A Tripod Ligand with Three Different "Legs" and Some Chiral Zinc Complexes Thereof

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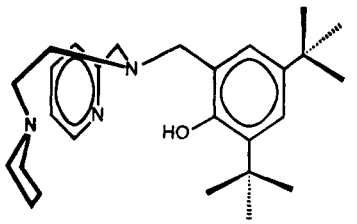
Stepwise alkylation of 2-picolylamine has yielded the unsymmetrical tripodal amine ligand (2-picolyl)(*N*-pyrrolidinylethyl)(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (**L**). In the presence of diethylzinc, **L** is deprotonated at the phenolic OH function with formation of the unstable complex **L**·Zn–Et (**1**). **1** can be used as an intermediate for the synthesis of chiral **L**·Zn–X complexes by protolysis. Thus, with 2,4-dibromophenol, **L**·Zn–$OC_6H_3Br_2$ (**2**) is obtained, and with diphenylphosphoric acid, **L**·Zn–$OPO(OPh)_2$ (**3**) is formed. The low symmetry of the ligand **L** allows detailed NMR assignments. Complex **2** was subjected to a crystal structure determination.

Introduction

Two attractive areas in the coordination chemistry of zinc are metal-mediated organic synthesis[1] and the modeling of metalloenzymes.[2] In both cases the design of the metal's coordination sphere is critical. Specifically in the bioinorganic chemistry of zinc, where basic coordination types and reactivity patterns have now been modeled,[2-10] stereocontrol by spatially demanding or chiral ligands is becoming a challenge. In this context it should be desirable not only that the ligands provide a protective pocket of the correct polarity around the zinc ion but also that the shape and electronic nature of this pocket direct the stereochemistry of the reactions of the metal-bound substrates.

While the methodology of stereocontrol by the ligands has been developed to a large extent for asymmetric organometallic catalysis[11] or more recently for self-assembly processes of some coordination compounds,[12] it is still in its beginnings for substrate reactions of classical complexes.[13] Specifically in the field of zinc-bound substrates (organometallic or bioinorganic) we are not aware of any such reactivity control. We are therefore trying to find or develop asymmetric ligands for this purpose. Our approach is based on our experience with encapsulating tripod ligands derived from the prototypes tris(aminomethyl)methane (tridentate, e.g. pyrazolylborates[6]) and tris(aminoethyl)amine (tetradentate, e.g. imidazolylmethylamines[14]). We have used variants of these types with two different donor sets, e.g. N_2S[15] and N_2O.[16] This paper now describes our first tripod ligand with three different donor "legs", the ligand **L**, and some preliminary zinc complex chemistry thereof.



L

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere in freshly distilled solvents. The experimental techniques and the standard IR and NMR equipment were described previously.[17] Starting materials were purchased from Aldrich. In order to obtain correct assignments for the NMR resonances, ^{1}H-^{1}H-homo-COSY, ^{1}H-^{1}H-NOESY, and ^{1}H-^{13}C-hetero-COSY measurements were performed for the ligand **L**.

Synthesis of the Chiral Ligand L. Ligand **L** was constructed from the two components (2-pyridylmethyl)(1-pyrrolidinylethyl)amine (**E1**) and (2,4-di-*tert*-butyl)(6-chloromethyl)phenol (**E2**); cf. formulas below.

Component E1. *N*-(2-Chloroethyl)pyrrolidine hydrochloride (5.10 g, 30.0 mmol) was dissolved in 2-picolylamine (13.1 g, 121 mmol), and the solution was stirred for 20 h. The resulting orange suspension was washed with 20 mL of a saturated aqueous K_2CO_3 solution. The organic phase was collected, dried over Na_2SO_4, and stirred for 30 min with solid K_2CO_3 (6.3 g, 45 mmol). Then the supernatant organic layer was removed with a pipet, stirred for 5 d, washed with saturated K_2-

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CO_3 solution, and dried again over Na_2SO_4. Distillation through a 10 cm Vigreux column at 115−130 °C/0.05 mmHg yielded 2.42 g (39%) of **E1** as a light yellow liquid which is hygroscopic and air-sensitive. **E1** was identified by its NMR spectrum. Satisfactory elementary analyses could be obtained for the zinc complex **E1**·$ZnBr_2$, which was precipitated from equimolar amounts of **E1** and $ZnBr_2$ in ethanol/ether (1:1) in 85% yield. ^{1}H-NMR of **E1** ($CDCl_3$): δ 1.76 (mm, 4H, pyrrolidine), 2.04 (s, 1H, NH), 2.49 (m, 4H, pyrrolidine), 2.64 (t, J = 5.8, 2H, ethylene), 2.78 (t, J = 5.8, 2H, ethylene), 3.93 (s, 2H, methylene), 7.12−7.60 (m, 2H, pyridine), 7.64 (t, J = 6.0, 1H, pyridine), 8.55 (d, J = 6.0, 1H, pyridine).

