Zinc Complexes of Tripodal N_3O Ligands☆

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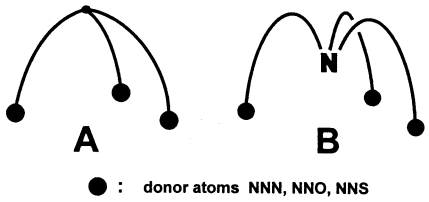
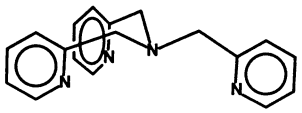
The tripodal N,O ligands bis(2-pyridylmethyl)(*o*-hydroxybenzyl)amine ($\mathbf{L}^1$) and bis(2-pyridylmethyl)(2-carboxyethyl)amine ($\mathbf{L}^2$) were tested for their ligating properties towards zinc. Zinc halides yielded $\mathbf{L}^1{\cdot}Zn{-}Hal$ (**1a**−**c**, Hal = Cl, Br, I) and $\mathbf{L}^2{\cdot}Zn{-}Hal$ (**2a**−**c**, Hal = Cl, Br, I). Subsequent treatment of $\mathbf{L}^1$ with $ZnEt_2$ or $Zn[N(SiMe_3)_2]_2$ and phenol, thiophenols or diphenylphosphate led to $\mathbf{L}^1{\cdot}Zn{-}OPh$ (**3**), $\mathbf{L}^1{\cdot}Zn{-}SAr$ (**4**) and $\mathbf{L}^1{\cdot}Zn{-}OPO(OPh)_2$ (**5**). Zinc salts of noncoordinating anions yielded oligonuclear ligand-bridged complexes $[\mathbf{L}^1{\cdot}Zn]ClO_4$ (**6**), $[\mathbf{L}^2{\cdot}Zn]ClO_4$ (**7**) and $[\mathbf{L}^2{\cdot}Zn]NO_3$ (**8**), of which **6** was identified as a phenolate bridged dimer and **8** as a η^1-η^2-carboxylate bridged polymer.

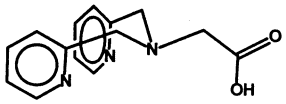
The challenge of modern coordination chemistry is the design of complexes in which an inert ligand matrix provides the metal ion with appropriate electronic properties and the right number of labile coordination sites to effect specific metal-mediated reactions. In practice this means the use of polydentate ligands, and specifically in the field of functionalized macrocycles a high level of sophistication has been reached for this purpose.

We are trying to contribute to this area of research in the field of zinc chemistry. Zinc ion catalysis, in organic synthesis as well as in biological systems, involves zinc complexes of low coordination numbers, e.g. 4 or 5[1]. Hence most macrocyclic ligands which favour coordination numbers 5 and 6 are not ideally suited for mechanistic or bioinorganic model studies here. The ligands of choice are the tripods of which very many have been synthesized in recent years. If constructed right, those of type **A** should favour tetrahedral zinc and those of type **B** should favour trigonal-bipyramidal zinc, each with one labile coordination site.



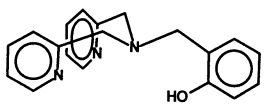
A typical representative of type **A** is the class of pyrazolylborate ligands[2] to which we have contributed synthetic, model complex, and complex reactivity studies[3]. One of the simplest representatives of type **B** is tris(picolyl)amine[4] which so far has been used sparsely in zinc chemistry[5]. In contrast to the pyrazolylborates, the type **B** tripods can easily be obtained with different donor "arms" in the same ligand. A recent example which has the additional advantage of bearing one negative charge is dipicolylglycinate[6] of which we have prepared the $[\mathbf{L}{\cdot}Zn{-}OH_2]^+$ complex and studied its reactivity[7].


tris(picolyl)amine

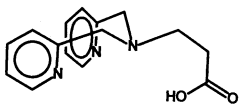


dipicolylglycine

Ligands like tris(picolyl)amine and dipicolylglycinate have an arrangement of donor atoms corresponding to that of ethylenediamine, i.e. they support valence angles near 90° and hence octahedral coordination at the metal ion, as we have experienced for zinc complexes of the latter[7]. In order to relax their bite, the length of their "arms" should be extended. Some reports on zinc complexes having type **B** ligands with "longer arms" seem to support this idea[8]. We therefore looked for such ligands to include them in our reactivity studies. Of the various possibilities we opted for the two dipicolylamine derivatives $H\mathbf{L}^1$ with a phenolate unit and $H\mathbf{L}^2$ with a carboxylate unit as the third "arm". Both could be expected to bind to zinc as the monoanions $\mathbf{L}^1$ and $\mathbf{L}^2$ and thereby ensure a reasonably good complex stability.



