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Zn–OH_2 and Zn–OH Complexes with Hydroborate-Derived Tripod Ligands: A Comprehensive Study

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The complete array of those hydrotris(pyrazolyl/thioimidazolyl)borate ligands that were developed and used in the author's laboratories, with N_3, N_2S, NS_2, and S_3 donor sets, was scanned for their ability to form Zn–OH_2 and Zn–OH complexes. The coordination motifs found were Zn–OH_2, Zn–OH, Zn–OH–Zn, and Zn–O_2H_3–Zn. Of these, the well-established Zn–OH motif was complemented with novel species bearing N_3, NS_2, and S_3 tripods. The Zn–OH_2 motif was observed only with pyrazolylborate ligands and only in unusual situations with coordination numbers higher than 4 for zinc. The new Zn–OH–Zn motif was realized for three different pyrazolylborates, for one NS_2 tripod, and for two S_3 tripods. Finally, it was verified that the Zn–O_2H_3–Zn motif again occurs only with pyrazolylborate ligands. The new complexes were identified by a total of 11 structure determinations.

Introduction

Among the many tripod−Zn complexes that were used to model zinc enzymes,[1] the tris(pyrazolyl)borate-ligated ones certainly were most productive. One reason for this is the fact that with suitably substituted Tp ligands the Zn−OH complexes as the essential mimics of the active state of hydrolytic zinc enzymes could be isolated and used for biomimetic chemistry.[2] For most of the other Zn-containing model systems, such a central model species, i.e., one containing a Zn−OH function in the pocket of the tripod ligand, could only be proposed as a necessary intermediate.[1]

The pyrazolylborate−zinc hydroxide complexes with their (N,N,N)Zn−X core in a strict sense represent only those zinc enzymes that bind Zn through three histidine units. In recent years, it has become evident, however, that an increasing number of zinc enzymes applies (N,N,S), (N,S,S), and (S,S,S) donor sets for the metal, using histidine and/or cysteinate.[1] Model systems for these enzymes are emerging, but with one or two exceptions, they have not yielded Zn−OH complexes yet.[1]

On the other hand, while simple Zn−OH_2 complexes are commonplace, an unsupported cationic TpZn·OH_2 species is still awaiting its isolation, with its closest representation being Parkin's $Tp^{tBu,Me}Zn-OH\cdots H\cdots HOB(C_6F_5)_3$.[3] The same holds true for tripod−Zn complexes with N/S donor sets, where again the tetrahedral Zn−aqua species have only been proposed, but not isolated yet, as intermediates.[1]

The challenge of making tetrahedral tripod−Zn−OH and tripod−Zn−OH_2 complexes with N_3, N_2S, NS_2, and S_3 donor sets should be manageable ever since the pyrazolylborate-related tripod ligands with N_2S,[4,5] NS_2,[6−8] and S_3 donor sets[9−12] have become available and applicable for Zn model complex chemistry. We have contributed to this,[4,7,11] and we recently have presented several new polar tris(pyrazolyl)borate ligands.[13,14] With all of these ligand types,

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we have tackled the above-mentioned challenge. This paper reports our findings, accumulated over the last 5 years.

A survey of the literature has shown that apart from the TpZn−OH species only one tripod−Zn−OH complex was fully characterized: Parkin's tris(1-phenylthioimidazolyl)borate−zinc hydroxide.[15] Three crystal structures of TpZn−OH_2 complexes were reported, our $Tp^{Py,Me}Zn(OH_2)[OPO(OPh)_2]$,[16] Parkin's $Tp^{tBu,Me}Zn(OH_2)[HOB(C_6F_5)_3]$,[3] and Carrano's $Tp^{COOEt,Me}Zn(OH_2)(OAc)$,[17] while the complex $Tp^{COOEt,Me}Zn(OH_2)_3(ClO_4)$ was mentioned among similar complexes of other metals.[17,18] This paper adds three aqua and six terminal hydroxo complexes, plus six examples of a new structural type, the OH-bridged dinuclear tripod−Zn complexes.

Results and Discussion

We had previously observed that the complex types TpZn−OH and $[TpZn-(\mu\text{-}O_2H_3)-ZnTp]^+$ can form from the Tp ligand and hydrated zinc perchlorate even without the addition of a base, although as a rule a stoichiometric amount of KOH favors their formation in good yields.[19−21] This implies that subtle changes of the acidity of the solutions, which can even be brought about by a variation of the solvent composition, can affect the accessibility of such species. On the one side, TpZn−OH is endangered in the presence of acids because the resulting $[TpZn\cdot OH_2]^+$ is prone to hydrolytic self-destruction of the Tp ligand. On the other side, the enforced formation of the hydroxo complex in the presence of a base goes along with an increased tendency for its dismutation to $Zn(OH)_2$ and $ZnTp_2$. These phenomena may explain why a compound containing isolated tetrahedral $TpZn\cdot OH_2$ cations has not been obtained yet and why attempts have failed to prepare TpZn−OH species by hydrolysis of TpZn−R.[3,19]

The complex types L·Zn−OH, L·Zn−OH_2, $(L\cdot Zn)_2OH$, and $(L\cdot Zn)_2O_2H_3$ described in this paper must all be involved in acid−base equilibria of the above-mentioned type. Accordingly, their formation is controllable only to a limited extent, and, accordingly, it has taken years of repeating experiments and varying conditions to isolate and characterize the specific complexes, yet finally in a reproducible way. In principle, all of their syntheses follow the same scheme: a zinc salt with nonnucleophilic anions, typically zinc perchlorate, is treated with the tripod ligand. Variations of the solvent and the possible presence of KOH are used to adjust the conditions for the isolation of the resulting complex. There is no case where all four complex types are accessible for one and the same tripod ligand, and there is no case where one complex type, once isolated, could be converted to another one.

