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New Polar Pyrazolylborate Ligands and Their Basic Zinc Complex Chemistry

Cristina Pérez Olmo,[a] Karin Böhmerle,[a] Gunther Steinfeld,[a] and Heinrich Vahrenkamp*[a]

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By refinement of Trofimenko's procedures, four new tris(pyrazolyl)borate (Tp) ligands bearing pyridyl and carboxamide substituents at the 3-positions of the pyrazole rings, were obtained. Two of them were identified by structure determinations of their potassium salts. Their coordinative properties were explored by preparing Tp*Zn-X complexes, with X = Cl, Br, I, NO_3, OAc, phenolate, thiophenolate and diorganophosphate, including the cationic complexes $[Tp^*Zn{\cdot}L]^+$ with L = methanol and pyrazole. From the spectra and structure determinations of these complexes it has become evident that the polar Tp* ligands favor coordination numbers higher than four for zinc, either by inducing bidentate coordination of the coligands X and L, using the carboxamide oxygen atoms for coordination, or by linking two Tp*Zn-X units through the pyridyl nitrogen atoms. As a result, the structural chemistry of these complexes is quite varied, and includes coordination dimers and polymers.

Introduction

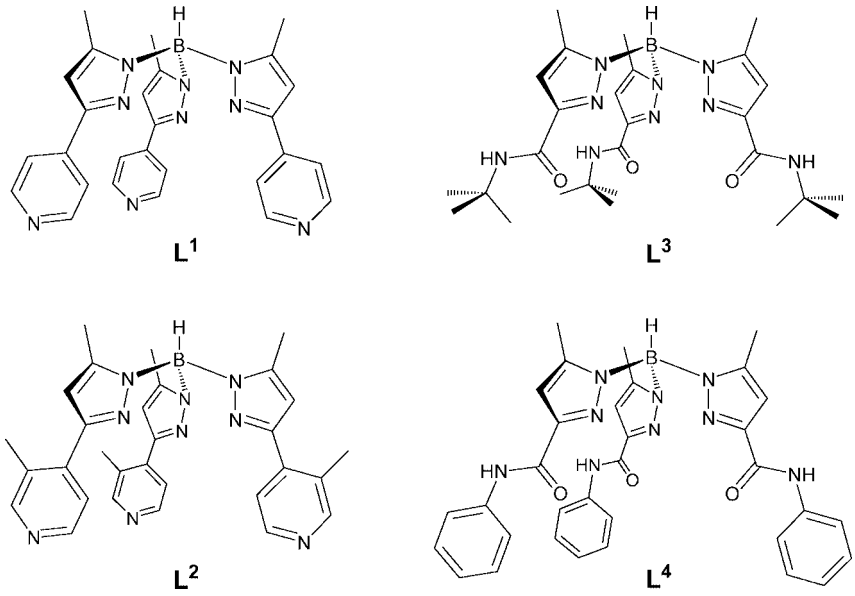
Trofimenko's tris(pyrazolyl)borate (Tp) ligands[1] have been the key to success in biomimetic zinc complex chemistry, in our own hands[2] as well as in those of our competitors,[3] as evidenced by Parkin's recent review.[4] One reason for this is the ease by which their structures can be varied, for example, by attaching various substituents at the 3- and 5-positions of their pyrazole rings. The substituents at the 3-positions create and control the protective pocket around the zinc ion, which is the "active center" of the enzyme model. Substituents as small as methyl groups at the 5-positions protect the B–N bonds, preventing hydrolytic self-destruction of the ligands due to the presence of zinc ions.

Until now most of the 3-substituted Tp ligands bear nonpolar, i.e. mostly hydrocarbon, substituents. This is due to the fact that most functional organic groups do not survive the reaction conditions during the Tp ligand synthesis that occurs in the presence of KBH_4 at 150–200 °C. The advantage of the nonpolar $Tp^{R,Me}$ ligands (with Me at the 5-positions and the variable R at the 3-positions) is that they can be relied upon to form tetrahedral zinc complexes including $Tp^{R,Me}$Zn-OH the essential enzyme model, and that the resultant ligand pocket around the zinc ion stabilizes many kinds of reaction products that model the intermediates of the zinc enzyme catalyzed processes.[2–4] Their disadvantage is that these "intermediates" form such stable zinc complexes that so far the $Tp^{R,Me}$Zn-OH species could not be used for catalytic processes, and that both the potassium salts and the zinc complexes of the Tp ligands are not soluble in water, thereby severely hampering their suitability as enzyme models.

Until now only a few attempts have been made to overcome these limitations. We have attached 3-pyridyl substituents to Tp ligands and studied their zinc complex chemistry,[5–7] and Ward did the same with 2-pyridyl groups.[8,9] Carrano reported Tp ligands with carboxylic ester and carboxamide substituents and a number of zinc complexes thereof;[10,11] unfortunately this work could not be reproduced by us.[12] In our eyes the most promising approach has been reported recently by Trofimenko and involved pyrrolidinocarbonyl substituents,[13] which have not yet been exploited in zinc complex chemistry. Insofar as zinc complexes of these Tp ligands with polar substituents have been studied, it was found that the benefit of their enhanced polarity comes along with a liability: the coordination number of zinc goes up to five or six, either by using the substituents' donor groups for coordination, or by the attachment of additional donor ligands.

In this paper we describe some attempts by our group to improve this situation. Our plan was to develop pyrazolylborate ligands whose polar substituents have a reduced tendency to coordinate to the zinc ion in the complex, but support the solubility of their zinc complexes in protic media by having the potential to form hydrogen-bonding interactions. The latter condition led to the choice of pyridyl and amide functionalities, and the former required these donor groups to point away from the metal ion, or to be sterically hindered. We succeeded in preparing four new ligands, **L^1**–**L^4** (Scheme 1). This paper demonstrates their suitability for

[a] Institut für Anorganische und Analytische Chemie der Universität Freiburg,
Albertstr. 21, 79104 Freiburg, Germany
Fax: +49-761-203-6001
E-mail: vahrenka@uni-freiburg.de



Scheme 1.

basic zinc complex chemistry. Their use for enzyme modeling will be the subject of a subsequent publication. It should be mentioned that the ligand hydridotris[3-(4′-pyridyl)pyrazolyl]borate, which is a relative of **L¹**, has recently been obtained and used in some complexes by Ward.[14]

Results and Discussion

Ligands L¹–L⁴

All four ligands were prepared according to Trofimenko's method, i.e. by heating the appropriate pyrazole with KBH_4. In case of **L¹** and **L²** the most cumbersome part of this synthesis was the preparation of the substituted pyrazoles, via the corresponding β-diketones, by previously reported procedures.[15–18] The best yields for the potassium salts of **L¹** and **L²** were obtained by heating KBH_4 with 4 equiv. of the pyrazole to 200 °C without solvent. In this way K**L¹** and K**L²** were obtained as colorless crystalline materials in yields of 40–50%. These compounds are insoluble in hydrocarbons, diethyl ether and chloroform, but soluble in DMSO, acetonitrile, methanol and water/methanol mixtures. The ligand K**L¹** possesses a rare property for pyrazolylborates in that it is, as expected, soluble in water.

The crystallinity of K**L¹** allowed its structure to be determined by X-ray diffraction. Figure 1 shows that the ligand **L¹** acts as a tripodal donor towards the potassium ion; however, the sideways coordination of the pyrazole nitrogen atoms N3 and N6 is weak. In addition, all the pyridyl nitrogen atoms are attached to different potassium ions. If one counts N3 and N6 as being coordinated at a single position, the potassium ions have a reasonably perfect octahedral coordination.