$H\mathbf{L}^1$



$H\mathbf{L}^2$

Both $H\mathbf{L}^1$[9] and $H\mathbf{L}^2$[10] have been described before and used for bioinorganic model studies[9][10][11][12][13]. The coordination chemistry of ligands like $\mathbf{L}^1$ with varying "arm lengths" was developed extensively by D. E. Fenton[13][14][15][16] including the modelling of the structure and reactivity of zinc enzymes[15][16] and the preparation of dinuclear copper and zinc complexes of $\mathbf{L}^1$[13][15]. One of the attractions in the zinc chemistry of $\mathbf{L}^1$ and $\mathbf{L}^2$ is that they

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allow to mimick the fivefold N_xO_y coordination of zinc in enzymes like the peptidase astacin [histidine (3×), tyrosine, H_2O][17] or Escherichia coli alkaline phosphatase [histidine (2×), aspartate (2×), H_2O][18]. With this in mind we intended to explore the basic zinc coordination chemistry of $\mathbf{L}^1$ and $\mathbf{L}^2$ (coordination numbers, ligand bridging) and to find complexes like $[\mathbf{L}\cdot Zn]^+$, $[\mathbf{L}\cdot Zn-OH_2]^+$ or $[\mathbf{L}\cdot Zn-OH]$ for reactivity studies involving a labile coordination site or a hydrolytically active function at the zinc ion.

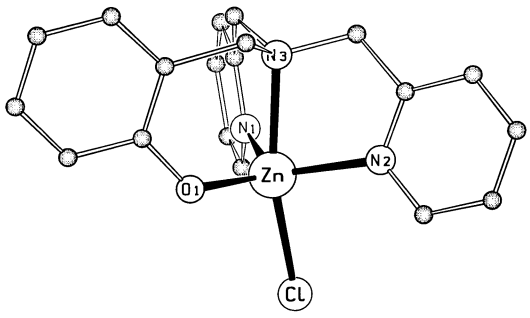
L·Zn−X Complexes

In order to test the ligating abilities of $\mathbf{L}^1$ and $\mathbf{L}^2$ their zinc halide complexes were prepared. This could be achieved with $ZnHal_2$ in methanol, using NaOH to deprotonate **L**H. All six complexes (**1** and **2**) were obtained. Complexes **1** are soluble in polar organic solvents like dichloromethane or ethanol, complexes **2** dissolve only in water or water/alcohol mixtures. The presence of the intact ligands **L** in the complexes is evident from their ^{1}H-NMR spectra (see experimental), their binding to zinc can be deduced from the low-field shifts of the signals for the pyridyl-H_α atoms.

$\mathbf{L}^1\cdot Zn-Hal$		$\mathbf{L}^2\cdot Zn-Hal$	
1a	Hal = Cl	**2a**	Hal = Cl
1b	Br	**2b**	Br
1c	I		

Proof for the molecular nature of complexes **L**·Zn−Hal was obtained by the structure determination of **1a**, see Figure 1. The geometry at zinc in **1a** is close to trigonal-bipyramidal, and it can be compared with that in related zinc complexes of tris(benzimidazolylmethyl)amine[19] or dipicolylglycinate[7]. This includes the bending along the trigonal axis (165°) and the lengthening of the axial Zn−N distance compared to the equatorial ones. The axial Zn−Cl distance (2.33 Å) seems long when compared to those in pyrazolylborate zinc complexes (2.14−2.18 Å)[20]. But it compares well with that in trigonal-bipyramidal (tren)Zn−Cl (2.31 Å)[21].

Figure 1. Molecular structure of $\mathbf{L}^1\cdot Zn-Cl$ (**1a**)[a]



[a] Bond lengths and angles around zinc: Zn−N1 2.109(5), Zn−N2 2.116(4), Zn−N3 2.240(4), Zn−O1 1.928(3), Zn−Cl 2.326(2) Å. − N1−Zn−N3 77.6(2), N2−Zn−N3 76.7(2), O1−Zn−N3 91.9(2), Cl−Zn−N3 165.1(1), Cl−Zn−N1 96.5(2), Cl−Zn−N2 95.3(1), Cl−Zn−O1 102.9(1), N1−Zn−N2 121.2(2), N1−Zn−O1 117.0(2), N2−Zn−O1 115.8(2)°.

In the subsequent derivatizations it turned out to be advantageous to use an acid-sensitive zinc compound {$ZnEt_2$ or $Zn[N(SiMe_3)_2]_2$} for the deprotonation of ligands **L**H. The resulting labile complexes {$\mathbf{L}\cdot Zn-Et$ or $\mathbf{L}\cdot Zn-N(SiMe_3)_2$} were then treated with the corresponding acid HX of the coligand X. This way the $\mathbf{L}^1\cdot Zn$ unit was converted to the phenolate **3** by treatment with $ZnEt_2$ and phenol. Likewise thiophenol could be incorporated as the thiophenolate **4a** via the $Zn-N(SiMe_3)_2$ intermediate. **4a** could, however, not be obtained in a pure form. Therefore alternatively *p*-chlorothiophenol was used, leading to **4b** which was fully characterized. Finally, using $ZnEt_2$ and diphenylphosphate the phosphate complex **5** was prepared. Complexes **3**−**5** are again soluble in moderately polar organic solvents, thereby indicating their molecular nature. Their ^{1}H-NMR spectra (see Experimental Section) are proof for their constitutions.