Results of the desired kind were obtained with the tripods offering N_3, NS_2, and S_3 donor sets. The reason that the bis(pyrazolyl)thioimidazolylborates[4] as N_2S tripods did not yield any one of the OH-containing Zn complexes must be sought in the fact that they contain unsubstituted pyrazolyl groups and, hence, cannot provide the encapsulating pocket around the Zn ion that seems to be essential in this field of chemistry. Similarly nonproductive were attempts to prepare the Zn−OH-containing complexes starting from precursors other than $Zn(ClO_4)_2$, for instance, by treating a L·Zn halide complex with freshly precipitated Ag_2O. Thus, although quite a number of the desired complexes have been found, the challenge remains to complete the various series by different preparative procedures or to reach the stage where the members of the series can be interconverted.

Aqua Complexes. While attempting to study the $TpZn(OH_2)$/TpZn(OH) equilibrium by potentiometric titration[22] for species with 3-*tert*-butyl- or 3-aryl-substituted Tp ligands, we observed that complete protonation of TpZn−OH, i.e., the formation of $[TpZn(OH_2)]^+$ in solution, leads to decomposition involving the autocatalytic hydrolytic destruction of the Tp ligand. Attempts to isolate any such $TpZn(OH_2)$ complex must therefore avoid acidic media or save the product by quick isolation. After many attempts with the former, we succeeded in one case with the latter. Mixing $KTp^{Ph,Me}$ with $Zn(ClO_4)_2\cdot 6H_2O$ in acetone, followed by the addition of $KBPh_4$ and precipitation of the product, allowed the isolation of **1**.

$$[Tp^{Ph,Me}Zn(H_2O)_3]BPh_4$$

1

Compound **1** could not be subjected to a crystal structure determination, and its spectral data only allow one to guess about its structure. The water resonance in the ^1H NMR spectrum at 2.03 ppm in $CDCl_3$ proves that there is no free water in solution (which in $CDCl_3$ gives rise to a signal at 1.47 ppm). The strong broad IR band at 3360 cm^{-1} indicates that the water molecules are involved in H bonds. Thus, the question of how many of the water molecules in **1** are directly bound to Zn and how many are attached to these by H bonds remains open.

In contrast to our "classical" pyrazolylborates that bear only hydrocarbon substituents, our new polar ones bearing 4-pyridyl or carboxamido substituents[14] made it easy to prepare the $TpZn(OH_2)$ complexes **2** and **3**, whose compositions (but not their solid-state structures) are indicated in the formula drawings below. Complex **2** was obtained by simply combining $KTp^{4-Py,Me}$ and $Zn(ClO_4)_2$, and complex **3** resulted from treatment of $Tp^{tBuA,Me}Zn-Br$ with $AgClO_4\cdot H_2O$. They show the presence of their Zn-bound water ligand by their IR bands at 3515 and 3361 cm^{-1}, respectively. In the polar

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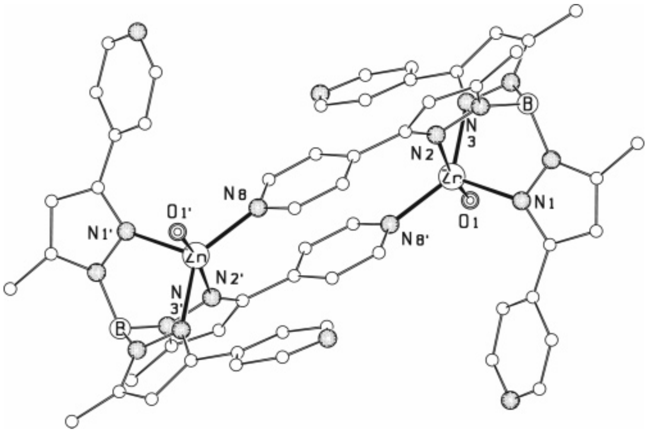
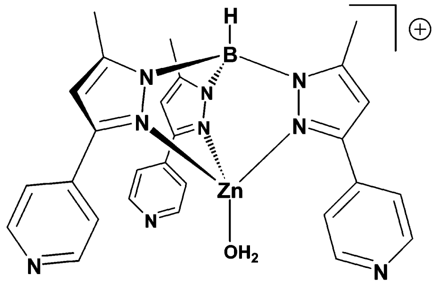


Figure 1. Structure of one of the two dimeric cations of **2** in the solid state. Bond lengths (Å): Zn−N1 2.031(5)/2.060(5), Zn−N2 2.352(5)/2.278(5), Zn−N3 2.025(5)/2.024(5), Zn−N8′ 2.005(5)/2.011(5), Zn−O 2.168(4)/2.139(4).

deuterated media necessary to record their NMR spectra, their OH signals could not be observed.