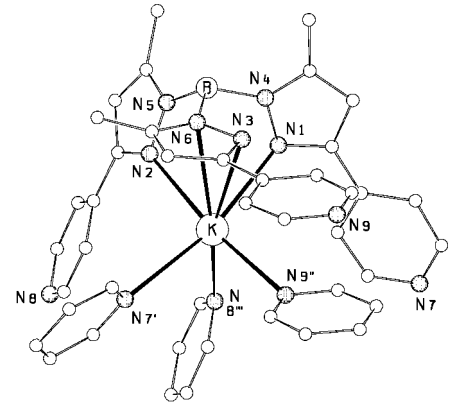
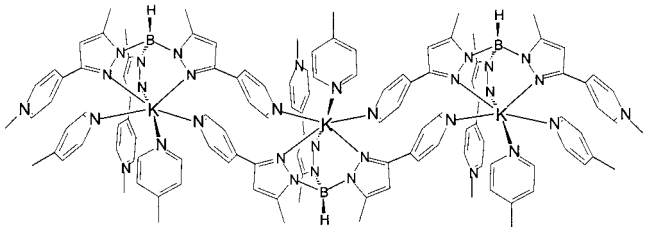


Figure 1. Coordination of the potassium ions in K**L¹**. Bond lengths [Å]: K–N1 2.897(3), K–N2 2.810(3), K–N3 3.022(3), K–N6 2.954(3), K–N7′ 3.152(4), K–N8′′′ 2.869(3), K–N9′′ 2.802(4).

Crystalline K**L¹** is a 3D coordination polymer. A substructure of this polymer is displayed in Scheme 2, showing that the pairwise coordination of the pyridyl nitrogen atoms to neighboring potassium ions creates a chain-like array. The third remaining pyridyl nitrogen atom of each **L¹** ligand is used to build the 3D network. In general, the structure of K**L¹** resembles the structures of our K**L** compounds, with **L** being 3-pyridyl-substituted pyrazolylborates.[5]

The preparation of the carboxamide-substituted ligands **L³** and **L⁴** was even more time-consuming than for **L¹** and **L²**. One reason for this was the multistep syntheses required for the preparation of the corresponding pyrazoles via diketopiperazines,[19–22] as outlined by Trofimenko.[13] Secondly, the unavoidable non-stoichiometric compositions of the KBH_4/pyrazole reaction mixtures resulted in purification problems for the K**L** products. As for **L¹** and **L²**, the pyrazoles had to be provided in excess during the reactions with KBH_4 in order to obtain reaction mixtures from which



Scheme 2.

the desired ligands could be isolated. Again, these reactions were performed without solvent, this time at temperatures around 150–160 °C. After the purification procedures, only K**L**^{4} could be obtained free from byproducts. One reason for the problems experienced in purifying K**L**^{3} is its high solubility,·K**L**^{3} is soluble in chloroform and more polar organic solvents,·K**L**^{4} is insoluble in chloroform and acetonitrile, but soluble in alcohols. Both compounds are soluble in alcohol/water mixtures, but not in water.

While K**L**^{3} could be identified, in the presence of its pyrazole, by its spectra, it had to be converted into the zinc halide complexes **2a** and **2b** (see below) to enable crystallographic proof of the **L**^{3} structure to be obtained, and to generate a starting material so its zinc complex chemistry could be investigated. In contrast, K**L**^{4} could be crystallized and subjected to structure determination by X-ray diffraction. The solvated crystals contain one K**L**^{4} unit, one water molecule, and 2.5 methanol molecules per asymmetric unit. The solvent molecules are severely disordered, so their positions in the coordination sphere of the potassium ion are ill-defined. In Figure 2 the water molecule, and the methanol molecule with the highest occupancy factor located near the potassium ion, are included in the drawing. While it is meaningless to discuss the coordination geometry of the metal ion, the binding of the pyrazolylborate ligand to the potassium ion is neatly defined. Unlike in K**L**^{1}, it coordinates in the established tripodal fashion. In addition, two of its three carboxamide substituents use their oxygen atoms for coordination to two different neighboring potassium ions, thereby making **L**^{4} a pentadentate ligand.

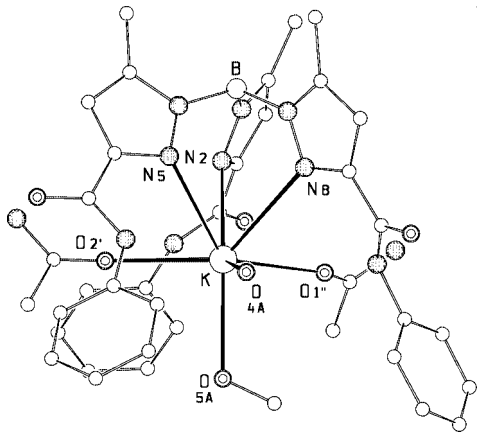
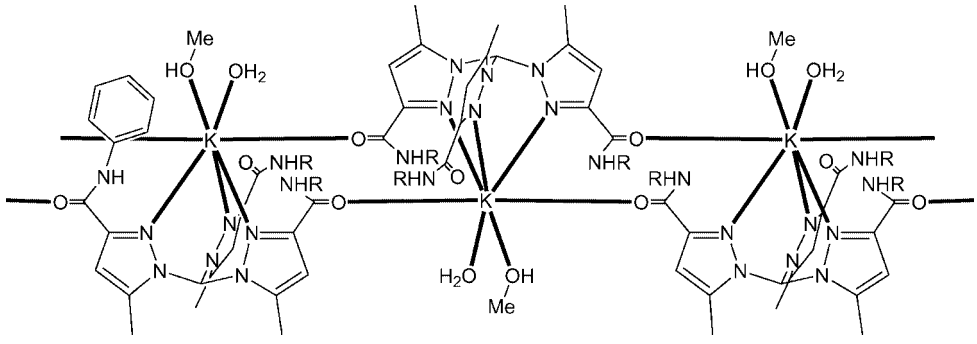


Figure 2. Coordination of the potassium ions in K**L**^{4}. Bond lengths [Å]: K–N2 2.802(2), K–N5 3.122(2), K–N8 3.040(2), K–O1′′ 2.860(2), K–O2′ 2.822(2), K–O4a 2.707(3), K–O5a 2.762(4).

Like in K**L**^{1}, the linking of neighboring complex units in K**L**^{4} occurs in a pairwise manner, resulting in a chain-like array, as shown in Scheme 3. Unlike in K**L**^{1}, there are no further links to create a 3D network, as the third carbonyl oxygen atom of each **L**^{1} unit remains uncoordinated.

Zinc Complexes of L^1

The coordinative properties of the new pyridyl-substituted Tp ligands were explored by preparing some zinc complexes of **L**^{1}. Thus, the halide complexes **1a**–**1c** resulted from the reaction of K**L**^{1} and the corresponding zinc halides. Their ^{1}H-NMR spectra in DMSO solution show split resonances for the pyrazolyl as well as the pyridyl protons, with intensity ratios between 2:1 and 5:1, and their ν(BH) IR bands in KBr are also split. This indicates different coordination modes for the "arms" of the **L**^{1} tripod, and possibly different coordination modes for different tripods, the simplest explanation for which is oligomerization, which was found in almost all the crystal structures reported in this paper. **1a**–**1c** did not yield suitable crystals for analysis, and therefore could not be used to verify this hypothesis.



Scheme 3.

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

The reactions between K$\mathbf{L^1}$ and zinc acetate or zinc nitrate led to complexes **1d** and **1e**. While the ^{1}H-NMR spectrum of **1d** is simple, indicating the monomeric nature of the complex, the spectrum of **1e** shows split resonances, just like those seen in the spectra of complexes **1b** and **1c**, with intensity ratios of 5:1, pointing to an as yet unidentified oligomeric state being present in solution.