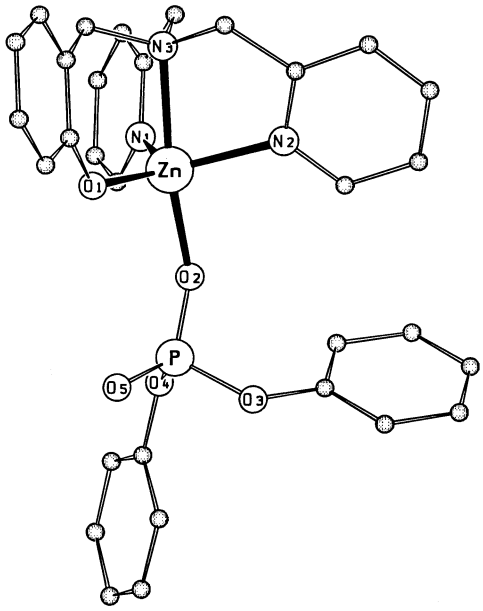
$\mathbf{L}^1\cdot Zn-OPh$ **3**	$\mathbf{L}^1\cdot Zn-SPh$ **4a**
$\mathbf{L}^1\cdot Zn-SC_6H_4-p\text{-}Cl$ **4b**	$\mathbf{L}^1\cdot Zn-O-PO(OPh)_2$ **5**

Crystals for a structure determination were obtained of **5**. Figure 2 shows that the coordination environment of zinc is very similar to that in **1a**, including the moderate deformation of the trigonal-bipyramidal geometry, the lengthening of the axial vs. equatorial Zn−X bonds and the bending of the N3−Zn−O2 axis. The orientation and the bonding situation of the phosphate ligand can be compared to that in a considerable number of pyrazolylborate−zinc−organophosphate complexes.[22] Specifically, the close similarity of the P−O2 and P−O5 bond lengths and the wide Zn−O−P angle are as observed before. This holds also for organophosphate complexes of dipicolylglycinate[7] and tris(picolyl)amine[5].

[L·Zn]$^+$ Complexes

The main purpose of this study was the preparation of zinc complexes in which the tripodal ligands **L** encapsulate the zinc ion such that they stabilize $[\mathbf{L}\cdot Zn]^+$ cations or cationic $[\mathbf{L}\cdot Zn-OH_2]^+$ complexes which can give access to reactive substrates **S** for zinc-mediated or zinc-catalyzed interconversions via intermediate complexes $[\mathbf{L}\cdot Zn-\mathbf{S}]$. To obtain such cationic complexes ligands **L** were treated with zinc salts of noncoordinating anions. In case of $\mathbf{L}^1$ and $\mathbf{L}^2$ this worked with $Zn(ClO_4)_2 \cdot 6\ H_2O$. When using methanol as a solvent and NaOH as a base the products **6** and **7** were isolated. Of these **6** was impure and insoluble while **7** could be recrystallized from water yet not obtained in the form of good single crystals. A form of **6** suitable for X-ray analysis was obtained by runing the reaction in CH_2Cl_2/methanol with KOH as a base, removing $KClO_4$ by filtration and allowing the product to crystallize from chloroform. This product **6** was not soluble in chloroform after isolation but could be subjected to NMR spectroscopy in DMSO. The ^{1}H-NMR and IR data of **6** and **7** (see Experimental Section) confirm the presence of **L** and ClO_4^- but give no indication of the complexes' structures. The insoluble form of **6** seems to be polymeric. **7** is likely to be a carboxylate-

Figure 2. Molecular structure of $\mathbf{L}^1$·Zn−OPO(OPh)$_2$ (**5**)[a]



[a] Pertinent bond lengths and angles: Zn−N1 2.073(4), Zn−N2 2.096(3), Zn−N3 2.221(3), Zn−O1 1.926(3), Zn−O2 2.030(3), P−O2 1.486(3), P−O3 1.598(3), P−O4 1.601(3), P−O5 1.461(3) Å. − N3−Zn−N1 79.5(1), N3−Zn−N2 77.5(1), N3−Zn−O1 91.7(1), N3−Zn−O2 168.5(1), N1−Zn−N2 111.9(1), N1−Zn−O1 121.0(2), N1−Zn−O2 93.3(2), N2−Zn−O1 122.6(2), N2−Zn−O2 97.4(1), O1−Zn−O2 99.8(1), Zn−O2−P 151.9(2)°.

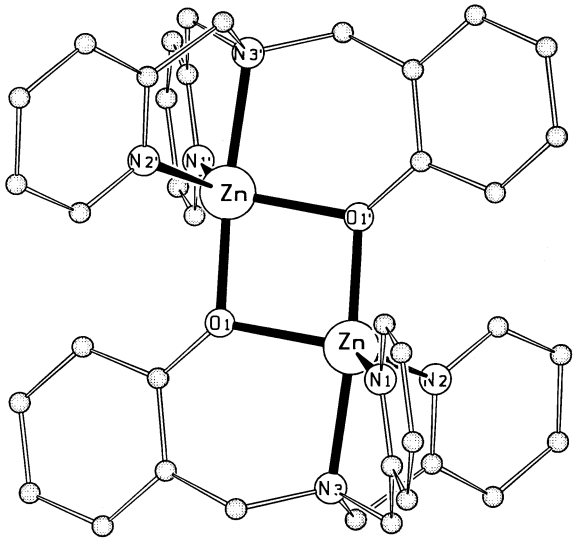
bridged oligomer, possibly a polymer like **8** (see below) or a trimer like the analogous dipicolylglycinate complex[7].