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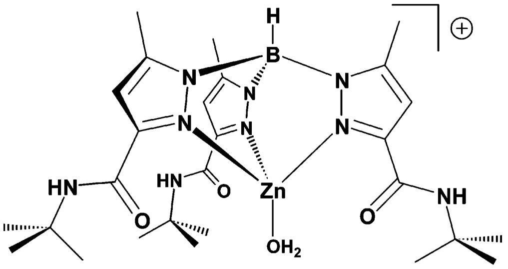

3

Both **2** and **3** were identified by structure determinations. The structure of one of the two independent units of **2** is shown in Figure 1. Like in almost all other Zn complexes of $Tp^{4-Py,Me}$,[14] association has occurred by using one of the pyridyl N atoms. In the case of **2**, the result of this is a dimer with five-coordinate Zn. The coordination geometry of the metal is trigonal-bipyramidal with the water ligand and one of the tripod's N atoms on the axis (angle ca. 170°), in accordance with their elongated bonds to Zn. Just like in many Zn complexes of the previously reported $Tp^{3-Py,Me}$, including the aqua/phosphate complex,[16] the increased polarity of the environment of Zn goes along with an increase of the coordination numbers. The main difference between the two independent units of **2** in the crystal is that in one of them the water ligand is H-bonded to another water molecule in the crystal, while in the other, it is H-bonded to a methanol molecule. It is noteworthy that the ^1H NMR solution data of **2** do not reflect the structure in the crystal. As was observed previously for other $Tp^{4-Py,Me}Zn$ complexes,[14] two sets of resonances are observed for the Tp ligand with an intensity ratio of 1:5, indicating other coordination patterns and/or equilibration in solution.

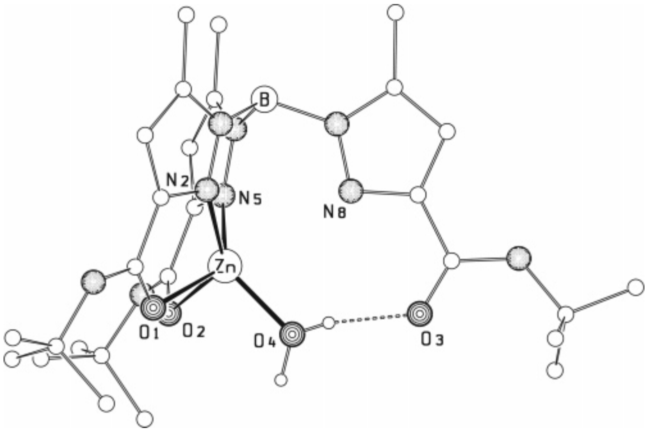

Figure 2. Structure of the cation of **3** in the solid state. Bond lengths (Å): Zn−N2 2.024(3), Zn−N5 2.019(3), Zn−O1 2.190(3), Zn−O2 2.276(3), Zn−O4 1.922(3), O4···O3 2.586(5).

The structure of **3** is quite different (see Figure 2). The *tert*-butylcarboxamido-substituted Tp ligand is using only two of its pyrazole donors for coordination, which is rare and previously unobserved for this type of ligand.[14] Instead, the two carbonyl O atoms of the two coordinating carboxamidopyrazoles are bound to Zn, creating two five-membered N,O chelate rings. This N_2O_2 donor arrangement constitutes the basis of a square pyramid, the apical position of which is occupied by the water ligand. This, in turn, is connected to the carbonyl O of the noncoordinating carboxamidopyrazole. Compared to the other Zn−ligand bonds, the Zn−O(H_2O) bond is remarkably short.

All three new aqua complexes described here display unusual structural features. It is likely that all three have a coordination number higher than 4 for the Zn ion, following the trend that harder donors (or a higher polarity) in the ligand sphere of Zn go along with higher coordination numbers. Thus, although the goal of making $TpZn(OH_2)$ complexes was achieved, the quest for a genuine tetrahedral $TpZn(OH_2)$ cation remains.

(μ-O_2H_3)Zn_2 Type. If one out of two $L\cdot Zn(OH_2)$ complex units is deprotonated, the composition of the bulk is $L_2Zn_2(O_2H_3)$. This would be the case if the pH of the solution is identical with the pK_a of the $L\cdot Zn(OH_2)$ species. We had verified this condition for TpZn complexes with 3-pyridyl- and cumenyl-substituted Tp's. As a result, we had isolated the dinuclear TpZn(μ-O_2H_3)ZnTp complexes.[20] Later Cohen had obtained the same result with our $Tp^{Ph,Me}$ ligand.[23]

During our attempts to grow single crystals of the aqua complex **1**, we experienced that, instead of **1**, only its relatives **4** and **9** (see below) could be precipitated in a crystalline form. A very small amount of **4** was obtained from dichloromethane/methanol; an equally small amount