$\mathbf{L^1}$Zn-OCOCH$_3$ **1d** $\mathbf{L^1}$Zn-ONO$_2$ **1e**

The solid-state nature of both **1d** and **1e** could be determined by X-ray methods. Complex **1d** is a monomer containing a semi-bidentate acetate ligand, see Figure 3. Its zinc coordination sphere offers no unusual features compared to the many (pyrazolylborate)zinc carboxylate structures in the Cambridge Structural Database. However, this makes **1d** an exception among the zinc complexes of $\mathbf{L^1}$.

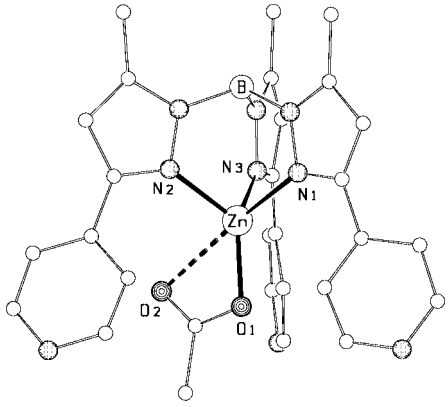


Figure 3. Molecular structure of **1d**. Bond lengths [Å]: Zn–N1 2.108(3), Zn(N2) 2.018(3), Zn–N3 2.018(3), Zn–O1 1.919(3), Zn–O2 2.534(3).

The nitrate complex **1e** is a 1D coordination polymer. Figure 4 shows the coordination sphere for one of the zinc ions in this polymer. Ligand $\mathbf{L^1}$ is nicely tripodal and the nitrate is symmetrically bound in a bidentate manner. One of the pyridyl nitrogen atoms coordinates to a neighboring zinc ion. This results in an octahedral coordination environment for the zinc ion, albeit a quite distorted one. The polymer chains comprise a zig-zag array of $\mathbf{L^1}$ZnONO$_2$ units linked by the pyridyl substituents.

The *p*-nitrophenolate complex **1f** and the bis(*p*-nitrophenyl)phosphate complex **1g** were prepared. It was thought that they would result from the hydrolytic cleavages of *p*-nitrophenyl acetate and tris(*p*-nitrophenyl)phosphate, reactions which were to be performed in subsequent studies with suitable $\mathbf{L^1}$ZnX compounds. For their unambiguous identification they were prepared from K$\mathbf{L^1}$, zinc perchlorate, and *p*-nitrophenolate and bis(*p*-nitrophenyl)phosphate, respectively.

The syntheses of **1f** and **1g** did not yield crystals suitable for structure determinations, and **1g** could not be obtained in an analytically pure form. Their ^{1}H-NMR spectra show

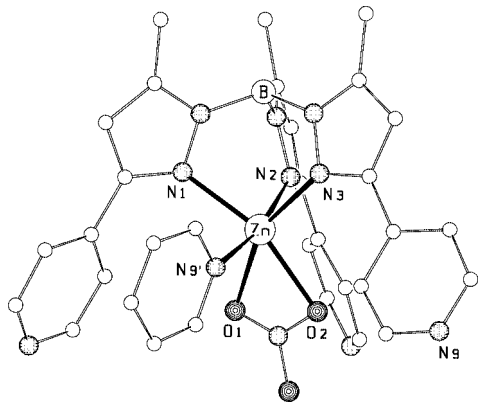


Figure 4. Monomeric fragment of polymeric **1e**. Bond lengths [Å]: Zn–N1 2.126(3), Zn–N2 2.263(3), Zn–N3 2.102(3), Zn–O1 2.189(3), Zn–O2 2.200(3), Zn-N9′ 2.250(3).

$\mathbf{L^1}$Zn-ONit **1f** $\mathbf{L^1}$Zn-OPO(ONit)$_2$ **1g**

no splitting of the pyrazolyl or pyridyl resonances, thereby indicating a monomeric structure. This was also the case for the corresponding zinc complexes with the 3-pyridyl-substituted Tp ligands. Of these, the nitrophenolate is a pyridyl-bridged dimer,[23] while the phosphate is a hydrated monomer with five-coordinate zinc ions.[24] The structures of **1f** and **1g** may be similar to either of these. Complex **1f** is precipitated with one water molecule per formula unit.

Finally, an attempt was made to obtain a zinc perchlorate complex of $\mathbf{L^1}$. To achieve this purpose, K$\mathbf{L^1}$ was treated with $Zn(ClO_4)_2$ in a dichloromethane/methanol solution. However, it became apparent that methanol is a better ligand for zinc than perchlorate, and the methanol complex **1h** was obtained. In the case of the related sulfur-containing tripod ligands, there is precedence for the preferred coordination of alcohol and perchlorate ligands.[25,26]

[$\mathbf{L^1}$Zn(CH$_3$OH)] ClO$_4$ **1h**

The ^{1}H-NMR spectrum of **1h**, just like the spectra for several other complexes of **1**, displays a splitting of the pyrazolyl and pyridyl resonances with intensity ratios of 1:5,

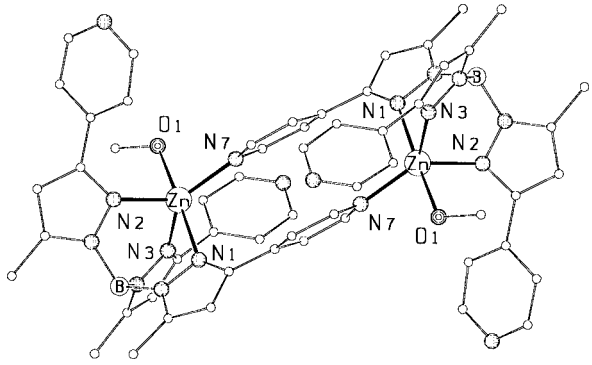


Figure 5. Structure of the dimeric cations of **1h**. Bond lengths [Å]: Zn–N1 2.210(2), Zn–N2 2.047(2), Zn–N3 2.047(2), Zn–O1 2.185(2), Zn–N7′ 2.034(2).

indicating the presence in solution of a complex with an unknown mode of oligomerization. In the solid state **1h** is dimeric, with the two complex units being held together by a pair of bridging pyridine rings that lie across a center of symmetry, see Figure 5. This type of coordination with trigonal-bipyramidal zinc ions has precedence in the zinc complexes of the 3-pyridyl-substituted Tp ligands.[6] The methanol ligand in **1h** is positioned on the axis of the trigonal bipyramid. It is linked by a hydrogen bond to a pyridyl nitrogen atom of a neighboring complex unit, such that a pairwise linkage across a center of symmetry exists. In this way a zig-zag array of complex units is seen in the solid state, that are bridged by pairs of pyridine donors and hydrogen bonds in an alternating fashion.

Zinc Complexes of L^3 and L^4

As mentioned above, ligand $\mathbf{L^3}$ had to be converted into a zinc halide complex in order to have a clean starting material for the synthesis of the $\mathbf{L^3}$Zn complexes. This was done by treating the crude reaction product, K$\mathbf{L^3}$, with zinc chloride and bromide, leading to **2a** and **2b**. Likewise, K$\mathbf{L^4}$ was easily converted with zinc chloride to yield **3a**. All three halide complexes show a rather low solubility, even in dichloromethane and methanol. This points to an oligomeric nature, but their ^{1}H-NMR spectra are simple, and thus yield no further information.

$\mathbf{L^3}$Zn-Cl **2a** $\mathbf{L^3}$Zn-Br **2b** $\mathbf{L^4}$Zn-Cl **3a**

The zinc nitrate complex of $\mathbf{L^3}$, **2c**, was prepared from **2b** and silver nitrate. The treatment of **2c** with potassium acetate yielded **2d**. The two corresponding complexes of $\mathbf{L^4}$, **3b** and **3c**, were synthesized in a more direct fashion from K$\mathbf{L^4}$ and the zinc salts. All four of these complexes are noticeably more soluble than the halide complexes, indicating a monomeric or dimeric nature, as observed for **1d** and **1h**. Only in case of **3c** did the ^{1}H-NMR spectrum yield structural information, as it showed split signals for the methyl groups of the pyrazole with a 2:1 intensity ratio. The simplest explanation for this is that dimerization has occurred with a pair of bridging carboxamide substituents. However, this must remain a speculative structural assignment until the structural chemistry of the zinc complexes of $\mathbf{L^3}$ and $\mathbf{L^4}$ can be based on a sufficient number of X-ray structure determinations.