Component E2. A solution of 2,4-di-*tert*-butyl phenol (20.0 g, 96.9 mmol) in toluene (60 mL) was cooled to 2 °C. HCl gas was bubbled through the solution with stirring for 5 min, during which time the liquid turned deep yellow. Paraformaldehyde (3.80 g, 127 mmol) was added with stirring in several portions. After being stirred for another 5 min, the reaction mixture was brought to room temperature, and a vigorous stream of HCl gas was passed through for 1 h. The paraformaldehyde was dissolved, and 3 mL of an aqueous phase was formed. After a further 45 min of stirring, the aqueous phase was removed and the organic phase was washed twice with water (10 mL) and once with 15 mL of an ice-cold saturated aqueous $NaHCO_3$ solution. Then the solution was dried over K_2CO_3 and the solvent removed *in vacuo*; 20.5 g (83%) of **E2** was left behind as a very viscous orange oil. **E2** was identified by its NMR spectrum and used without further purification. ^{1}H-NMR ($CDCl_3$): 1.29 (s, 9H, *tert*-butyl), 1.43 (s, 9H, *tert*-butyl), 4.69 (s, 2H, CH_2), 7.04 (d, J = 2.9, 1H, phenyl), 7.30 (d, J = 2.9, 1H, phenyl).

Ligand L. Component **E1** (4.47 g, 21.8 mmol) and component **E2** (5.58 g, 21.9 mmol) in a solvent mixture of triethylamine (10 mL) and dioxane (15 mL) were refluxed for 3 d. After being cooled to 40 °C, the solution was pipeted off the amine hydrochloride precipitate and evaporated to dryness *in vacuo*. The waxlike brown residue was dissolved in ether (68 mL) and triethylamine (10 mL), the solution filtered, and the filtrate evaporated to dryness again and kept in an oil pump vacuum for 2 h; 8.71 g (94%) of **L** remained as a brown raw product. This was dissolved at 40 °C in nonane (14 mL), and the solution was allowed to cool overnight. The first fraction of **L** thus obtained (2.32 g, 25%) consisted of large (2−5 mm) deep-yellow crystals, mp 82 °C, which after filtration, washing with a small amount of hexane, and cleaning (from some brown oil) with filter paper were analytically pure. Cooling the mother liquor to −30 °C for 2 d yielded a second fraction of **L** (2.02 g, 22%), which after the same workup was also analytically pure. Further fractions could only be obtained as a mixture of crystals and oil. For NMR data see the Results. Anal. Calc for $C_{27}H_{41}N_3O$: C, 76.55; H, 9.76; N, 9.92. Found: C, 77.27; H, 9.80; N, 10.02.

Identification of L·Zn−Et (1). Ligand **L** (0.20 g, 0.47 mmol) was dissolved in hexane (5 mL), and diethylzinc (0.64 mL, 0.71 mmol) was added as a 1.1 M solution in hexane. After being refluxed for 1 h, the solution was allowed to stand overnight. The mother liquor was removed from the yellowish precipitate of **1** (0.18 g, 75%) with a pipet. The ^{1}H-NMR spectrum of **1** (see Results) showed only small amounts of impurities. Upon attempted recrystallization from various solvents, insoluble precipitates of decomposition products were formed.

In order to prove that **1** contains the unchanged ligand **L**, the raw product **1** (0.14 g, 0.27 mmol) was dissolved in benzene (4 mL). Pentane (5 mL) was added and the solution filtered off from small amounts of a yellowish precipitate. The solution was evaporated to dryness. The residue was treated with water (2 mL), glacial acetic acid (0.1 mL), and dichloromethane (10 mL), and the mixture was stirred for a few minutes. The dichloromethane phase was separated from the mixture and evaporated to dryness again. Ligand **L** (0.10 g, 87%) remained as a yellow glassy raw material, which was identified by its ^{1}H and ^{13}C NMR spectra.

L·Zn−OC$_6$H$_3$Br$_2$ (2). Ligand **L** (153 mg, 0.36 mmol) and 2,4-dibromophenol (92 mg, 0.37 mmol) were dissolved in toluene (8 mL). Diethylzinc (0.33 mL, 0.36 mmol) was added as a 1.1 M solution in hexane. The reaction mixture was kept for 1 d at room temperature and for 2 d at −1 °C, during which time a colorless precipitate formed. The mother liquor was removed with a pipet, and the precipitate was washed with 3 mL of pentane and dried in vacuo for 2 min. Complex **2** (224 mg, 75%) remained as a toluene solvate in the form of colorless crystals. Anal. Calc for $C_{33}H_{43}Br_2N_3O_2Zn$·C_7H_8: C, 57.81; H, 6.19; N, 5.06. Found: C, 57.50; H, 6.18; N, 5.02. Pumping for extended periods of time produced a white powder of **2** (mp 206 °C) which according to NMR and elemental analysis was not completely free of toluene.