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of **9** resulted from acetone/water. In both cases, no acid or base was added to the crystallization solutions, which implies that the acid/base properties of the solvent mixtures alone account for the partial deprotonation of **1**. The formation of **4** corresponds to the above-mentioned deprotonation of one out of two $TpZn(OH_2)$ units, with the subsequent linking of TpZn(OH) and $TpZn(OH_2)$ via a H bond. The formation of **9** involves the same 50% deprotonation and subsequent substitution of water from $TpZn(OH_2)$ by TpZn(OH).

$$[Tp^{Ph,Me}Zn{-}OH\cdots H\cdots HO{-}ZnTp^{Ph,Me}]BPh_4$$

4

The crystal structure of **4** was determined (see the Supporting Information). The structural details of the $Zn{-}O_2H_3{-}Zn$ core (Zn−O 1.884(2) and 1.892(2) Å; O···O 2.43 Å) closely resemble those of Cohen's identical complex with perchlorate counterions[23] and also those of our three previous structure determinations of similar $(TpZn)_2(\mu\text{-}O_2H_3)$ complexes.[20] In a way, complex **4** is a better representation of the desired tetrahedral $TpZn(OH_2)$ species than complex **1**, insofar as it can be described, just like Parkin's $TpZn{-}OH_2\cdots OHB(C_6F_5)_3$,[3] as a $TpZn(OH_2)$ species stabilized by a H bond to a base whose corresponding acid is of strength similar to that of this $TpZn(OH_2)$.

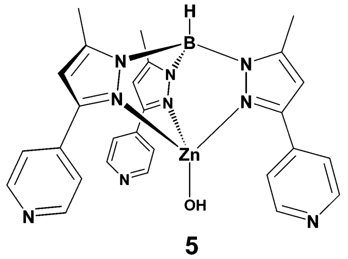
In the context of this work, complex **4** was the only occurrence of the $(\mu\text{-}O_2H_3)Zn_2$ type. However, its "water-free" equivalent represented by complexes **9**−**14** (see below) provides ample evidence that our tripod−Zn−OH species are protonated (and likewise their implied counterparts $tripod{-}Zn{-}OH_2$ are deprotonated) near neutral pH. This, in turn, implies that the $TpZn{-}OH_2$ species have pK_a's near 7, as confirmed by our preliminary potentiometric measurements,[22] an essential quality making the TpZn−OH complexes viable models of hydrolytic zinc enzymes.[2]

Hydroxo Complexes. The formation of the hydroxo complexes (tripod)Zn−OH corresponds to the deprotonation of all $(tripod)Zn(OH_2)$ species in solution. Accordingly, the five previously reported hydroxo complexes with Tp ligands[13,21,24−26] and the one with a tris(thioimidazolyl)borate ligand[15] were prepared from the tripod, a simple zinc salt and a base. However, in many cases, particularly with the NS_2 and S_3 tripods, this did not yield the desired result because of the high tendency of formation of the $Zn(tripod)_2$ complexes, causing the dismutation of (tripod)Zn−OH to $Zn(tripod)_2$ and $Zn(OH)_2$.

The availability of the new polar tris(pyrazolyl)borate ligands[14] as well as further NS_2[7,8] and S_3 tripods[11,12] gave us an opportunity to search for further (tripod)Zn−OH complexes with them. This search yielded the four new compounds **5**−**8**, whose compositions (but not necessarily their structures) are shown as formula drawings here. Again their synthesis is seemingly straightforward: zinc perchlorate or nitrate is treated with the tripod and base. Yet, it took some adjustment of the reaction conditions to get the desired products (Chart 1).

Except for the two cases mentioned below, complexes **5**−**8** did not yield crystals suitable for structure determinations. They could be identified by their ^1H NMR spectra. One would have wished to observe NMR or IR data of their OH functions, as was possible for the TpZn−OH complexes with hydrocarbon-substituted Tp ligands, which show sharp IR bands near 3600 cm^{-1} and ^1H NMR signals near 0 ppm. However, the presence of water or methanol in the isolated compounds and/or H/D exchange in the NMR solvents wiped out the OH NMR signals and shifted the OH IR bands, just as in the previous Zn−OH complexes with polar Tp ligands or the one case with a S_3 tripod.[13,15,17,25] The observed broad OH bands in the IR spectra in the 3200−3400-cm^{-1} range are indicative of H-bonded species. The lack of spectroscopic evidence for the Zn−OH units is overcome, however, by the structure determinations of **5a** and **8** and, equally important, by the hydrolytic activity of all four new complexes.[27]

Chart 1



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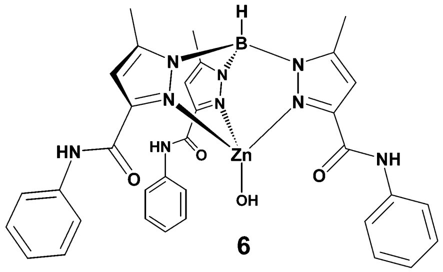