$\mathbf{L^3}$Zn-ONO_2 **2c** $\mathbf{L^3}$Zn-$OCOCH_3$ **2d**
$\mathbf{L^4}$Zn-ONO_2 **3b** $\mathbf{L^4}$Zn-$OCOCH_3$ **3c**

As noted above, the *p*-nitrophenolate complex **2e** and the *p*-nitrothiophenolate complex **2f** were prepared in order to have reference materials for their identification in product mixtures during subsequent studies of zinc-catalyzed hydrolytic ester cleavage reactions. Compounds **2e** and **2f** resulted from the reaction between **2b**, KOH, and the corresponding phenols (as yellow powders). Complex **2e** was not obtained analytically pure. Again, little information could be gathered concerning their structures. They are more soluble in solvents of low polarity than the other complexes of $\mathbf{L^3}$ and $\mathbf{L^4}$, and hence may be monomeric.

$\mathbf{L^3}$Zn-ONit **2e** $\mathbf{L^3}$Zn-SNit **2f**

As for $\mathbf{L^1}$, a simple reaction of $\mathbf{L^3}$ aimed at preparing a perchlorate complex did not yield the desired product, but instead a solvated cationic zinc complex of $\mathbf{L^3}$ was produced. Treating the raw product K$\mathbf{L^3}$, which contains considerable amounts of 3-*tert*-butylcarboxamido-5-methylpyrazole (Pz*), with zinc perchlorate in dichloromethane/methanol produced a small amount of the pyrazole complex **2g**, which could be identified by its spectra.

[$\mathbf{L^3}$Zn(Pz*)] ClO_4 **2g**

Unlike the other complexes of $\mathbf{L^3}$ and $\mathbf{L^4}$, **2g** was produced as crystals suitable for X-ray structure determination. The result is displayed in Figure 6. Complex **2g** is mononuclear. Ligand $\mathbf{L^3}$ is coordinated to the zinc ion in the normal tripodal fashion, with the notable detail that all three carboxamide oxygen atoms are pointing towards the zinc ion. The pyrazole coligand is bidentate and produces a five-membered O,N chelate ring. Thereby **2g** resembles the large number of TpZn chelate complexes which are frequently discussed as models for enzyme-inhibitor complexes.[27,28] The coordination of the zinc ion can be described as reasonably close to trigonal-bipyramidal, with N8 and O4 on the axis forming the long Zn–X bonds. Additional rigidity in the structure comes from a hydrogen bond between the NH group of the pyrazole coligand and one carboxamide oxygen atom. Thus, the structure of **2g** has yielded two valuable pieces of information with respect to the subsequent use of ligands like $\mathbf{L^3}$ and $\mathbf{L^4}$ for modeling zinc enzymes: firstly, these ligands can form mononuclear zinc complexes and secondly, the carboxamide functional groups can show polar interactions and hydrogen bonding at, or near, the zinc center.

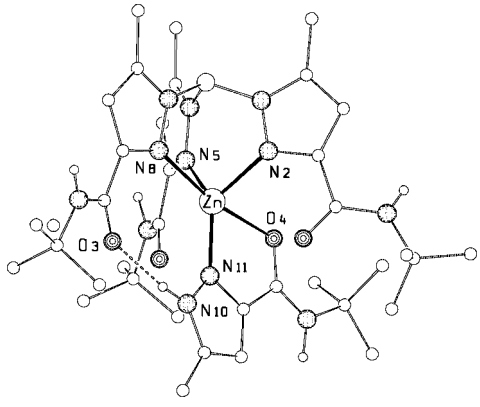


Figure 6. Molecular structure of complex **2g**. Bond lengths [Å]: Zn–N2 2.036(5), Zn–N5 2.036(5), Zn–N8 2.269(5), Zn–N11 1.979(5), Zn–O4 2.312(4), N10···O3 2.602(6).

Conclusions

The four new pyrazolylborate ligands described in this paper have been found to have conventional properties (i.e. they coordinate to the zinc ion in the tripodal fashion) as well as novel features that qualify them for a biomimetic zinc complex chemistry (i.e. they contain further donor functional groups, they allow for variable metal coordination numbers, they engage in various kinds of hydrogen bonds, and they form complexes which are soluble in water-containing solvents or even in pure water). Just like the previously described Tp ligands with 3-pyridyl substituents they allow, or more accurately they enforce, coordination numbers higher than four for zinc. The well-established term "tetrahedral enforcer", which qualifies many Tp ligands, does not hold for **L**^{1}–**L**^{4}.

Variability in coordination numbers and geometries, as seen for the zinc complexes described herein, is a prerequisite for catalytic activity. This, together with the increased solubility in water-containing solvents, indicates that zinc complexes of **L**^{1}–**L**^{4} with coordinated water or hydroxide, or with labile coligands X, should qualify as new, or better, models for, hydrolytic zinc enzymes. In this context, the carboxamide-substituted ligands **L**^{3} and **L**^{4} deserve special attention. Their CO–NH functionality mimics the peptide environment of the zinc ion in an enzyme in terms of its hydrogen-bonding ability, as well as in its polarity and donor quality. We therefore believe that the carboxamide-substituted pyrazolylborates should lead to significant advancements in enzyme modeling with zinc complexes, and once again Swiatoslaw Trofimenko has to be praised for being the first person to prepare such ligands.

Experimental Section

General: For general working and measuring procedures see ref.[29] Zinc salts and organic starting materials were obtained commercially.

Pyrazoles: The synthesis of the two pyrazoles needed for the synthesis of **L**^{1} and **L**^{2} started with the Claisen condensation of acetone with ethyl isonicotinate (commercially available) and ethyl 2-methylisonicotinate[15] to yield the corresponding diketones.[16] Their reaction with hydrazine hydrate, as previously described,[17,18] resulted in 5-methyl-3-(4′-pyridyl)pyrazole and 5-methyl-3-[4′-(6′-methyl)pyridyl]pyrazole in good yields. The two pyrazoles needed for the synthesis of **L**^{3} and **L**^{4} were obtained from the same intermediate, 2,7-dimethyldipyrazolo[1,5-*a*;1′,5′-*a*′]pyrazine-4,9-dione, which was synthesized according to literature procedures.[13,19–22] Treatment of this with *tert*-butylamine or aniline in refluxing toluene, as previously described,[13,22] resulted in 3-(*tert*-butylcarboxamido)-5-methylpyrazole and 3-(phenylcarboxamido)-5-methylpyrazole, respectively, in very good yields.

Tripod Ligands

KL^{1}**:** A mixture of 6.28 g (39.44 mmol) of 5-methyl-3-(4′-pyridyl)-pyrazole and 532 mg (9.86 mmol) of KBH_4 was stirred in a three-necked 100-mL flask equipped with an immersing thermometer. The temperature was slowly increased to 200 °C over a period of 30 min. At 140–160 °C, the mixture melted and the gas evolution became brisk. The melt was stirred continuously at 200 °C until it started to turn brown (ca. 3 h) and then slowly cooled to room temperature. The resulting glassy residue was carefully powdered and refluxed in 100 mL of toluene for 30 min, in order to remove unreacted pyrazole impurities. The mixture was filtered while hot, and the light brown residue was washed 3 times with 5 mL of boiling toluene and once with 5 mL of petroleum ether (30–50 °C). Recrystallization from 50 mL of acetonitrile at –20 °C yielded 2.59 g (50%) of K**L**^{1} as colorless crystals, m.p. 328 °C. $C_{27}H_{25}BKN_9$ (525.46): calcd. C 61.72, H 4.80, N 23.99; found C 61.23, H 4.85, N 23.87. ^{1}H NMR ([D$_6$]DMSO): δ = 2.02 [s, 9 H, Me(pz)], 6.44 [s, 3 H, H(pz)], 7.58 (dd, J = 4.5 and 1.5 Hz, 6 H, Py), 8.42 (dd, J = 4.5 and 1.5 Hz, 6 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2446 m (BH), 1605 vs (Py) cm^{-1}.