$[\mathbf{L}^1\cdot Zn]ClO_4$ **6** $\qquad$ $[\mathbf{L}^2\cdot Zn]ClO_4$ **7**

The structure determination of the soluble form of **6** showed it to be a chloroform-solvated dimer (see Figure 3). The unit cell contains two independent centrosymmetric dinuclear entities which differ slightly in their conformations but only marginally in the coordination environments of the zinc ions (bond lengths ±0.01 Å , angles ±2°). The coordination geometry of zinc is trigonal-bipyramidal, and all details associated therewith correspond to those for **1a** and **5**. The phenolate oxygen atoms provide the bridging function, as has been observed before, typically in zinc complexes of dinucleating ligands with central phenolate units[23]. The basic type of $[N_3Zn(\mu\text{-}O)_2]$ coordination is realized in $[\mathbf{L}\cdot Zn{-}OH]_2^{2+}$ with L = triazacyclononane[24] or tris(picolyl)amine[5] and zinc in a square-pyramidal environment. The Zn−N and Zn−O distances in **6** compare well with those in the reference compounds. The closest relation to **6** exists in the corresponding copper derivative of $\mathbf{L}^1$ which, however, contains square-pyramidal copper[13]. Fenton has also described two phenoxide-bridged dizinc complexes derived from $\mathbf{L}^1$-related tripod ligands with longer arms[15]:

When using zinc nitrate, a pure product, **8**, could only be obtained with $\mathbf{L}^2$. The structure determination showed this to be a polymeric methanol solvate with noncoordinating

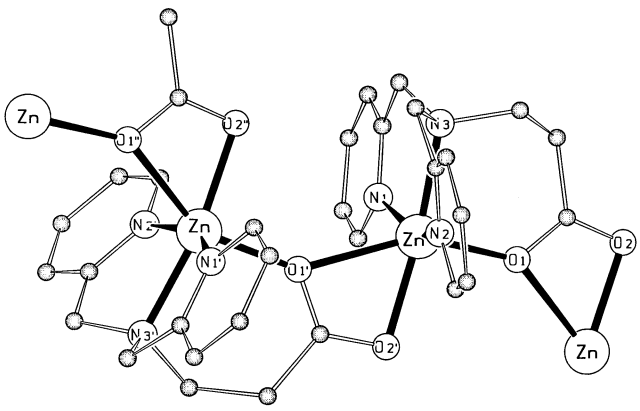
Figure 3. Molecular structure of the cations of **6**[a]



Average bond lengths and angles about zinc: Zn−O1 2.029(3), Zn−O1′ 2.002(4), Zn−N1 2.066(4), Zn−N2 2.066(4), Zn−N3 2.161(4), Zn···Zn 3.064(2) Å. N3−Zn−N1 80.4(2), N3−Zn−N2 79.9(2), N3−Zn−O1 93.0(2), N3−Zn−O1′ 172.5(2), N1−Zn−N2 126.6(2), N2−Zn−O1 122.8(2), N2−Zn−O1′ 99.6(2), O1−Zn−N1 112.6(2), O1′−Zn−N1 106.0(2), O1−Zn−O1′ 81.0(2), Zn−O1−Zn′ 99.0(2)°.

nitrate anions (see Figure 4). The linkage between the monomeric units is provided by the carboxylate groups in a manner which to our knowledge has not been observed for zinc before: one oxygen atom is bridging while the other is coordinated to the neighbouring zinc ion (η^1-η^2-carboxylate bridging)[25]. In contrast the trimeric complex $[\mathbf{L}\cdot Zn]ClO_4$ with L = dipicolylglycinate has one oxygen coordinating the ipso zinc ion and the other the neighbouring one[7]. The coordination geometry of the zinc ions in **8** is severley distorted octahedral with O1−Zn−O2 (58.7°) as the smallest and N3−Zn−O1′ (113.9°) as the largest *cis* angles and *trans* angles of 169.6 (N3−Zn−O2′), 150.0 (O1−Zn−O1′), and 154.8° (N1−Zn−N2). Carboxylate bridging between zinc ions is quite common[26], and all types of bridging[27] except for the η^1-η^2 type have been observed.

Figure 4. Solid-state arrangement of polymeric $[\mathbf{L}^2\cdot Zn]^+$ in **8**[a]



[a]Bond lengths: Zn−N1 2.084(3), Zn−N2 2.076(3), Zn−N3 2.179(3), Zn−O1 2.013(2), Zn−O1′ 2.302(2), Zn−O2′ 2.132(2) Å.

As can be seen from the Zn−N and Zn−O bond distances the coordination of $\mathbf{L}^2$ to zinc can be viewed as that in a trigonal-bipyramidal $\mathbf{L}^2$·Zn−X complex, i.e. the Zn−N3 bond is longer than the three other Zn−L bonds. Carboxylate atom O2′ then occupies the second axial ligand position, viz. Zn−O2′ is comparable in length to Zn−N3. The Zn−O1′ bond, i.e. the one that provides bridging to the neighbouring zinc ion, is the weakest, and O1 also occupies the most distorted octahedral ligand position. The distorted nature of the bridging assembly points to weak bridging, in accordance with the solubility of **8** in methanol.