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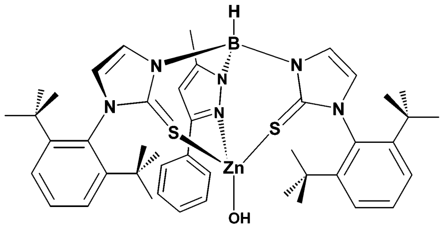

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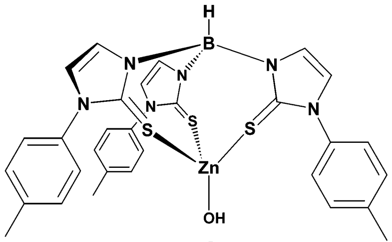

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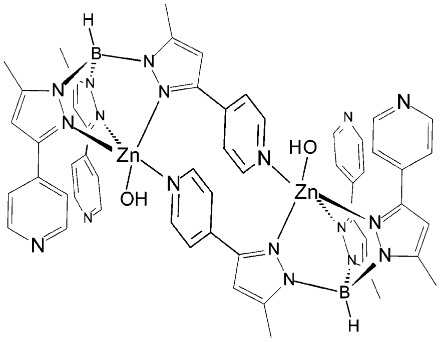

Figure 3. Proposed structure for complex **5**.

In the ^{1}H NMR spectrum of complex **5**, there is a 2:1 splitting of all nonmultiplet resonances. This supports the notion that **5**, like the parent aqua complex **2** and the related methanol complex,[14] is a dimer, in which one pyridyl substituent of each TpZn unit is coordinated to a second such unit, creating the dimeric structure displayed in Figure 3.

Compound **5** was obtained only when the reaction solutions were permanently cooled in an ice bath. When this was not the case, partial decomposition took place with the formation of $Zn(OH)_2$ as a cloudy precipitate. This indicated dismutation with concomitant formation of $Zn(Tp^{4-Py,Me})_2$. Confirmation for that came after isolation of the species remaining in solution, which turned out to be the 2:1 association product **5a**.

$$Zn(Tp^{4-Py,Me})_2{\cdot}2Tp^{4-Py,Me}Zn{-}OH$$

5a

Complex **5a** seems to exist with the same composition in the solid state as well as in solution, as evidenced by the occurrence of four sets of ^{1}H NMR signals with 2:2:1:1 intensity ratios. The result of the structure determination of **5a** (see the Supporting Information) is shown schematically in Figure 4. The central $ZnTp_2$ unit uses two of its six pyridyl substituents to coordinate to the external TpZn−OH units. This gives the two symmetry-related TpZn−OH units an extremely elongated trigonal-bipyramidal coordination, with one pyrazole arm almost detached from the metal. The Zn−N distances reflect this situation: they are 2.19−2.28 Å at the octahedral central Zn, and the three "normal" ones at the external zinc atoms are 2.04−2.12 Å, while the elongated Zn−N interaction is 2.81 Å long. The Zn−O distance of 1.874(3) Å corresponds to those in the other tetrahedral TpZn−OH complexes.[15,19,21]

We assume the structures of complexes **6** and **7** to correspond to the formula drawings shown above. The ^{1}H NMR data of complex **6** show no peculiarities, indicating that **6** is a normal tetrahedral TpZn−OH complex. The ^{1}H NMR spectrum of the (NS_2)Zn−OH compound **7** shows separate resonances of equal intensity for the *tert*-butyl groups. We have no convincing explanation for this, other than that the bulky *tert*-butyl groups enforce rigid orientations of the two *tert*-butylphenyl substituents. It would have been advantageous to have a structure determination of **7** because this (NS_2)Zn−OH complex is the first of its kind. However, the lability of **7** in solution, related again to the tendency for dismutation, prevented the growing of suitable single crystals.

For the (S_3)Zn−OH complex **8**, the dismutation tendency could be kept under control, and crystals for a structure determination could be obtained. Figure 5 shows the structure. The molecules of **8** have crystallographically imposed trigonal symmetry, and the coordination of Zn is close to ideally tetrahedral. The Zn−O bond is slightly longer than those in the TpZn−OH complexes[19,21] but corresponds to that in Parkin's related (S_3)Zn complex Tm^{Ph}Zn−OH[15] (1.90 Å). Most molecular features of **8** correspond to those of Parkin's compound, including the presence of three H-bonded methanol molecules in the vicinity of the OH group. The H atom of the OH group could not be located crystallographically because of its disordered position due to the 3-fold molecular symmetry.

This paper describes only the syntheses and structures of the new OH_2- and OH-containing complexes. The motivation for their investigation, as mentioned above, was their hoped-for applicability as models of hydrolytic zinc enzymes. Our investigations toward this end, particularly with the (tripod)-Zn−OH species, have borne some fruit already, and they will be published subsequently.[27]

OH-Bridged Dinuclear Complexes. The dinuclear (tripod)Zn complexes with a Zn−OH−Zn center, hitherto represented by just one example,[17] were an unexpected outcome of this study. However, they turned out to be the easiest to prepare and to crystallize. All tripod types used here yielded this type of complex, and all six new compounds could be subjected to structure determinations.