KL^{2}**:** 5-Methyl-3-[4′-(6′-methyl)pyridyl]pyrazole (2.66 g, 15.35 mmol), and 207 mg (3.84 mmol) of KBH_4 were mixed by stirring in a three-necked 50-mL flask equipped with an immersing thermometer. The temperature was slowly increased to 200 °C over a period of 30 min. The melt was continuously stirred at 200 °C until it started to turn brown (ca. 3 h) and then slowly cooled to room temperature. The resulting glassy residue was carefully powdered and refluxed in 50 mL of toluene for 30 min, in order to remove unreacted pyrazole impurities. The mixture was filtered while hot, and the light brown residue was washed 3 times with 5 mL of boiling toluene and once with 5 mL of petroleum ether (30–50 °C). Recrystallization from 50 mL of undried acetonitrile at –20 °C yielded 871 mg (40%) of K**L**^{2} as colorless crystals, m.p. 319 °C (dec.). $C_{30}H_{31}BKN_9{\cdot}H_2O$ (567.54 + 18.02): calcd. C 61.54, H 5.68, N 21.53; found C 61.05, H 5.76, N 21.33. ^{1}H NMR ([D$_6$]DMSO): δ = 1.99 [s, 9 H, Me(pz)], 2.41 [s, 9 H, Me(py)], 6.41 [s, 3 H, H(pz)], 7.38 (d, J = 5.1 Hz, 3 H, Py), 7.45 (s, 3 H, Py), 8.28 (d, J = 5.1 Hz, 3 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2486 m (BH), 1612 vs (Py) cm^{-1}.

KL^{3}**:** 3-(*tert*-butylcarboxamido)-5-methylpyrazole (3.03 g, 16.65 mmol), and 0.28 g (5.08 mmol) of KBH_4 were mixed by stirring in a 100-mL three-necked flask equipped with an immersing thermometer, and slowly heated until melting, which occurred at 130 °C. The temperature was raised to 160 °C over a period of 2 h, after which time the gas evolution ceased. After cooling, the solid residue was carefully powdered and stirred in chloroform overnight. Then the suspension was filtered and the filtrate concentrated to dryness, leaving behind 2.34 g of a colorless mixture of K**L**^{3} and the unreacted pyrazole. According to NMR analysis, the mixture contained 1.78 g (59%) of K**L**^{3}. Attempts at further purification resulted in increasing the amount of impurities present. ^{1}H NMR of K**L**^{3} (CD_3OD): δ = 1.38 (s, 27 H, *t*Bu), 2.05 [s, 9 H, Me(pz)], 6.39 [s, 3 H, H(pz)] ppm. IR of K**L**^{3} (KBr): $\tilde{\nu}$ = 3396 m (NH), 2444 m (BH), 1652 vs (CO) cm^{-1}.

KL^{4}**:** A mixture of 3.29 g (16.35 mmol) of 3-methyl-5-(phenylcarboxyamido)pyrazole and 221 mg (4.09 mmol) of KBH_4 was stirred in a three-necked 50-mL flask equipped with an immersing thermometer. The temperature was slowly increased to 150 °C over a period of 30 min, at which point the mixture melted. The melt was continuously stirred at 150 °C until no more hydrogen was evolved (ca. 2 h), and then heated to 160 °C over a period of 30 min. It was then cooled to room temperature. The resulting glassy residue was carefully powdered and refluxed in 30 mL of acetonitrile for 30 min in order to remove unreacted pyrazole impurities. The mixture was filtered while hot, and the residue was washed 3 times with 5 mL of boiling acetonitrile and once with 2 mL of water. Recrystallization from 40 mL of methanol/dichloromethane (1:2) at –20 °C yielded 300 mg (11%) of K**L**^{4} as large crystals, m.p. 250 °C. $C_{33}H_{31}BKN_9O_3{\cdot}H_2O$ (651.58 + 18.02): calcd. C 59.19, H 4.97, N 18.83; found C 59.43, H 5.14, N 18.44. ^{1}H NMR ([D$_6$]DMSO): δ

= 2.01 [s, 9 H, Me(pz)], 6.46 [s, 3 H, H(pz)], 7.01 (m, 3 H, Ph), 7.27 (m, 6 H, Ph), 7.64 (d, J = 7.6 Hz, 6 H, Ph), 9.25 (s, 3 H, NH) ppm. IR (KBr): $\tilde{\nu}$ = 3365 s (NH), 2470 m (BH), 1653 vs. (CO) cm^{-1}.

Zinc Complexes of L^1

1a: A solution of 46 mg (0.33 mmol) of $ZnCl_2$ in 5 mL of methanol was added dropwise to a solution of 160 mg (0.30 mmol) of KL^1 in 20 mL of methanol/dichloromethane (1:1) over a period of 5 min. After 6 h of stirring, a small amount of a cloudy precipitate was removed by filtration, and the clear filtrate was slowly concentrated at room temperature to yield, after 2 d, 116 mg (65%) of **1a** as colorless needles, m.p. 238 °C. $C_{27}H_{25}BClN_9Zn{\cdot}1.5H_2O$ (587.21 + 27.02): calcd. C 52.80, H 4.59, N 20.52; found C 52.63, H 4.48, N 20.66. ^{1}H NMR ([D$_6$]DMSO): δ = 2.02 [s, 6 H, Me(pz)], 2.54 [s, 3 H, Me(pz)], 6.44 [s, 2 H, H(pz)], 6.65 [s, 1 H, H(pz)], 7.58 (d, J = 6.0 Hz, 4 H, Py), 7.70 (d, J = 5.5 Hz, 2 H, Py), 8.41 (d, J = 6.0 Hz, 4 H, Py), 8.59 (d, J = 6.0 Hz, 2 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2553 and 2496 w (BH), 1619 s (Py) cm^{-1}.

1b: A solution of 150 mg (0.67 mmol) of $ZnBr_2$ in 10 mL of methanol/dichloromethane (1:1) was added dropwise to a stirred solution of 318 mg (0.61 mmol) of KL^1 in 20 mL of methanol/dichloromethane (1:1) over a period of 30 min. A white solid precipitated immediately, but the mixture was allowed to react for 6 h. Then the solvent was removed in vacuo and the residue was dissolved in chloroform/methanol (90:10) under reflux. After storage at 5 °C for 2 d, a precipitate of **1b**, 298 mg (78%), as colorless needles formed, m.p. 252 °C. $C_{27}H_{25}BBrN_9Zn$ (631.66): calcd. C 51.34, H 3.99, N 19.96; found C 50.77, H 4.11, N 19.53. ^{1}H NMR ([D$_6$]DMSO): δ = 2.07 [s, 1.5 H, Me(pz)], 2.53 [s, 7.5 H, Me(pz)], 6.46 [s, 0.5 H, H(pz)], 6.63 [s, 2.5 H, H(pz)], 7.61 (m, 6 H, Py), 8.42 (d, J = 5.3 Hz, 1 H, Py), 8.62 (d, J = 4.9 Hz, 5 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2557 and 2499 w (BH), 1621 vs (Py) cm^{-1}.