Conclusions

The results of this paper indicate that ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ are suitable for monofunctional zinc complexes L·Zn−X. Anionic coligands X providing Zn−Cl, −Br, −I, −OR, −SR, and −oxoanion linkages can be incorporated. The structures of the complexes are trigonal-bipyramidal with the pivotal N atom of the tripod and the coligand X on the axial positions. The complexes derived from $\mathbf{L}^1$ complement previous work on zinc complexes of similar tripodal ligands with one phenolate and two pyridyl donors[13][14][15][16].

In terms of functionality and possibly catalytic activity the complexes derived from $\mathbf{L}^2$ seem to be better suited. In case of $\mathbf{L}^1$ phenolate bridging and consequently oligomerization seem to be so preferred that we could not obtain a soluble $[\mathbf{L}^1{\cdot}Zn]^+$ complex or a species $[\mathbf{L}^1{\cdot}Zn{-}\mathbf{S}]^+$ with a labile solvent ligand **S** like H_2O. On the other hand the oligomeric $[\mathbf{L}^2{\cdot}Zn]^+$ complexes **7** and **8** are soluble in methanol and/or water indicating the presence of species $[\mathbf{L}^2{\cdot}Zn{-}\mathbf{S}]^+$. If such a species is [L·Zn−OH] it should be a catalyst for the cleavage of esters or peptides[15][28]. Our subsequent work in this field will therefore focus on the solution chemistry of the $\mathbf{L}^2$·Zn complexes, their acid-base behaviour and their reactivity towards hydrolysable substrates.

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Experimental Section

General experimental methods and measuring techniques: see ref.[29]. The ligands $\mathbf{L}^1$[9] and $\mathbf{L}^2$[10] were prepared according to the published procedures.

1a: 400 mg (1.31 mmol) of $\mathbf{L}^1$ and 52 mg (1.31 mmol) of NaOH were dissolved in 40 ml of methanol. 177 mg (1.31 mmol) of $ZnCl_2$ in 10 ml of methanol were added, and the mixture was stirred for 2 h. Upon addition of 200 ml of ether the raw product **1a** was precipitated and filtered off. Recrystallization from methanol/water (1:1) yielded 218 mg (41%) **1a** as colourless crystals, m.p. 263°C (dec.). − $C_{19}H_{18}ClN_3OZn$ (405.2), calcd.: C 56.32, H 4.48, N 10.37, found: C 55.76, H 4.40, N 10.15. − ^{1}H NMR ($CDCl_3$): δ = 3.76 [s, 2 H, NCH_2Ph], 3.85 [d, J = 15.6 Hz, 2 H, NCH_2Py], 4.10 [d, J = 15.6 Hz, 2 H, NCH_2Py], 6.42−7.10 [m, 4 H, Ph], 7.29 [d, J = 7.8 Hz, 2 H, H_δ(Py)], 7.47 [dd, J = 5.4 Hz, 6.5 Hz, 2 H, H_β(Py)], 7.87 [dd, J = 7.8 Hz, 5.4 Hz, 2 H, H_γ(Py)], 9.45 [d, J = 6.5 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1604s, 1479vs, 1438s, 1309vs.

1b: Like **1a** from 200 mg (0.66 mmol) of $\mathbf{L}^1$, 26 mg (0.66 mmol) of NaOH, and 149 mg (0.66 mmol) of $ZnBr_2$. Yield 229 mg (77%) of **1b**, colourless crystals, m.p. 259°C. − $C_{19}H_{18}BrN_3OZn$ (449.7), calcd.: C 50.75, H 4.03, N 9.34, found: C 48.80, H 3.88, N 9.06. − ^{1}H NMR ($CDCl_3$): δ = 3.73 [s, 2 H, NCH_2Ph], 3.85 [d, J = 15.8 Hz, 2 H, NCH_2Py], 4.08 [d, J = 15.8 Hz, 2 H, NCH_2Py], 6.39−7.08 [m, 4 H, Ph], 7.30 [d, J = 9.2 Hz, 2 H, H_δ(Py)], 7.43 [dd, J = 6.6 Hz, 5.2 Hz, 2 H, H_β(Py)], 7.86 [dd, J = 9.2 Hz, 6.6 Hz, 2 H, H_γ(Py)], 9.47 [d, J = 5.2 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1605s, 1480vs, 1451m, 1433m, 1307s.

1c: Like **1a** from 200 mg (0.66 mmol) of $\mathbf{L}^1$, 26 mg (0.66 mmol) of NaOH, and 211 mg (0.66 mmol) of ZnI_2. Yield 268 mg (82%) of **1c**, colourless crystals, m.p. 168°C. − $C_{19}H_{18}IN_3OZn$ (496.7), calcd.: C 45.95, H 3.65, N 8.46, found: C 44.37, H 3.55, N 8.12. − ^{1}H NMR (DMSO): δ = 3.84 [s, 2 H, NCH_2Ph], 4.15 [s, 4 H, NCH_2Py], 6.39−7.06 [m, 4 H, Ph], 7.65−7.69 [m, 4 H, H_β(Py), H_δ(Py)], 8.17 [dd, J = 7.5 Hz, 6.6 Hz, 2 H, H_γ(Py)], 8.79 [d, J = 4.2 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1609s, 1482vs, 1441m, 1293m, 1273s.