L·Zn−OPO(OPh)$_2$ (3). Ligand **L** (151 mg, 0.36 mmol) and diphenylphosphoric acid (148 mg, 0.59 mmol) were dissolved in toluene (10 mL). Diethylzinc (0.54 mL, 0.59 mmol) was added as a 1.1 M solution in hexane. The reaction mixture was kept at room temperature for 2 d while a colorless precipitate formed. The mother liquor was removed with a pipet. The precipitate was washed with toluene (10 mL) and pentane (10 mL) and dried in vacuo. Complex **3** (134 mg, 27%) remained as a colorless crystalline powder, mp 152 °C. Anal. Calc for $C_{39}H_{50}N_3O_5PZn$: C, 63.57; H, 6.84; N, 5.70. Found: C, 62.48; H, 6.72; N, 5.36.

Structure Determination. Crystals of **2** were obtained by dissolving the above-mentioned, nearly toluene-free powder in ethanol/water (2:1) and slow evaporation of the ethanol through a perforated septum. Diffraction data were recorded with the $\omega/2\theta$ scan mode in the 2θ range 3−47° on a Nonius CAD4 diffractometer fitted with a molybdenum tube (λ = 0.710 73 Å) and a graphite monochromator at 294 K. An absorption correction based on ψ scans[18] was applied. Scattering factors were obtained from common sources.[19] The structure was solved with Patterson methods and refined anisotropically.[20] Hydrogen atoms were included on fixed positions (C−H = 0.96 Å) and treated with a common isotropic temperature factor. The drawing was made with the SCHAKAL program.[21]

The asymmetric unit in the space group $P\bar{1}$ contains two molecules of **2**. They are roughly related by a pseudotranslation along c. This translation symmetry is most noticeably broken by the orientation of the dibromophenyl rings (rotation about the phenolic C−O bond), the disposition of the tripod ligand (O−Zn−N angles in the equatorial plane of the trigonal-bipyramidal coordination about zinc), and the orientation of the *tert*-butyl groups (different torsion angles). The overall appearances of both molecules are so similar, however, that they can be represented by one drawing. In both independent molecules, the locations of the outer parts of the dibromophenyl rings and parts of the *tert*-butyl groups are poorly defined, as evidenced by the high and very anisotropic thermal parameters. The immediate coordination sphere of zinc is well-defined, however, in both cases. Table 1 lists the crystallographic details, and Table 2 gives the atomic parameters of **2**.

Results

Preparations. The aim of the synthetic procedure leading to ligand **L** was to obtain a tripod which (i) contained three different "legs", (ii) possessed the three "legs" in the form of an N_2O donor set in order to model metalloenzymes with such a donor set, (iii) would be anionic in its complexes to enhance stability, i.e. contained an acidic OH. In contrast to our synthesis of the dipicolylglycine ligand,[16] we chose a phenolic OH as the acidic function. Otherwise the synthetic approach was the same as before;[16] i.e., we started with a functionalized amine containing the final anchoring point of the tripod as an NH_2 group. This time the amine was 2-picolylamine. Straightforward alkylation with (2-chloroethyl)pyrrolidine yielded the new intermediate **E1** containing two "legs" of the final tripod. The third "leg" was introduced in the form of the new (chloromethyl)phenol **E2** which bears two *tert*-butyl groups in order to increase the solubility of **L** in organic solvents and to improve the encapsulating properties of the tripod. **E2** was obtained by chloromethylation of 2,4-di-*tert*-butylphenol with paraformal-

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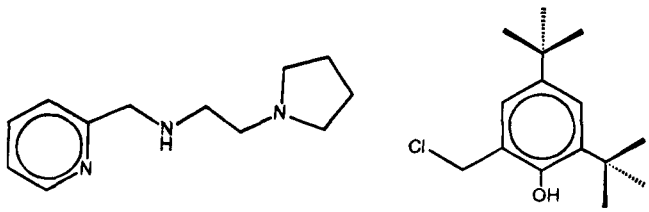
Table 1. Crystallographic Data for **2**

formula	$C_{33}H_{43}Br_2N_3O_2Zn$
mol wt	738.9
crystal size, mm	0.2 × 0.2 × 0.2
color	colorless
space group	*P*1
Z	4
a, Å	13.519(3)
b, Å	15.205(3)
c, Å	18.781(4)
α, deg	70.08(3)
β, deg	83.25(3)
γ, deg	67.05(3)
V, Å^3	3341.8(9)
density calcd, g/cm^3	1.47
density found, g/cm^3	1.40
μ, cm^{-1}	31.59
hkl range	$\pm h, \pm k, +l$
no. of reflns measd	9441
no. of indep reflns ($I \geq 2\sigma(I)$)	4637
no. of variables	739
R, unweighted	0.081
residual electron density, e/Å^3: max, min	+1.00, −1.03

dehyde and HCl. Combination of **E1** and **E2** produced ligand **L** in an overall yield of 18% based on 2-picolylamine. The final asset of ligand **L** turned out to be its ease of crystallization.