1c: The preparation of **1c** was analogous to that of **1b**, but with ZnI_2 (127 mg, 0.40 mmol) in place of $ZnBr_2$. Recrystallization from chloroform/methanol (90:10) at 5 °C yielded 184 mg (75%) of **1c** as colorless needles, m.p. 226 °C. $C_{27}H_{25}BIN_9Zn$ (678.66): calcd. C 47.78, H 3.71, N 18.57; found C 47.09, H 3.83, N 19.00. ^{1}H NMR ([D$_6$]DMSO): δ = 2.00 [s, 1.5 H, Me(pz)], 2.54 [s, 7.5 H, Me(pz)], 6.46 [s, 0.5 H, H(pz)], 6.63 [s, 2.5 H, H(pz)], 7.56 (m, 6 H, Py), 8.41 (d, J = 6.0 Hz, 1 H, Py), 8.72 (dd, J = 4.6 Hz and 1.4 Hz, 5 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2557 and 2491 w (BH), 1617 s (Py) cm^{-1}.

1d: A solution of 174 mg (0.79 mmol) of $Zn(OAc)_2{\cdot}2H_2O$ in 5 mL of methanol was added dropwise to a solution of 379 mg (0.72 mmol) of KL^1 in 20 mL of methanol/dichloromethane (1:1) over a period of 5 min. After 6 h of stirring, a small amount of a cloudy precipitate was removed by filtration, and the clear filtrate was concentrated to dryness in vacuo. Recrystallization from 15 mL of methanol at 5 °C yielded 401 mg (91%) of **1d** as large colorless crystals, m.p. 242 °C. $C_{29}H_{28}BN_9O_2Zn$ (610.80): calcd. C 57.03, H 4.62, N 20.64; found C 56.49, H 4.82, N 20.42. ^{1}H NMR ([D$_6$]-DMSO): δ = 1.51 (s, 3 H, Ac), 2.56 [s, 9 H, Me(pz)], 6.64 [s, 3 H, H(pz)], 7.60 (dd, J = 4.6 and 1.4 Hz, 6 H, Py), 8.60 (d, J = 6.0 Hz, 6 H, Py) ppm. IR(KBr): $\tilde{\nu}$ = 2558 m (BH), 1608 vs (Py) cm^{-1}.

1e: A solution of 146 mg (0.49 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ in 5 mL of methanol was added dropwise to a solution of 234 mg (0.45 mmol) of KL^1 in 20 mL of methanol over a period of 5 min. A white solid precipitated immediately, but the mixture was stirred for 6 h. Then the solvent was removed in vacuo and the residue was dissolved in chloroform/methanol (90:10) under reflux. After storage at 5 °C for 5 d, a precipitate of **1e**, 188 mg (69%), as colorless crystals formed, m.p. 210 °C (dec.). $C_{27}H_{25}BN_{10}O_3Zn{\cdot}H_2O$ (613.76 + 18.02): calcd. C 51.33, H 4.31, N 22.17; found C 51.47, H 4.01, N 22.05. ^{1}H NMR ([D$_6$]DMSO): δ = 2.01 [s, 1.5 H, Me(pz)], 2.55 [s, 7.5 H, Me(pz)], 6.45 [s, 0.5 H, H(pz)], 6.62 [s, 2.5 H, H(pz)], 7.56 (m, 6 H, Py), 8.41 (d, J = 5.7 Hz, 1 H, Py), 8.72 (d, J = 5.9 Hz, 5 H, Py). IR(KBr): $\tilde{\nu}$ = 2550 m (BH), 1613 s (Py) cm.

1f: To a stirred mixture of 266 mg (0.50 mmol) of KL^1 and 207 mg (0.55 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ in 30 mL of methanol/dichloromethane/water (1:1:0.5) at 0 °C was added a solution of 42 mg (0.75 mmol) of KOH in methanol/dichloromethane (1:1). After 1 h of stirring at 0 °C, a solution of 68 mg (0.49 mmol) of *p*-nitrophenol in 5 mL of methanol was added. After 6 h of stirring and subsequent filtration, all volatiles were removed in vacuo, and the residue was recrystallized from 15 mL of methanol/dichloromethane (1:2) at –20 °C, yielding 314 mg (93%) of **1f** as a light yellow powder, m.p. 254 °C (dec.). $C_{33}H_{29}BN_{10}O_3Zn{\cdot}H_2O$ (689.86 + 18.02): calcd. C 55.99, H 4.41, N 19.79; found C 56.15, H 4.42, N 19.74. ^{1}H NMR ($CDCl_3$): δ = 1.66 (br. s, 2 H, H_2O), 2.62 [s, 9 H, Me(pz)], 5.88 (d, J = 9.1 Hz, 2 H, Ph), 6.43 [s, 3 H, H(pz)], 7.51 (m, 8 H, Py, Ph), 8.41 (dd, J = 4.5 and 1.4 Hz, 6 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2559 w (BH), 1607 s (Py), 1584 s and 1304 vs (NO) cm^{-1}.

1g: The method for the preparation of **1g** is like the synthetic procedure for **1f**. The reaction mixture contained 266 mg (0.50 mmol) of KL^1, 207 mg (0.55 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$, 42 mg (0.75 mmol) of KOH, and 183 mg (0.54 mmol) of bis(*p*-nitrophenyl)phosphoric acid in 35 mL of methanol/dichloromethane (2:1) at 0 °C. After 2 h of stirring and subsequent filtration, all volatiles were removed in vacuo and the raw product was suspended in 5 mL of chloroform. The suspension was filtered again and the filtrate concentrated to dryness, leaving behind 134 mg (31%) of impure **1g** as a light yellow powder, m.p. 231 °C. Attempts at purification by recrystallization were unsuccessful. ^{1}H NMR ($CDCl_3$): δ = 2.60 [s, 9 H, Me(pz)], 6.40 [s, 3 H, H(pz)], 6.85 (d, J = 8.9 Hz, 4 H, Ph), 7.52 (d, J = 5.9 Hz, 6 H, Py), 7.98 (d, J = 9.1 Hz, 4 H, Ph), 8.61 (d, J = 5.7 Hz, 6 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 2566 w (BH), 1621 s (Py), 1591 s and 1346 vs (NO) cm^{-1}.

1h: Compound KL^1, 210 mg (0.40 mmol), was dissolved in 30 mL of methanol/dichloromethane (1:1), and a solution of 163 mg (0.44 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ in 5 mL methanol was added dropwise over a period of 10 min. A slurry of $KClO_4$ precipitated immediately. This was filtered off and the clear filtrate was stirred for 6 h. After this time, a large amount of colorless solid had precipitated. This precipitate was filtered off and dried in vacuo to yield 180 mg (66%) of **1h** as a colorless powder, m.p. 284 °C. The mother liquor was concentrated in vacuo to ca. 20 mL and kept at 5 °C overnight to yield 10 mg (4%) of **1h** as X-ray quality crystals. $C_{28}H_{29}BClN_9O_5Zn{\cdot}H_2O$ (683.25 + 18.02): calcd. C 47.96, H 4.46, N 17.98; found C 47.75, H 4.36, N 17.60. ^{1}H NMR ([D$_6$]DMSO): δ = 2.01 [s, 1.5 H, Me(pz)], 2.55 [s, 7.5 H, Me(pz)], 3.34 (s, 3 H, MeOH), 6.45 [s, 0.5 H, H(pz)], 6.62 [s, 2.5 H, H(pz)], 7.56 (m, 6 H, Py), 8.41 (d, J = 5.9 Hz, 1 H, Py), 8.73 (d, J = 5.9 Hz, 5 H, Py) ppm. IR (KBr): $\tilde{\nu}$ = 3572 m (OH), 3428 bs (H_2O), 2574 m (BH), 1623 s (Py), 1094 vs (ClO) cm^{-1}.