2a: 200 mg (0.74 mmol) of $\mathbf{L}^2$ and 30 mg (0.74 mmol) of NaOH were dissolved in 10 ml of methanol. 101 mg (0.74 mmol) of $ZnCl_2$ in 10 ml of methanol were added. A flask containing diethyl ether was then connected to the reaction flask by a glass tube. After 2 d, the product had precipitated and was filtered off. Recrystallization from methanol/water (1:1) yielded 96 mg (35%) **2a** as colourless microcrystals, m.p. 258°C (dec.). − $C_{15}H_{16}ClN_3O_2Zn$ (371.2), calcd.: C 48.54, H 4.34, N 11.32, found: C 48.07, H 4.16, N 10.95. − ^{1}H NMR (D_2O): δ = 2.15 [t, J = 7.1 Hz, 2 H, $CH_2(C_2)$], 3.89 [t, J = 7.1 Hz, 2 H, $CH_2(C_1)$], 4.23 [s, 4 H, NCH_2Py], 7.45−7.56 [m, 4 H, H_β(Py), H_δ(Py)], 8.00 [dd, J = 7.8 Hz, 7.7 Hz, 2 H, H_γ(Py)], 8.57 [d, J = 5.2 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1605vs, 1441m, 1395m.

2b: Like **2a** from 150 mg (0.55 mmol) of $\mathbf{L}^2$, 22 mg (0.55 mmol) of NaOH, and 124 mg (0.55 mmol) of $ZnBr_2$. Yield 98 mg (43%) of **2b**, colourless microcrystals, m.p. 259°C (dec.). − $C_{15}H_{16}BrN_3O_2Zn$ (415.6), calcd.: C 43.35, H 3.88, N 10.11, found: C 42.43, H 3.81, N 9.79. − ^{1}H NMR (D_2O): δ = 1.99 [t, J = 6.9 Hz, 2 H, $CH_2(C_2)$], 2.75 [t, J = 6.9 Hz, 2 H, $CH_2(C_1)$], 4.12 [s, 4 H, NCH_2Py], 7.36−7.43 [m, 4 H, H_β(Py), H_δ(Py)], 7.87 [dd, J = 7.8 Hz, 7.7 Hz, 2 H, H_γ(Py)], 8.43 [d, J = 4.1 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1600vs, 1440m, 1365m.

2c: Like **2a** from 200 mg (0.74 mmol) of $\mathbf{L}^2$, 30 mg (0.74 mmol) of NaOH, and 236 mg (0.74 mmol) of ZnI_2. Yield 282 mg (82%) of **2c**, colourless needles, m.p. 223°C (dec.). − $C_{15}H_{16}IN_3O_2Zn$ (462.6), calcd.: C 38.95, H 3.49, N 9.08, found: C 38.39, H 3.93, N 8.57. − ^{1}H NMR (D_2O): δ = 2.18 [t, J = 5.8 Hz, 2 H, $CH_2(C_2)$], 2.93 [t, J = 5.8 Hz, 2 H, $CH_2(C_1)$], 4.28 [s, 4 H, NCH_2Py], 7.50−7.60 [m, 4 H, H_β(Py), H_δ(Py)], 8.03 [dd, J = 7.8 Hz, 7.7 Hz, 2 H, H_γ(Py)], 8.60 [d, J = 4.8 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1607s,1539vs, 1441m.

3: 200 mg (0.66 mmol) of $\mathbf{L}^1$ were dissolved in 10 ml of toluene. Diethylzinc (0.66 ml, 0.66 mmol) was added as a 1 M solution in hexane. Then, 62 mg (0.66 mmol) of phenol dissolved in 5 ml of toluene were added while stirring. Upon addition of the phenol the raw product **3** was precipitated and filtered off. Recrystallization from ethanol/water (1:1) yielded 162 mg (53%) of **3** as colourless crystals, m.p. 224°C. − $C_{25}H_{23}N_3O_2Zn$ (462.9), calcd.: C 64.87, H 5.01, N 9.08, found: C 63.74, H 4.98, N 8.97. − ^{1}H NMR ($CDCl_3$): δ = 3.68 [s, 2 H, NCH_2Ph], 3.70 [d, J = 15.8 Hz, 2 H, NCH_2Py], 4.00 [d, J = 15.8 Hz, 2 H, NCH_2Py], 6.42−7.23 [m, 13 H, Ph, H_β(Py), H_δ(Py), O-Ph], 7.72 [dd, J = 7.1 Hz, 6.3 Hz, 2 H, H_γ(Py)],

8.90 [d, J = 5.7 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1607s, 1591s, 1478vs, 1454m, 1437m, 1308vs.