E1 **E2**

When preparing zinc complexes of **L**, our goals were (i) to obtain an enzyme model in the form of a **L**·Zn−OH complex and (ii) to find an entry to chiral organozinc chemistry. Both goals have been reached only partially so far, but our investigations have shown that chemistry derived thereof is possible.

In analogy to our syntheses of pyrazolylborate Zn−OH complexes,[6] we tried various combinations of **L**, $Zn(ClO_4)_2$, and KOH which so far did not allow us to isolate **L**·Zn−OH or (**L**·Zn−OH_2)ClO_4 although NMR spectra of the reaction solutions seem to indicate the presence of such species. Similarly, one of the entries to pyrazolylborate−zinc alkyl compounds, the reaction of the ligand with diethylzinc,[22] was not as easy with **L**. It did produce a compound, though, which according to its NMR spectrum (see below) we assume to be complex **1**.

L·Zn−Et
1

This complex was obtained as a yellowish precipitate from hexane which is highly air and moisture sensitive and which decomposed in benzene solution within 1−2 h. Chemical proof for the existence of **1** and for the fact that it contains the unchanged ligand **L** was obtained by hydrolytic destruction with acetic acid after which **L** could be recovered as a raw material in 87% yield.

The high sensitivity of **1** which renders a larger scale organic chemistry difficult proved to be advantageous for derivatizations which could not be started with the as yet unaccessible **L**·Zn−OH complex. Thus the acidic "substrate models" 2,4-dibromophenol and diphenylphosphoric acid which we had intended to use in condensation reactions with the "enzyme model" **L**·Zn−OH did react proteolytically with intermediately formed **1**. The resulting complexes **2** and **3**,which were obtained in

L·Zn−$OC_6H_3Br_2$ **2** **L**·Zn−$OPO(OPh)_2$ **3**

good to reasonable yields, contain the Zn−O−substrate combinations which we intended to make. Both **2** and **3** are air- and moisture-stable zinc complexes which according to their spectra (see below) contain the coligands bound in a unidentate fashion.

Spectra. The IR spectra of **L** and its complexes offer little information. A typical indicator of complex formation by pyridine-*N* coordination[23] is observed: the strong band of **L** at 1590 cm^{-1} is shifted to 1604−1607 cm^{-1} for the complexes. Other than that, only the strong phosphate bands for **3** at 1262, 1244, and 1210 cm^{-1} give direct evidence related to the complex constituents. The phosphate ligand in **3** is also characterized by its ^{31}P-NMR resonance at −13.6 ppm which is little, but significantly, different from that of diphenylphosphoric acid at −9.3 ppm.

The unsymmetrical nature of **L** gives rise to many resonances in the ^{1}H- and ^{13}C-NMR spectra which secure the identification of its derivatives and give some information on the bonding of the coligands. Tables 3 and 4 list the data which were verified with 2D-NMR experiments.

The best indication of the chirality of ligand **L** in its complexes and hence the complexes as a whole is obtained from the ^{1}H-NMR resonances. Thus the two H atoms of the CH_2 group of Zn−Et in **1** are diastereotopic, giving rise to two closely spaced quartet signals. Likewise the N−CH_2−pyridine and N−CH_2−phenol methylene groups produce two signals each with strong geminal couplings in all three complexes, reflecting the rigid structures of the complexes and the chemical nonequivalence of the CH_2 protons. This is not the case for the free ligand due to possible inversion at the central nitrogen and free rotation about its C−N bonds. For the same reason, the four ethylene H atoms which are nearly isochronous in the free ligand all become nonequivalent in the complexes, as a result of which they produce broad multiplet patterns for **1**−**3**. Thus, while the free ligand **L** should be called prochiral rather than chiral, the chirality of the complexes **1**−**3** is well-documented.