As mentioned above, the formation of the Zn−OH−Zn species can be understood as a reaction that competes with the formation of the $Zn{-}O_2H_3{-}Zn$ species: one out of two $Zn(OH_2)$ units is deprotonated, and the resulting Zn−OH unit behaves as a ligand, replacing the water molecule of the second $Zn(OH_2)$ unit. In line with this, our first Zn−OH−Zn complex of this type was found accidentally: compound **9** resulted in the form of just a few crystals from attempts to crystallize the aqua complex **1** from acetone/water, with the yield being so low that the structure determination is the only identification of **9**. Having realized the existence of this complex type, compounds **10**−**12** followed in quick succession. All three resulted in good yields from the combination of zinc perchlorate with the tripod ligand without the addition of a base. Finally, the two (S_3 tripod)Zn complexes **13** and **14** required the addition of KOH to result in good yields. Of the six new complexes, three (**12**−**14**) have no counterpart among the Zn−OH or $Zn(OH_2)$ complexes and two (**10** and **11**) are relatives of the Zn−OH complexes ($Tp^{Fu,Me}$Zn−OH[13] and **6** described here). Only **9**, which contains our most thoroughly investi-

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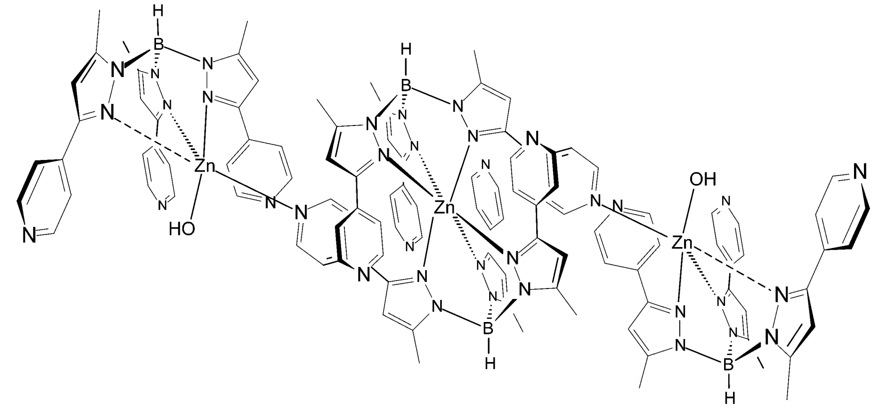


Figure 4. Schematic drawing of the crystal structure of complex **5a**.

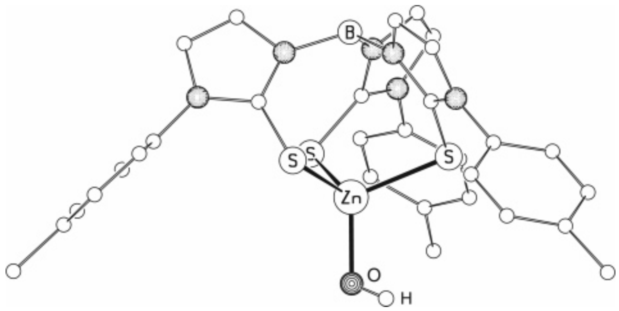


Figure 5. Molecular structure of complex **8**. Bond lengths (Å): Zn−S 2.342(2), Zn−O 1.906(9).

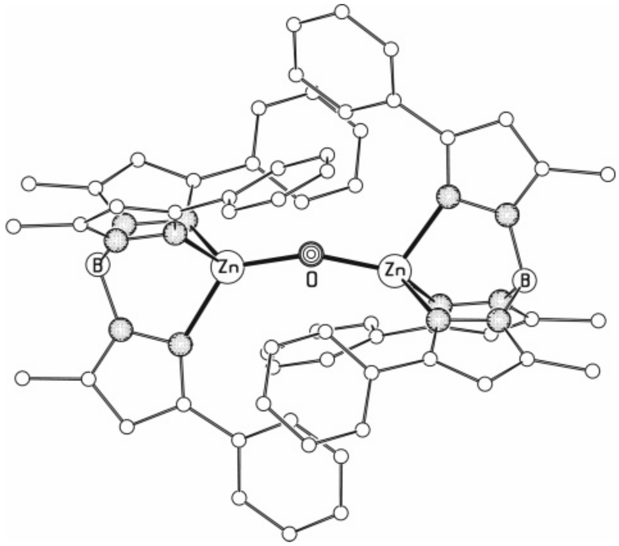
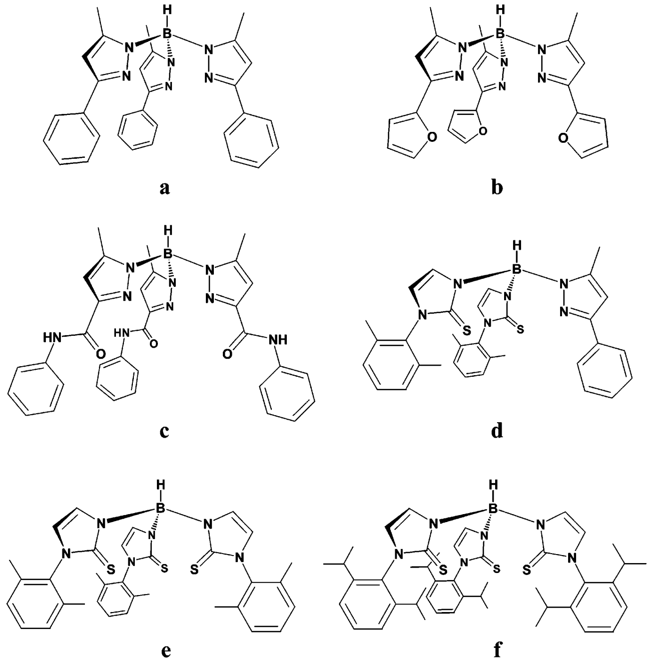


Figure 6. Structure of the dinuclear cation of **9**.