4a: 200 mg (0.66 mmol) of $\mathbf{L}^1$ were dissolved in 10 ml of toluene. $Zn[N(SiMe_3)_2]_2$ (255 mg, 0.66 mmol) were added. Then, 67 µl (73 mg, 0.66 mmol) of thiophenol dissolved in 5 ml of toluene were added while stirring. Upon addition of the thiophenol the raw product **4a** was precipitated and filtered off. Recrystallization from ethanol yielded 130 mg (41%) of **4a** as a colourless solid, m.p. 104°C. − $C_{25}H_{23}N_3OSZn$ (479.0), calcd.: C 62.70, H 4.84, N 8.77, found: C 57.38, H 4.17, N 7.91. − ^{1}H NMR ($CDCl_3$): δ = 3.67 [s, 2 H, NCH_2Ph], 3.78 [d, J = 15.7 Hz, 2 H, NCH_2Py], 3.98 [d, J = 15.7 Hz, 2 H, NCH_2Py], 6.30−7.73 [m, 15 H, Ph, H_β(Py), H_δ(Py), H_γ(Py), S-Ph], 9.02 [d, J = 5.4 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1603s, 1478vs, 1437m, 1312s.

4b: Like **4a** from 200 mg (0.66 mmol) of $\mathbf{L}^1$, 255 mg (0.66 mmol) of $Zn[N(SiMe_3)_2]_2$, and 95 mg (0.66 mmol) of 4-chloro-thiophenol. Yield 149 mg (44%) of **4b** as colourless crystals, m.p. 142°C. − $C_{25}H_{22}ClN_3OSZn$ (513.4), calcd.: C 58.49, H 4.32, N 8.19, found: C 58.47, H 4.39, N 7.91. − ^{1}H NMR ($CDCl_3$): δ = 3.67 [s, 2 H, NCH_2Ph], 3.80 [d, J = 15.8 Hz, 2 H, NCH_2Py], 3.91 [d, J = 15.8 Hz, 2 H, NCH_2Py], 6.35−7.28 [m, 12 H, Ph, H_β(Py), H_δ(Py), S-Ph], 7.70 [dd, J = 9.5 Hz, 8.7 Hz, 2 H, H_γ(Py)], 9.00 [d, J = 5.5 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1604s, 1477vs, 1438m, 1309s, 1093s.

5: Like **3** from 200 mg (0.66 mmol) of $\mathbf{L}^1$, 0.66 ml (0.66 mmol) of diethylzinc as a 1 M solution in hexane, and 164 mg (0.66 mmol) of diphenylphosphate. Yield 303 mg (74%) of **5** as colourless crystals, m.p. 91°C. − $C_{31}H_{28}N_3O_5PZn \cdot 2\ H_2O \cdot CH_3OH$ (618.9 + 36.0 + 32.0), calcd.: C 55.95, H 5.28, N 6.12, found: C 56.09, H 4.51, N 6.31. − ^{1}H NMR ($CDCl_3$): δ = 3.77 [s, 2 H, NCH_2Ph], 3.81 [d, J = 15.8 Hz, 2 H, NCH_2Py], 4.03 [d, J = 15.8 Hz, 2 H, NCH_2Py], 6.42−7.46 [m, 18 H, Ph, H_β(Py), H_δ(Py), P-O-Ph], 7.78 [dd, J = 7.6 Hz, 6.4 Hz, 2 H, H_γ(Py)], 9.04 [d, J = 4.4 Hz, 2 H, H_α(Py)]. − ^{31}P NMR ($CDCl_3$): δ = −11.63. − IR (KBr): $\tilde{\nu}$ = 1608s, 1595s, 1485vs, 1453m, 1437m, 1296s, 1267s, 1205s, 1104vs.

6: 200 mg (0.66 mmol) of $\mathbf{L}^1$ were dissolved in 10 ml of methylene chloride. 37 mg (0.66 mmol) of KOH in 5 ml of methanol were added, and the mixture was stirred for 10 min. Then, 244 mg (0.66 mmol) of $Zn(ClO_4)_2 \cdot 6\ H_2O$ in 5 ml of methanol were added while stirring. The solution became cloudy and was then refluxed for 30 min. After this, another 37 mg (0.66 mmol) of KOH in 5 ml methanol were added and the solution stirred overnight. The precipitate formed was removed by filtration. The filtrate was evaporated to dryness . Recrystallization from chloroform yielded 90 mg (23%) of **6** as colourless crystals, m.p. 274°C (dec.). − $C_{19}H_{18}ClN_3O_5Zn \cdot CHCl_3$ (469.2 + 119.4), calcd.: C 40.81, H 3.25, N 7.14, found: C 40.23, H 3.16, N 6.93. − ^{1}H NMR (DMSO): δ = 3.76 [s, 2 H, NCH_2Ph], 4.08 [s, 4 H, NCH_2Py], 6.36−6.99 [m, 4 H, Ph], 7.58−7.62 [m, 4 H, H_β(Py), H_δ(Py)], 7.91 [dd, J = 7.9 Hz, 7.7 Hz, 2 H, H_γ(Py)], 8.70 [d, J = 4.3 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1611s, 1485s, 1445m, 1274m, 1090vs.