While the ^{1}H-NMR resonances of the pyrrolidine and most of the pyridine ring protons are of little diagnostic value, the 6-CH (pyridine H_α) resonance gives significant information about the bonding of the coligands. It is shifted by 0.9 and 0.7 ppm to lower field for complexes **2** and **3** relative to free **L**. On the basis of the structure determination of **2** (see below), this can be related to the relative orientations of the pyridine ring and the aromatic rings of the coligands. In solid **2** the two rings are close to being coplanar, which means that they mutually exert maximal downfield NMR shifts. This orientation seems to be maintained in solutions of **2** and seems to be similar in solutions of **3**. This in turn means that there is limited orientational freedom in the protective pocket created around the zinc ion by ligand **L**, thus making chirality effects due to ligand **L** possible.

The ^{13}C-NMR spectra show only small signal shifts due to coordination. Thus they are mainly of diagnostic value. For **L** all aromatic resonances were assigned. From this and the

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **2**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Zn1	2306(1)	1272(1)	9189(1)	49(1)	Zn2	1654(1)	1206(1)	4203(1)	45(1)
O11	3572(7)	198(7)	9052(5)	51(6)	O21	1498(7)	−7(7)	4193(5)	51(6)
O12	1622(8)	1864(8)	8169(6)	67(7)	O22	1855(8)	1838(8)	3104(5)	56(7)
N11	2642(9)	612(9)	10463(7)	51(7)	N21	1737(9)	580(8)	5501(6)	47(8)
N12	820(9)	1219(10)	9658(8)	61(8)	N22	3101(9)	1210(8)	4466(7)	47(7)
N13	2505(10)	2517(8)	9342(7)	55(8)	N23	372(9)	2462(9)	4446(7)	51(7)
Br11	−426(2)	3188(2)	7185(1)	87(1)	Br21	2342(2)	3469(2)	1817(1)	91(2)
Br12	2500(3)	4170(3)	5012(1)	165(4)	Br22	−1366(2)	3760(2)	545(2)	153(2)
C1	3776(10)	−754(11)	9499(7)	40(7)	C1A	2097(11)	−909(10)	4649(8)	45(8)
C2	3792(10)	−1011(11)	10289(8)	47(8)	C2A	2086(11)	−1130(11)	5441(7)	46(9)
C3	3931(11)	−1979(11)	10752(8)	52(9)	C3A	2629(12)	−2080(11)	5933(8)	52(10)
C4	4058(11)	−2749(11)	10479(9)	53(9)	C4A	3249(11)	−2866(11)	5659(9)	52(8)
C5	4101(11)	−2495(11)	9686(9)	52(9)	C5A	3265(12)	−2650(11)	4877(9)	53(9)
C6	3961(11)	−1555(11)	9197(8)	49(9)	C6A	2736(12)	−1721(11)	4374(8)	49(9)
C7	3950(14)	−1336(13)	8338(9)	72(13)	C7A	2820(13)	−1537(12)	3518(9)	62(12)
C8	4777(14)	−849(14)	7948(10)	82(13)	C8A	3565(18)	−2475(14)	3330(11)	105(19)
C9	2819(15)	−596(14)	7990(8)	81(15)	C9A	1707(15)	−1205(13)	3165(9)	77(15)
C10	4231(16)	−2263(13)	8100(10)	85(16)	C10A	3269(15)	−683(14)	3134(9)	79(14)
C11	4186(13)	−3814(11)	10983(8)	57(12)	C11A	3855(13)	−3923(11)	6202(10)	66(11)
C12	3935(18)	−3884(13)	11803(9)	91(20)	C12A	5055(15)	−4191(16)	6146(15)	140(13)
C13	5296(15)	−4535(12)	10914(11)	87(15)	C13A	3572(19)	−4684(15)	6010(14)	116(20)
C14	3403(15)	−4180(13)	10716(11)	86(14)	C14A	3527(20)	−4024(17)	7038(10)	121(23)
C15	3693(11)	−224(10)	10614(8)	51(9)	C15A	1387(12)	−290(10)	5757(8)	52(10)
C16	2647(13)	1453(12)	10682(10)	65(10)	C16A	986(13)	1420(10)	5756(8)	59(12)
C17	3133(14)	2101(12)	10047(9)	66(12)	C17A	48(12)	2027(12)	5222(9)	62(10)
C18	3106(15)	2994(14)	8690(10)	80(13)	C18A	−538(13)	2958(14)	3916(10)	74(10)
C19	2280(18)	3958(13)	8202(11)	92(19)	C19A	−420(17)	3910(15)	3372(13)	101(15)
C20	1190(18)	3973(14)	8540(11)	99(20)	C20A	636(18)	3856(13)	3623(12)	98(18)
C21	1462(13)	3368(12)	9344(10)	74(11)	C21A	788(15)	3244(12)	4400(9)	73(14)
C22	1786(12)	277(11)	10857(9)	60(10)	C22A	2825(12)	301(11)	5778(8)	55(10)
C23	769(12)	795(11)	10405(9)	51(9)	C23A	3422(11)	879(11)	5193(8)	50(9)
C24	−216(15)	776(14)	10718(11)	81(13)	C24A	4302(12)	993(12)	5415(9)	59(10)
C25	−1119(15)	1210(15)	10274(13)	86(12)	C25A	4874(12)	1460(13)	4874(10)	67(9)
C26	−1052(13)	1650(13)	9533(12)	76(10)	C26A	4566(13)	1781(13)	4131(10)	67(12)
C27	−58(14)	1634(12)	9236(10)	68(12)	C27A	3688(12)	1668(11)	3943(9)	56(9)
C28	1817(13)	2310(13)	7479(10)	67(11)	C28A	1211(12)	2190(11)	2546(9)	55(10)
C29	1028(12)	2987(12)	6925(8)	58(10)	C29A	1231(13)	2984(11)	1888(8)	55(11)
C30	1208(19)	3560(14)	6193(9)	85(19)	C30A	508(16)	3433(13)	1317(9)	71(13)
C31	3072(22)	2714(21)	6481(14)	102(20)	C31A	−286(17)	3081(17)	1353(12)	90(15)
C32	2311(26)	3342(22)	6010(13)	109(26)	C32A	−394(16)	2300(16)	1949(13)	84(14)
C33	2903(15)	2143(15)	7206(11)	81(13)	C33A	381(14)	1838(12)	2532(10)	69(13)

