordination numbers mostly in the carboxylate resonances at 180.8 ppm for **6** and 176.7 ppm for **7**. The solution NMR data do not allow a straightforward interpretation, neither with respect to the structure of nor the connectivity in the complexes. The ¹H and ¹³C NMR spectra are very similar for all complexes **4**–**7** for the L·Zn unit, thereby proving nothing but the presence of this unit. The NMR data for the imidazole coligands in **6** and **7** differ rather little from those for the free imidazoles; cf. for ¹³C (free imidazole in brackets): imidazole, 137.1 (135.6), 122.1(121.5); 2-methylimidazole, 146.3 (145.5), 121.2 (121.1), 12.3 (12.2). Furthermore, the 4 and 5 positions of the imidazoles which become inequivalent due to complexation cannot be distinguished in the NMR spectra. This feeds the suspicion that in solution a dissociation of the imidazoles or their rapid exchange with water molecules is occurring

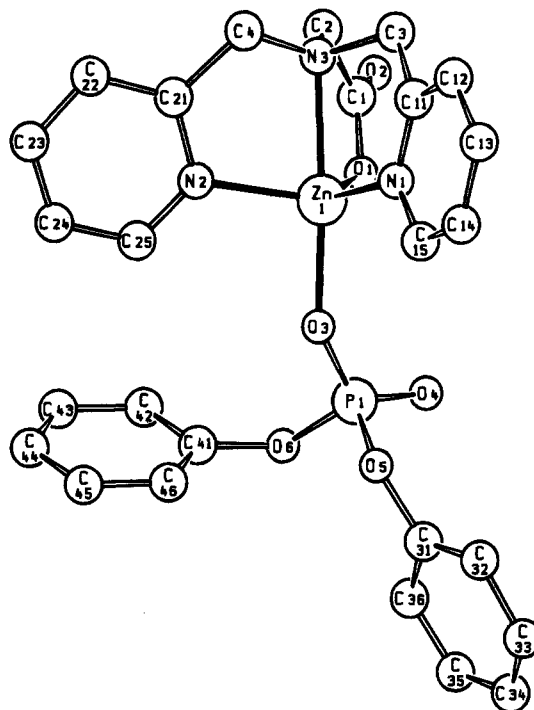


Figure 7. Molecular structure of **8**. Selected bond lengths (Å) and angles (deg): Zn(1)–O(1) 1.946(5); Zn(1)–O(3) 1.975(5); Zn(1)–N(1) 2.046(5); Zn(1)–N(2) 2.080(5); Zn(1)–N(3) 2.225(6); P(1)–O(3) 1.483(5); P(1)–O(4) 1.467(5); P(1)–O(5) 1.587(5); P(1)–O(6) 1.601(5); O(1)–Zn(1)–O(3) 100.2(2); O(1)–Zn(1)–N(1) 121.5(2); O(3)–Zn(1)–N(1) 101.8(2); O(1)–Zn(1)–N(2) 118.5(2); O(3)–Zn(1)–N(2) 97.2(2); N(1)–Zn(1)–N(2) 111.5(2); O(1)–Zn(1)–N(3) 81.6(2); O(3)–Zn(1)–N(3) 176.4(2); N(1)–Zn(1)–N(3) 79.8(2); N(2)–Zn(1)–N(3) 79.2(2); O(3)–P(1)–O(4) 123.4(3); O(3)–P(1)–O(5) 101.8(3); O(4)–P(1)–O(5) 110.7(3); O(3)–P(1)–O(6) 109.2(3); O(4)–P(1)–O(6) 104.6(3); O(5)–P(1)–O(6) 106.2(3).

thereby making the cationic solution species similar or identical to those in solutions of **5**. Further support for this assumption comes from the conductivity measurements which for **6** and **7** have yielded values (110 and 98 cm²/Ω·mol, respectively, at infinite dilution) which within the error limit are the same as that for **5**.

The incorporation of a phosphate ligand was possible by reaction of **5** with sodium diphenyl phosphate in ethanol/water. Unlike all other complexes with the L·Zn unit, the resulting **8** is a neutral molecular compound as evidenced by its structure determination and by its reasonable solubility in nonaqueous solvents. Its geometrical relation to **7** (both trigonal bipyramidal) is supported by the solid state ¹³C-NMR resonance for the carboxylate group at 175.6 ppm. The presence of the **L** and diphenyl phosphate ligands in **8** is evidenced by the NMR data (see Experimental Section). The characteristic IR bands of the phosphate show up in the IR (KBr) at 1270 and 1212 cm⁻¹.



Compound **8** consists of uncharged molecules [L·ZnOPO₃-(C₆H₅)₂] (see Figure 7) and of water molecules which are not linked to the complex moieties. The metal atom adopts the same slightly distorted trigonal-bipyramidal coordination geometry as has been described above for the compounds **5** and **7**. Diphenyl phosphate acts as a monodentate ligand occupying the fifth site of the metal's coordination sphere in the *trans* position with respect to the nitrogen bridgehead N3.

The Zn–O bond of the phosphate ligand is rather long compared with other such bonds.^{37,38} Correspondingly the two P–O bonds which do not bear phenyl substituents are of almost

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equal length (average 1.475 Å), again unlike the situation in the reference compounds.^{37,38} This indicates that the diphenyl phosphate ligand is still quite anionic and has a rather low degree of single bond location in the P–O–Zn unit.