Chart 2



	[(tripod)Zn−OH−Zn(tripod)] X					
no.	**9**	**10**	**11**	**12**	**13**	**14**
tripod	**a**	**b**	**c**	**d**	**e**	**f**
X	BPh_4	ClO_4	ClO_4	ClO_4	ClO_4	ClO_4

gated Tp ligand, has counterparts in all other classes: Zn-(OH_2) (**1**), Zn−O_2H_3−Zn (**4**), and Zn−OH (Chart 2).[20]The ν(OH) IR bands of complexes **9**−**14** do not yield characteristic information. They are weak and broad, located between 3300 and 3500 cm^{-1}. In some, but not all, cases, this relates to the existence of H bonds between the OH groups and either cocrystallized solvent molecules or donor functions on the tripod. Unambiguous identification of the complexes came from the six structure determinations, particularly from the location of the counterions therein, which ruled out the presence of uncharged (tripod)Zn−O−Zn(tripod) compounds. All crystallographic information is documented in the Supporting Information. For two representative examples, **9** and **13**, the molecular structures are displayed in Figures 6 and 7.

The structural details of all six complexes are closely related. Each contains two pseudotetrahedral (tripod)Zn−O units that display the usual attachment of the tripod ligands to zinc. As Table 1 shows, all Zn−O bond lengths fall into a very narrow range, with a slight tendency to get longer with an increasing S content of the tripod ligand. Compared to corresponding mononuclear (tripod)Zn−OH complexes[19,21,24] including **8**, they are only 0.02−0.04 Å longer.

The noteworthy feature of the Zn−OH−Zn complexes is the bent arrangement of the Zn−OH−Zn unit. This is certain for **9** and **11**−**13**, and it had to be revealed by resolving disorder in **10** (where the Zn−O−Zn array is on the crystallographic 3-fold axis) and **14** (where the O atom seems to be on an inversion center). As Table 1 shows, the bending

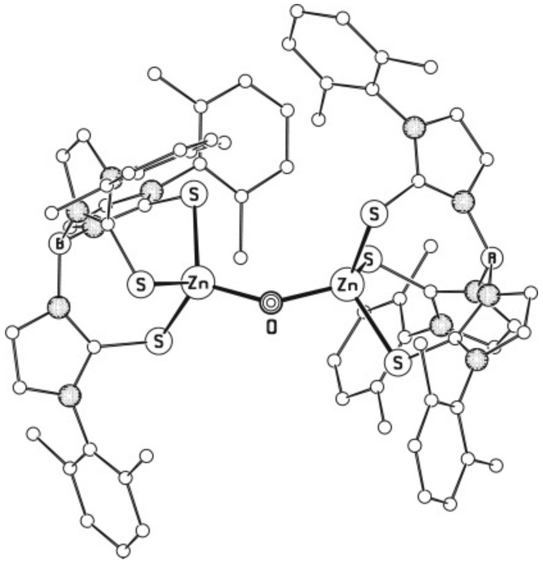


Figure 7. Structure of the dinuclear cation of **13**.

Table 1. Structural Characteristics of the Zn−OH−Zn Complexes

	Zn−O (Å)	Zn−O−Zn (deg)
9	1.909(2)/1.908(2)	156.2(5)
10[a]	1.877(16)	156.0(4)
11	1.885(5)/1.901(5)	120.3(2)
12	1.911(5)/1.913(5)	130.1(3)
13	1.925(5)/1.943(5)	139.5(3)
14[a]	1.82(3)/1.99(2)	160(1)

[a] Disordered positions for the O atom.

angles vary between 120 and 160°, which corresponds to the situation in the two (tridentate)Zn−OH−Zn(tridentate) complexes in the literature (134 and 160°).[17,28] This, of course, is a reflection of the sterical demands of the intertwining tripod ligands but, more importantly, of the "softness" of large bonding angles at O, for which phenomenon the silicates provide the most striking examples.

Conclusions

Another title of this paper could have been "Derivatizing Water in the Presence of Tripod−Zinc Complexes", which expresses both the motivation for and the results of the studies described here. New Zn−OH$_x$ combinations were found for our old tripods, the nonpolar tris(pyrazolyl)borates, and the new ones, the functionalized tris(pyrazolyl)borates as well as the NS$_2$ and S$_3$ tripods, were found to be equally able to derivatize water in all possible ways.