[a] Defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. ^{1}H-NMR Data ($CDCl_3$; **1** in C_6D_6; δ (ppm)/*J* (Hz))

	L	1	2	3
4-*t*-Bu	1.27 s	1.43 s	1.25	1.24 s
2-*t*-Bu	1.45 s	1.86 s	1.34 s	1.47 s
C−CH_2 (pyrrol)	1.75 m	1.49 m, br	1.74 m, br	1.68 m, br
N−CH_2 (pyrrol)	2.39 m	2.25 m, br	2.50−2.95[a]	2.43−2.94[a]
CH_2 (ethylene)	2.688 t/3.4	2.56−2.91[a]	2.50−2.95[a]	2.43−2.94[a]
CH_2 (ethylene)	2.691 t/3.4	2.56−2.91[a]	2.50−2.95[a]	2.43−2.94[a]
CH (CH_2−phenol)	3.75 s	3.41 d/11.8	3.54 d/11.6	3.51 d/10.3
CH (CH_2−phenol)	3.75 s	3.62 d/11.8	4.20 d/11.6	4.11 d/10.3
CH (CH_2−py)	3.76 s	3.57 d/14.8	3.74 d/16.2	3.76 d/16.6
CH (CH_2−py)	3.76 s	3.90 d/14.8	4.08 d/16.2	4.07 d/16.6
3-CH (phenol)	6.88 d/2.4	6.86 d/2.9	6.82 d/2.5	6.77 d/2.4
5-CH (phenol)	7.21 d/2.4	7.53 d/2.9	7.18 d/2.5	7.13−7.40[a]
3-CH (py)	7.31 d/7.8	6.45−6.52[a]	7.21−7.24[a]	7.13−7.40[a]
5-CH (py)	7.11 m	6.45−6.52[d]	7.35 m	7.13−7.40[a]
4-CH (py)	7.58 m	6.85 m[a]	7.79 m	7.72 m
6-CH (py)	8.48 d/4.9	8.19 d/4.4	9.36 d/4.6	9.15 d/5.0
coligand signals		0.60 q/8.2	7.10 dd/8.8, 2.6	7.13−7.40[a]
		0.62 q/8.2	5-CH	arom
		Zn−CH_2	7.21−7.24[a]	7.01 m (2H)
		1.71 t/8.2	6-CH	para CH
		C−CH_3	7.49 d/2.6	
			3-CH	

[a] Overlapping multiplets from different resonances.

Table 4. ^{13}C-NMR Data ($CDCl_3$; δ (ppm))

	L	2	3
CH_3 (*t*-Bu)	29.58	29.53	29.94
	29.67	31.87	31.86
C (*t*-Bu)	34.04	33.85	33.80
	34.90	35.23	35.33
C−CH_2 (pyrrol)	23.30	22.78	22.15
N−CH_2 (pyrrol)	53.71	55.62	55.80
CH_2 (ethylene)	51.79	51.79	52.37
CH_2 (ethylene)	52.75	54.10	53.55
CH_2 (phenol)	57.36	57.86	57.99
CH_2 (py)	60.07	59.56	59.38
aromatic range[a]	121.99[5], 122.14[f]	121.44, 122.14	120.38, 120.98
	122.93[c], 123.74[3]	123.12, 124.07	122.99, 123.12
	124.38[e], 135.60[b]	124.12, 125.30	124.13, 124.38
	136.21[4], 140.15[d]	125.61, 129.06	125.36, 129.11
	148.60[6], 153.84[a]	130.89, 133.51	134.98, 138.95
	158.97[2]	138.72, 139.52	139.62, 150.87
		151.23, 155.64	152.98, 155.45
			164.04