Zinc Complexes of L^3 and L^4

2a: To a stirred solution of 1.59 g of impure KL^3 (ca. 2.0 mmol of KL^3) in 10 mL of methanol was added dropwise a solution of 0.44 g (3.2 mmol) of $ZnCl_2$ in 3 mL of methanol. After 4 h of stirring, the volume was reduced to 3 mL in vacuo. The precipitate was filtered off and washed with 5 mL of water. After drying in vacuo, it was suspended in 4 mL of THF and 1 mL of methanol. The remaining precipitate was filtered off and dried in vacuo, yielding 430 mg (27%) of **2a** as a colorless powder, m.p. 278 °C. $C_{27}H_{48}BClN_9O_3Zn{\cdot}0.5H_2O$ (653.35 + 9.01): calcd. C 48.96, H 6.70, N 19.03; found C 48.80, H

6.74, N 18.86. ^{1}H NMR (CD_3OD): δ = 1.48 (s, 27 H, *t*Bu), 2.46 [s, 9 H, Me(pz)], 6.54 [s, 3 H, H(pz)] ppm. IR (KBr): $\tilde{\nu}$ = 3398 m (NH), 2505 w (BH), 1648 vs and 1605 vs (CO) cm^{-1}.

2b: The method of synthesis for **2b** is like the procedure for the preparation of **2a**. From 1.97 g (ca. 2.5 mmol) of **KL^3** and 0.90 g (4.03 mmol) of $ZnBr_2$, 650 mg (38%) of **2b** was obtained as a colorless powder, m.p. 260 °C. $C_{27}H_{48}BBrN_{10}O_6Zn{\cdot}1.5H_2O$ (679.80 + 27.03): calcd. C 44.74, H 6.40, N 17.39; found C 44.94, H 6.22, N 17.39. ^{1}H NMR (CD_3OD): δ = 1.48 (s, 27 H, *t*Bu), 2.46 [s, 9 H, Me(pz)], 6.55 [s, 3 H, H(pz)] ppm. IR(KBr): $\tilde{\nu}$ = 3397 w (NH), 2500 w (BH), 1650 vs and 1605 vs (CO) cm^{-1}.

3a: A solution of 22 mg (0.16 mmol) of $ZnCl_2$ in 2 mL of methanol was added dropwise to a solution of 96 mg (0.15 mmol) of **KL^4** in 10 mL of methanol/dichloromethane (1:1). After 3 h of stirring, a small amount of cloudy precipitate was removed by filtration, and the clear filtrate was slowly concentrated at room temperature to yield after 1 d 91 mg (87%) of **3a** as colorless needles, m.p. 216 °C. $C_{33}H_{31}BClN_9O_3Zn{\cdot}H_2O$ (713.32 + 18.02): calcd. C 54.20, H 4.55, N 17.05; found C 53.74, H 4.66, N 17.05. ^{1}H NMR ($CDCl_3$): δ = 1.57 (br. s, 2 H, H_2O), 2.53 [s, 9 H, Me(pz)], 6.80 [s, 3 H, H(pz)], 7.14 [m, 3 H, Ph], 7.33 (m, 6 H, Ph), 7.74 (d, *J* = 7.8 Hz, 6 H, Ph), 8.89 (s, 3 H, NH) ppm. IR (KBr): $\tilde{\nu}$ = 3315 s (NH), 2511 w (BH), 1648 vs and 1598 vs (CO) cm^{-1}.

2c: A solution of 30 mg (0.19 mmol) of $AgNO_3$ in 2 mL of methanol was slowly added dropwise to a stirred solution of 0.13 g (0.19 mmol) of **2b** in 15 mL of methanol at 0 °C. After 30 min, the precipitate was filtered off and the filtrate concentrated to dryness, leaving behind 100 mg (77%) of **2c** as a colorless hygroscopic powder, m.p. 190 °C (dec.). $C_{27}H_{48}BN_9O_3Zn{\cdot}2H_2O$ (679.90 + 36.04): calcd. C 45.30, H 6.62, N 19.56; found C 45.34, H 6.68, N 19.08. ^{1}H NMR (CD_3OD): δ = 1.48 (s, 27 H, *t*Bu), 2.46 [s, 9 H, Me(pz)], 6.55 [s, 3 H, H(pz)] ppm. IR (KBr): $\tilde{\nu}$ = 3294 m (NH), 2557 w (BH), 1642 s and 1608 s (CO) cm^{-1}.

2d: A solution of 8 mg (0.08 mmol) of KOAc in 1 mL of methanol was added dropwise to a stirred solution of 50 mg (0.07 mmol) of **2c** in 4 mL of dichloromethane. After 2 h of stirring, the precipitate was filtered off and the filtrate concentrated to dryness. The residue was washed with 1 mL of water and dried in vacuo, leaving behind 35 mg (74%) of **2d** as a colorless powder, m.p. 188 °C. $C_{29}H_{46}BN_9O_5Zn{\cdot}2H_2O$ (676.94 + 36.04): calcd. C 48.85, H 7.07, N 17.68; found C 48.96, H 7.12, N 17.40. ^{1}H NMR (CD_3OD): δ = 1.47 (s, 27 H, *t*Bu), 1.90 (s, 3 H, OAc), 2.46 [s, 9 H, Me(pz)], 6.54 [s, 3 H, H(pz)] ppm. IR (KBr): $\tilde{\nu}$ = 3293 w (NH), 2559 w (BH), 1648 vs and 1605 s (CO) cm^{-1}.

3b: A solution of 50 mg (0.17 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ in 5 mL of methanol was added dropwise to a solution of 100 mg (0.15 mmol) of **KL^4** in 10 mL of methanol. After 3 h of stirring, a small amount of cloudy precipitate was removed by filtration, and the clear filtrate was concentrated to dryness in vacuo. Recrystallization from 10 mL of methanol/dichloromethane (1:1) at 5 °C yielded 87 mg (77%) of **3b** as a white powder, m.p. 190 °C. $C_{33}H_{31}BN_{10}O_6Zn$ (739.87): calcd. C 53.57, H 4.22, N 18.93; found C 52.93, H 4.31, N 19.01. ^{1}H NMR($CDCl_3$): δ = 2.39 [s, 9 H, Me(pz)], 6.54 [s, 3 H, H(pz)], 6.76 (m, 9 H, Ph), 7.03 (d, *J* = 8.2 Hz, 6 H, Ph), 9.80 (s, 3 H, NH) ppm. IR (KBr): $\tilde{\nu}$ = 3282 m (NH), 2566 w (BH), 1648 s and 1601 s (CO) cm^{-1}.

3c: A solution of 35 mg (0.16 mmol) of $Zn(OAc)_2{\cdot}2H_2O$ in 2 mL of methanol was added dropwise to a solution of 94 mg (0.14 mmol) of **KL^4** in 10 mL of methanol/dichloromethane (2:1). After 3 h of stirring, a small amount of cloudy precipitate was removed by filtration, and the clear filtrate was slowly concentrated at room temperature to yield after 1 d 93 mg (88%) of **3c** as colorless crystals, m.p. 216 °C. $C_{35}H_{34}BN_9O_5Zn$ (736.91): calcd. C 57.05, H 4.65, N 17.11; found C 56.29, H 4.75, N 16.84. ^{1}H NMR ($CDCl_3$): δ = 1.75 (s, 3 H, OAc), 2.39 [s, 3 H, Me(pz)], 2.52 [s, 6 H, Me(pz)], 6.69 [m, 5 H, H(pz) + Ph], 7.08 (m, 6 H, Ph), 7.28 (m, 4 H, Ph), 7.67 (d, *J* = 7.6 Hz, 4 H, Ph), 8.95 (br. s, 1 H, NH) ppm. IR (KBr): $\tilde{\nu}$ = 3307 m (NH), 2573 w (BH), 1650 s and 1600 s (CO) cm^{-1}.