7: 200 mg (0.74 mmol) of $\mathbf{L}^2$ and 30 mg (0.74 mmol) of NaOH were dissolved in 10 ml of methanol. 244 mg (0.74 mmol) of $Zn(ClO_4)_2 \cdot 6\ H_2O$ in 10 ml of methanol were added, and the mixture was stirred for 10 min. The solution became cloudy and after 5 min, **7** precipitated as a white solid. Recrystallization from water yielded 171 mg (53%) of **7** as colourless microcrystals, m.p. 296°C (dec.). − $C_{15}H_{16}ClN_3O_6Zn$ (435.2), calcd.: C 41.40, H 3.71, N 9.66, found: C 41.14, H 3.49, N 9.56. − ^{1}H NMR (D_2O): δ = 2.10 [t, J = 7.0 Hz, 2 H, $CH_2(C_2)$], 2.85 [t, J = 7.0 Hz, 2 H, $CH_2(C_1)$], 4.19 [s, 4 H, NCH_2Py], 7.40−7.50 [m, 4 H, H_β(Py), H_δ(Py)], 7.96 [dd, J = 7.9 Hz, 7.7 Hz, 2 H, H_γ(Py)], 8.51 [d, J = 5.0 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1607s, 1548s 1484m, 1441m, 1088vs.

8: 200 mg (0.74 mmol) of $\mathbf{L}^2$ and 30 mg (0.74 mmol) of NaOH were dissolved in 10 ml of methanol.193 mg (0.74 mmol) of

Table 1. Crystallographic details

	1a	**5**	**6**	**8**
formula	$C_{19}H_{18}ClN_3OZn$	$C_{31}H_{29}N_3O_5PZn \cdot CH_3OH \cdot 2\ H_2O$	$C_{38}H_{36}Cl_2N_6O_{10}Zn_2 \cdot 2\ CHCl_3$	$C_{15}H_{16}N_4O_5Zn \cdot CH_3OH$
mol. mass	405.18	686.98	1177.10	429.73
cryst. from	CH_2Cl_2/hexane	CH_3OH/H_2O	$CHCl_3$	CH_3OH
crystal size [mm]	0.3 × 0.5 × 1.0	0.4 × 0.5 × 0.5	0.3 × 0.4 × 0.5	0.5 × 0.6 × 0.6
space group	$P-1$	$P-1$	$P-1$	$P2_1/n$
Z	2	2	2	4
a [Å]	6.835(1)	9.503(2)	12.641(5)	9.968(2)
b [Å]	12.586(2)	12.855(3)	14.085(8)	7.866(2)
c [Å]	13.168(2)	13.453(3)	15.555(11)	23.089(5)
α [°]	107.26(1)	90.87(3)	89.92(5)	90
β [°]	101.38(1)	93.49(3)	68.06(5)	94.79(3)
γ [°]	102.32(1)	106.90(3)	66.09(4)	90
V [Å^3]	1014.8(3)	1568.6(6)	2311(2)	1804.0(7)
d(calc.) [g·cm^{-3}]	1.33	1.45	1.69	1.58
temp. (K)	293	293	183	293
µ(Mo-$K\alpha$) [mm^{-1}]	1.35	0.89	1.56	1.40
Θ range [°]	3.7−26.0	2.4−26.1	2.7−26.0	2.7−26.0
hkl range	h: −8 to 8 k: −15 to 14 l: 0 to 16	h: −11 to 0 k: −15 to 15 l: −16 to 16	h: −15 to 14 k: −17 to 0 l: −19 to 19	h: 0 to 12 k: 0 to 9 l: −28 to 28
refl. measd.	4152	6556	9423	3735
indep. refl.	3972	6164	9035	3524
obs. refl. [$I>2\sigma(I)$]	3392	4621	6879	2881
parameters	226	406	595	244
refl. refined	3972	4621	9021	3524
R (obs. refl.)	0.065	0.053	0.051	0.040
R (all refl.)	0.211	0.163	0.175	0.119
min. / max. residual el. density [e·Å^{-3}]	+1.1 / −1.2	+0.8 / −0.8	+1.0 / −1.1	+1.0 / −0.7

$Zn(NO_3)_2 \cdot 4\ H_2O$ in 10 ml of methanol were added. A flask containing diethyl ether was then connected to the reaction flask by a glass tube. After 2 d, crystallization yielded 191 mg (65%) of **8** as colourless crystals, m.p. 238°C (dec.). − $C_{15}H_{16}N_4O_5Zn \cdot CH_3OH$ (397.7 + 32.0), calcd.: C 44.72, H 4.69, N 13.04, found: C 43.24, H 4.13, N 13.36. − ^1H NMR (D_2O): δ = 2.17 [t, J = 5.6 Hz, 2 H, $CH_2(C_2)$], 3.91 [t, J = 5.6 Hz, 2 H, $CH_2(C_1)$], 4.27 [s, 4 H, NCH_2Py], 7.52−7.59 [m, 4 H, H_β(Py), H_δ(Py)], 8.03 [dd, J = 7.7 Hz, 7.6 Hz, 2 H, H_γ(Py)], 8.59 [d, J = 4.8 Hz, 2 H, H_α(Py)]. − IR (KBr): $\tilde{\nu}$ = 1609s, 1541m, 1384vs, 1363vs.

Structure Determinations[30]: Crystals were obtained from the reaction solutions. Diffraction data were recorded with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 0.7107 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite[31]. Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$. Drawings were produced with SCHAKAL[32]. Table 1 lists the crystallographic data.

☆ Dedicated to Prof. *H. Nöth* on the occasion of his 70th birthday.

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