[a] Assignments: 2−6 = pyridine C2−C6; a−f = phenol C1−C6.

nonoccurrence of resonances near 148.6 ppm (pyridine C_α) for **2** and **3**, it can be concluded that the ring anisotropy shifts observed in the ^{1}H-NMR spectra for pyridine CH_α are active here as well. As the coligands in **2** and **3** contain only aromatic carbon, their assignment in the spectra was not attempted. Complex **1** was not stable enough for ^{13}C-NMR measurements.

Structure Determination. The structure determination was undertaken to verify the conclusion from the NMR data that **L** acts as a tetradentate tripod and to acquire information about the orientational freedom at the fifth coordination site of the metal atom. The choice of complex **2** for this purpose was

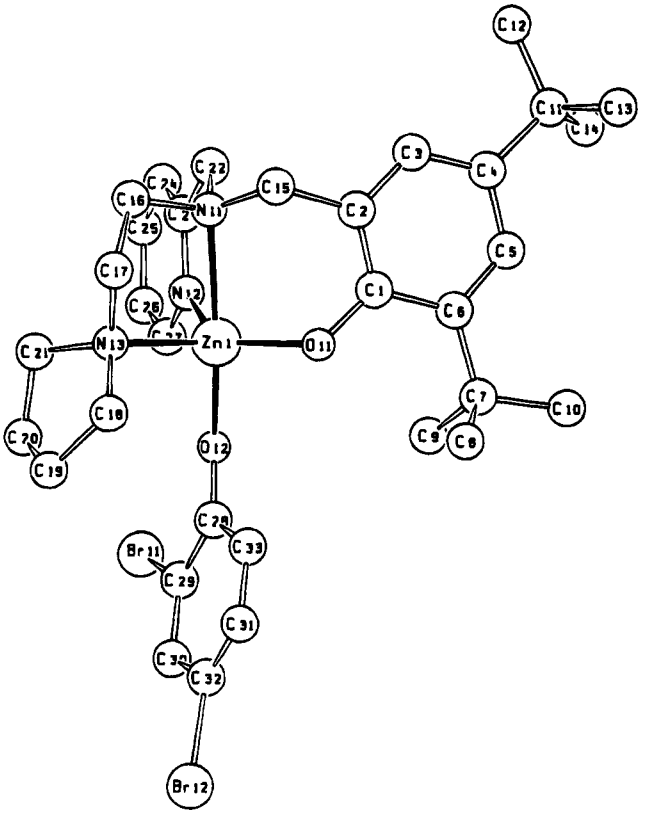

Figure 1. Structure of molecule 1 of complex **2**.

Table 5. Selected Bond Distances (Å) and Angles (deg) in **2**

	molecule 1	molecule 2
Zn1–O11	1.914(9)	1.942(9)
Zn1–O12	1.982(11)	1.994(9)
Zn1–N11	2.282(12)	2.295(11)
Zn1–N12	2.116(12)	2.076(11)
Zn1–N13	2.128(12)	2.164(12)
O11–C1	1.34(2)	1.33(2)
O12–C28	1.29(2)	1.27(2)
N11–C15	1.47(2)	1.49(2)
N11–C22	1.46(2)	1.47(2)
N11–C16	1.47(2)	1.48(2)
N13–C17	1.47(2)	1.47(2)
N13–C21	1.50(2)	1.48(2)
N13–C18	1.52(2)	1.46(2)
C15–C2	1.48(2)	1.52(2)
C22–C23	1.49(2)	1.52(2)
C16–C17	1.53(2)	1.49(2)
O11–Zn1–O12	101.3(4)	100.8(4)
O11–Zn1–N11	89.1(4)	88.8(4)
O11–Zn1–N12	129.1(5)	122.5(4)
O11–Zn1–N13	117.6(4)	124.5(4)
O12–Zn1–N11	164.7(4)	166.9(4)
O12–Zn1–N12	88.7(5)	90.7(4)
O12–Zn1–N13	102.7(5)	100.5(4)
N11–Zn1–N12	76.0(5)	76.6(4)
N11–Zn1–N13	82.0(5)	81.0(4)
N12–Zn1–N13	108.2(5)	107.8(4)
Zn1–O12–C28	139.3(11)	130.1(9)
Zn1–O11–C1	120.5(8)	120.8(8)

fortuitous, as the occurrence of two slightly different molecules in the asymmetric unit has offered the possibility of achieving just this goal. Figure 1 shows molecule 1; Table 5 lists the important molecular parameters for both molecules.