2e: A solution of 11 mg (0.15 mmol) of *p*-nitrophenol in 2 mL of methanol was deprotonated by the addition of a solution of 9 mg (0.16 mmol) of KOH in 1 mL of methanol. This intensive yellow solution was added to a solution of 0.11 g (0.15 mmol) of **2b** in 12 mL of methanol. After 3 h, the clear solution was concentrated under vacuum until the first turbidity appeared, at this time the solution had been reduced to 3 mL. Addition of 3 mL of dichloromethane caused a pale yellow precipitate to form. After filtration, the filtrate was concentrated to dryness. A yellow-brown powder (68 mg) remained, which consisted mainly of **2e**, but could not be purified by recrystallization. ^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 27 H, *t*Bu), 2.44 [s, 9 H, Me(pz)], 6.36 [s, 3 H, H(pz)], 6.55 (s, 1 H, NH), 6.65 (d, *J* = 9.0 Hz, 2 H, Ph), 7.96 (d, *J* = 9.0 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3332 w (NH), 2559 w (BH), 1647 s and 1606 s (CO) cm^{-1}.

2f: The procedure for the preparation of **2f** is like the method for the synthesis of **2e**. From 20 mg (0.13 mmol) of *p*-nitrothiophenol, 8 mg (0.14 mmol) of KOH, and 0.09 g (0.13 mmol) of **2b**, 67 mg (67%) of **2f** resulted. Recrystallization from benzene/dichloromethane reduced this amount to 18 mg (18%) of pure **2f**, m.p. 234 °C. $C_{33}H_{47}BN_{10}O_5SZn$ (772.05): calcd. C 51.34, H 6.13, N 18.14; found C 51.08, H 6.20, N 17.90. ^{1}H NMR (CD_3OD): δ = 1.35 (s, 27 H, *t*Bu), 2.44 [s, 9 H, Me(pz)], 6.50 [s, 3 H, H(pz)], 7.29 (d, *J* = 8.9 Hz, 2 H, Ph), 7.68 (d, *J* = 8.9 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 3305 m (NH), 2482 w (BH), 1645 s and 1604 vs (CO) cm^{-1}.

2g: A solution of 1.89 g (5.08 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ in 3 mL of methanol was added to a stirred solution of 2.57 g of raw **KL^3** contaminated with 3-(*tert*-butylcarboxamido)-5-methylpyrazole (ca. 2.7 mmol of **KL^3**) in 10 mL of dichloromethane. After 2 h of stirring, the precipitate was filtered off and the filtrate was concentrated to dryness. The residue was dissolved in 5 mL of dichloromethane/methanol (20:1) and the mixture subjected to slow concentration. After one week, 140 mg (6%) of **2g** had precipitated as colorless crystals, m.p. 250 °C. $C_{36}H_{58}BClN_{12}O_8Zn{\cdot}CH_3OH$ (898.57 + 32.04): calcd. C 47.75, H 6.71, N 18.06; found C 47.37, H 6.67, N 18.04. ^{1}H NMR (CD_3OD): δ = 1.40 [s, 9 H, *t*Bu(Pz*)], 1.45 (s, 27 H, *t*Bu), 2.34 [s, 3 H, Me(Pz*)], 2.48 [s, 9 H, Me(pz)], 6.55 [s, 4 H, H(Pz*) and H(pz)] ppm. IR (KBr): $\tilde{\nu}$ = 3397 (m, NH), 3356 m (NH), 2561 w (BH), 1676 s and 1647 vs and 1557 vs (CO), 1076 vs (ClO) cm^{-1}.

Structure Determinations:[30] Crystals were obtained by the slow evaporation of solvents: acetonitrile for **KL^1**, dichloromethane/methanol for **KL^2** and **1h**, methanol for **1d**, chloroform/methanol for **1e** and anhydrous dichloromethane for **2g**. In those cases where the crystals contained solvent, care had to be taken to avoid solvent loss. Diffraction data were recorded at room temperature for **KL^2** and **2g**, and at –50 °C for **KL^1**, **1d**, **1e** and **1h** with a Bruker Smart CCD diffractometer. The datasets for **KL^1**, **KL^2**, **1h** and **2g** were subjected to an empirical absorption correction (SADABS).[31] The structures were solved with direct methods and refined anisotropically using the SHELX program suite.[31] Serious disorder problems concerning the cocrystallized solvent molecules hampered the refinements of **KL^2** and **1h**. In the case of **1h** we had to resort to using Spek's SQUEEZE program, which includes the total electron

Table 1. Crystallographic details.

	KL[1]	**KL[4]**	**1d**	**1e**	**1h**	**2 g**
Empirical formula	$C_{27}H_{25}BKN_9 \cdot CH_3CN$	$C_{33}H_{31}BKN_9O_3 \cdot H_2O \cdot 2.5CH_3OH$	$C_{29}H_{28}BN_9O_2Zn \cdot CH_3OH$	$C_{27}H_{25}BN_{10}O_3Zn$	$C_{28}H_{29}BClN_9O_5Zn$	$C_{36}H_{58}BClN_{12}O_8Zn \cdot 2CH_2Cl_2$
Formula mass	566.51	749.71	642.84	613.75	683.25	1068.45
Crystal size [mm]	0.2×0.15×0.1	0.15×0.2×0.3	0.25×0.15×0.05	0.1×0.15×0.2	0.3×0.2×0.1	0.15×0.15×0.25
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$Pbca$
Z	4	2	4	4	2	8
a [Å]	11.375(2)	13.211(2)	12.936(4)	9.918(3)	10.838(2)	18.560(2)
b [Å]	16.015(3)	13.332(2)	16.933(6)	9.280(3)	12.544(2)	22.349(3)
c [Å]	16.499(3)	13.378(2)	16.460(4)	29.539(8)	16.023(3)	25.651(3)
α [°]	90	105.313(2)	90	90	90.583(3)	90
β [°]	103.399(3)	102.689(2)	120.67(2)	97.220(4)	101.794(3)	90
γ [°]	90	114.741(2)	90	90	94.111(3)	90
V [Å^3]	2924(1)	1911.8(4)	3101(2)	2697(1)	2126.3(6)	10640(2)
d(calcd.) [g·cm^{-3}]	1.29	1.28	1.38	1.51	1.07	1.33
μ(Mo-K_α) [mm^{-1}]	0.22	0.20	0.84	0.96	0.68	0.77
hkl range	h: –15 to 8	h: –17 to 16	h: –17 to 17	h: –13 to 12	h: –14 to 14	h: –8 to 25
	k: –20 to 22	k: –17 to 17	k: –22 to 22	k: –12 to 12	k: –16 to 16	k: –24 to 30
	l: –20 to 23	l: –17 to 18	l: –22 to 21	l: –38 to 39	l: –21 to 21	l: –34 to 20
Refl. measd.	19542	17246	28041	22184	18887	38586
Indep. refl.	8052	8887	7663	6429	9849	13078
Obsd. refl. [$I > 2\sigma(I)$]	3088	4891	3942	3589	5623	3502
Parameters	371	525	403	379	438	602
Refl. refined	8052	8887	7663	6429	9849	13078
R_1 (obsd. refl.)	0.068	0.055	0.058	0.053	0.053	0.070
wR_2 (all refl.)	0.238	0.172	0.174	0.158	0.156	0.236
Resid. electron dens. [e/Å^{-3}]	+0.4/–0.4	+0.7/–0.5	+0.7/–0.7	+0.6/–0.8	+1.0/–0.4	+0.9/–0.8

density, but not the specific atomic positions in the refinement.[32] Drawings were produced with SCHAKAL.[33] Table 1 lists the crystallographic details.

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