The solution data of **8** again point at least to a partial dissociation of the phosphate from zinc in water. While the ³¹P-NMR resonance at –9 ppm is in the range of that of all monophosphates including diphenyl phosphoric acid (–13 ppm), the ¹H and ¹³C NMR spectra (see Experimental Section) again do not show much difference from that of **5** except for the inconclusive aromatic phosphate resonances. Despite its molecular nature in the solid state, **8** has a good solubility in water where its conductivity (47 cm²/Ω·mol, at infinite dilution) is about half of that of **5–7**. A discussion of this value forbids itself, however, as the concentration dependence of the conductivity of **8** is zero; i.e., it does not follow Kohlrausch's square root law.^{18,39}

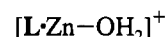
Discussion and Conclusions

The indirect synthesis of ligand **L** in its zinc complexes has opened the way to a controlled and large-quantity chemistry of this (N,N,O)[–]-tripod which was not obtained pure or in sufficient amounts before. While it remains to be tested whether this approach to making L·M complexes can be applied to metals other than zinc, we have found that in the case of zinc a derivative chemistry can be built up starting from the simple L·Zn complexes, specifically the perchlorate.

While simple in composition (L·Zn⁺ or L·Zn–X), the complexes **4–8** show a quite varied structural chemistry in the solid state. Two of them (**4**, **6**) have an octahedral and three (**5**, **7**, **8**) a trigonal-bipyramidal coordination to zinc, and the complex **5** for which the composition [L·Zn]X would indicate CN 4 achieves CN 5 by trimerization in the solid state. It is noteworthy that of the two simple [L·Zn] complexes the nitrate **4** contains bis-hydrated zinc while the perchlorate **5** crystallizes with no zinc-bound water. Similarly the small difference between imidazole and 2-methylimidazole makes the former coexist with one water molecule in **6** while the latter does not in **7**. In both pairs of complexes the difference in coordination goes along with a different kind of hydrogen bond network in the crystals. Thus it has been demonstrated again how subtle the influences on the coordination geometry of zinc are and how little we control them yet.

In contrast to the structural variety in the solid state there is possibly a quite uniform picture of the L·Zn coordination in aqueous solution. An extensive array of methods had to be used to find out about this. ¹³C-NMR spectroscopy was the method which could be applied to the solid state and to the solution as well. The probe of choice was the resonance of the carboxylate group which for the solid samples shows up in three different shift ranges: at ca. 188 ppm for **5** (bridging carboxylate), at ca. 181 ppm for **4** and **6** (octahedral), and at ca. 176 ppm for **7** and **8** (trigonal-bipyramidal). Conversely, in aqueous solution all five complexes show this resonance between 177.6 and 177.9 ppm which, as calibrated by the solid state data, corresponds to a trigonal bipyramidal coordination of zinc. The

other data support this assignment. Solution NMR fails to provide strong evidence for the coordination of the coligands to zinc in **6–8**, and according to the electrical conductivity measurements **4–7** seem to form similar species. Even the apparently molecular complex **8** seems to form ions in solution. In this context it is worth mentioning that due to preliminary potentiometric data⁴⁰ all complexes **4–8** show an apparent pK_a between 9.1 and 9.3 which may be related to the acidity of a zinc-bound water molecule. The simplest explanation for all these observations is the occurrence of a simple hydrated L·Zn cation in all solutions, be it as the only species or as a major constituent of an equilibrium mixture. The circumstantial evidence, specifically ¹³C-NMR, indicates that this species is the trigonal-bipyramidal complex **9**.



9

In relation to zinc-containing enzymes, **9** is a key species, as it models the resting enzyme with a water molecule on the "catalytic" position. Although we are aware that in the enzymes the protein environment provides different conditions for metal–substrate stabilities and reactivities, our observations with the ternary complexes **6–8** allow two statements related to the function of such enzymes: (1) Imidazole ligands are not bound very firmly in an aqueous environment which might not be expected considering the suggested mechanism of action of superoxide dismutase.⁷ (2) The phosphate unit is also not bound very well despite its negative charge, as would be expected for catalytic conversions in phosphatases.⁸

The apparently weak binding of substrates to the L·Zn⁺ unit may explain why we were unable to incorporate serine monophosphate or adenosine monophosphate in complexes like **8**. To our surprise we could also not deprotonate the imidazole in **7** in order to attach a L·Cu unit for building a Zn–Im–Cu model of superoxide dismutase. Such a model was obtained elsewhere using the closely related ligand *N,N*-bis(2-aminoethyl)glycinate without isolating an intermediate zinc complex.¹⁴ This again points to the subtleties governing this type of zinc coordination chemistry.

Nevertheless we consider the availability of a hydrated L·Zn⁺ species of the likely constitution **9** as the major achievement of this work. Generated from the easily accessible **5** this species should open the way to a derivative chemistry producing L·Zn–X complexes of a variety similar to that for L = pyrazolyl borate⁴¹ but this time with the new anionic (N,N,O) ligand donor set.

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Supplementary Material Available: A table of concentration/conductivity values for **1** and **4–8**, a fully labeled structural diagram of **5**, and tables containing the details of data acquisition and refinement, complete interatomic distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated parameters of hydrogen atoms for all six structure determinations (38 pages). Ordering information is given on any current masthead page.

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