The coordination of the zinc ion in **2** is trigonal bipyramidal to a reasonably good approximation. Ligand **L** and zinc form two five-membered and one six-membered chelate rings. The "bite" angles of the five-membered rings (N11–Zn1–N12 and N11–Zn1–N13) are characteristically smaller than that of the six-membered ring (N11–Zn–O11). The Zn–N bond to the bridgehead nitrogen is the longest Zn–ligand bond, and all three intraligand angles involving the bridgehead nitrogen are smaller than 90°, which is characteristic of such tripod ligands.[14,16] The equatorial Zn–N bond lengths and both Zn–O distances are also in the normal range for such complexes with an N_3O_2 donor set.[7,16,24,25]

The unique features of **2** are thus the position and orientation of the dibromophenolate coligand. As the O12–Zn1–N11, O12–Zn1–N13, and O12–Zn1–O11 angles show, the bromophenolate ligand is bending away from the phenolate and pyrrolidine "legs" of the tripod, which are spatially more demanding than the pyridine "leg". This is also evident from the position of bromine substituent Br11 below the pyridine ring and the near-to-copolanar arrangement of the bromophenolate and pyridine rings (interplanar angle 11° in molecule 1 and 21° in molecule 2). Thus the bromophenolate ligand is locked in the ligand pocket around the zinc ion. Its degree of freedom can be judged from the variation of pertinent intra- and interligand angles among the two molecules of **2**. The largest variations here concern the interplanar angles just mentioned, the O11–Zn1–N12 and O11–Zn1–N13 angles, and the angle at the bromophenolate oxygen, Zn1–O12–C28. They are all in the 10° range and interrelated; i.e., a large Zn1–O12–C28 angle correlates with a small O11–Zn1–N13 angle, etc. All this points to the interpretation that the rotation about the Zn1–O12 bond is significantly limited due to the spatial requirements of ligand **L** as well as the coligand phenol's bromine substituents.

Discussion and Conclusions

Ligand **L** whose synthesis is not too cumbersome offers a good opportunity to prepare and investigate chiral classical complexes. In the coordinated form it is one of the few ligands that owe their chirality not to chiral centers on the back side of the donor atoms but to the chiral nature of the pivotal donor atom itself. The NMR spectra of **1**–**3** have shown the asymmetric nature of **L** and the rigidity of its complexes in solution. The structure determination of **2** has shown that the spatial nature of **L** is such that it imposes orientational restraints on coligands bound to the fifth coordination position of the zinc ion. The possibility of optical induction by stoichiometric or catalytic reactions of zinc complexes of **L** is thereby indicated.

The steric and electronic nature of **L** gives rise to a zinc complex chemistry which is noticeably different from that of the related ligand dipicolylglycine.[16] While the latter ligand allows coordination numbers 5 and 6 in quite similar compounds and its zinc complexes seem to dissociate to $[L{\cdot}Zn]^+$ species in solution, the ligand **L** described here seems to produce reliably inert molecular **L**·Zn–X species which are all trigonal bipyramidal. This may have to do with the fact that zinc complexes of dipicolylglycine are quite polar and require solvents like water while **L** and its complexes are formed and must be handed in nonpolar solvents.

We did not devote much effort in developing organozinc chemistry derived from **L**. Instead we used the lability of the ethylzinc complex **1** to prepare the coordination compounds **2** and **3**. **1** is unusual in that it is an organozinc compound of coordination number 5. Unlike in the (pyrazolylborato)zinc alkyls, which are quite stable,[22,26] the increased number of

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donors in **1** seems to labilize the organic part of the molecular complex too much to allow convenient handling.

The phenolate and phosphate complexes **2** and **3** bear relevance to enzymes containing five-coordinated zinc with mixed N/O donor sets. Thus the peptidase astacin[27] was found to have zinc of CN 5 in the active center bound to the phenolate oxygen of tyrosine. Likewise, some phosphatases have N_3O_2 donor sets including the Zn−O(phosphate) linkage.[28] This is why the acidic 2,4-dibromophenol and the diphenylphosphoric acid were chosen to make the first zinc complexes of **L**.

The successful synthesis and application of ligand **L** increase the accessibility of two goals of this work: to prepare stable stereocontrolled Zn−R compounds and to make an enzyme model of the type **L**·Zn−OH or **L**·Zn−OH_2. Whether the further goal of making optically active complexes of **L** can be achieved remains to be seen.

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Supplementary Material Available: A fully labeled structural diagram of molecule 2 of complex **2** and tables containing the details of data acquisition and refinement, all interatomic distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated parameters of hydrogen atoms (4 pages). Ordering information is given on any current masthead page.

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