Of the four bonding combinations observed here, Zn−OH$_2$, Zn(O$_2$H$_3$)Zn, Zn−OH, and Zn−OH−Zn, the first one is still more a challenge than a reality for the (tripod)Zn units, and the last one, which was almost unprecedented, turned out to be the simplest to prepare. It should be noted that the "final step", the formation of a Zn−O−Zn species for which we have one example,[29] was not observed here.

It cannot be said that systematic procedures have been developed for the synthesis of any of the four product types. Each preparation was found empirically. It is most likely that two or three of the product types were present as parts of equilibrium mixtures in each reaction solution. Subtle differences in their acid−base behavior and their solubility must then have decided which species was isolated. The three different realizations of the Tp^{Py,Me}Zn−(OH$_x$) system, **2**, **5**, and **5a**, shed light on the intricacies involved. Yet, in the end, things were rather simple again: most of the specific tripods used yielded just one type of product.

The next step in the chemistry of these compounds must be Zn catalysis, i.e., their investigation toward stoichometric or catalytic cleavage of hydrolyzable substrates. We have made some preliminary studies toward this end,[27] but most of it will be left to our successors. There is no doubt that the acid−base equilibria underlying the preparative chemistry will be equally decisive for the reactivity of the isolated Zn(OH$_x$) compounds.

Experimental Section

General Data. All experimental techniques and the standard IR and NMR equipment were as described previously.[30] The tripod ligands in the form of their potassium salts were prepared as published.[7,8,11−14,26] A common problem with these types of complexes is that the C values in the elemental analyses are inconsistent. Therefore, when they were off by more than 1%, at least one more value (normally for S or Zn) was obtained.

Caution! *Perchlorate salts are potentially explosive. They should only be handled with utmost care in small amounts and with suitable safety equipment.*

1. A solution of 199 mg (0.38 mmol) of KTp^{Ph,Me} in 20 mL of acetone was mixed with a solution of 143 mg (0.38 mmol) of Zn(ClO$_4$)$_2$·6H$_2$O in 4 mL of O-free water. After the solution was stirred for 1 h, 130 mg (0.38 mmol) of NaBPh$_4$ was added to the clear solution. The mixture was stirred overnight and then reduced in vacuo to 8 mL, upon which a precipitate formed. This was filtered off and dried in vacuo, leaving behind 192 mg (57%) of **1** as a colorless powder. Mp: 124 °C. IR (KBr): 3363 (vs, b, H$_2$O), 2554 (m, BH). ^{1}H NMR (CDCl$_3$): 2.03 [s, 6H, H$_2$O], 2.58 [s, 9H, Me(pz)], 6.26 [s, 3H, H(pz)], 6.79−7.41 [m, 35H, Ar]. Anal. Calcd for C$_{54}$H$_{54}$N$_2$N$_6$O$_3$Zn (M_r = 922.07): C, 70.34; H, 5.90; N, 9.11. Found: C, 70.90; H, 5.78; N, 9.04.

2. A total of 165 mg (0.31 mmol) of KTp$^{4-Py,Me}$ was dissolved in 20 mL of methanol/dichloromethane (1:1), and 128 mg (0.34 mmol) of Zn(ClO$_4$)$_2$·6H$_2$O in 5 mL of water was added dropwise. The mixture was stirred for 2 h at room temperature, and then the precipitated KClO$_4$ was filtered off. The filtrate was concentrated in vacuo to half of the initial volume and then slowly evaporated at room temperature to yield 151 mg (72%) of **2** as colorless crystals (mp 300 °C). Cocrystallized water could not be completely removed by prolonged pumping. IR (KBr): 3515 (m, b, H$_2$O), 2567 (m, BH), 1622 (s, Py). ^{1}H NMR (DMSO-d_6): 2.00 [s, 1.5H, Me(pz)], 2.55 [s, 7.5H, Me(pz)], 6.46 [s, 0.5H, H(pz)], 6.63 [s, 2.5H, H(pz)], 7.67 [m, 6H, Py], 8.53 [d, J = 6.0 Hz, 1H, Py], 8.84 [d, J = 5.9 Hz, 5H, Py]. Anal. Calcd for C$_{27}$H$_{27}$BClN$_9$O$_5$Zn·H$_2$O (669.22 + 18.02): C, 47.19; H, 4.25; N, 18.34. Found: C, 47.01; H, 4.15; N, 18.19.

3. A solution of 45 mg (0.20 mmol) of AgClO$_4$·H$_2$O in 2 mL of methanol was added to a solution of 140 mg (0.20 mmol) of

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Table 2. Crystallographic Data

	2	**3**	**4**	**5a**	**8**	**9**
formula	$C_{54}H_{54}B_2Cl_2N_{18}O_{10}Zn_2 \cdot CH_3OH \cdot H_2O$	$C_{27}H_{50}BClN_9O_8Zn \cdot 0.5CH_2Cl_2$	$C_{84}H_{79}B_3N_{12}O_2Zn_2$	$C_{108}H_{102}B_4N_{36}O_2Zn_3 \cdot 2H_2O \cdot 3.5CH_2Cl_2$	$C_{30}H_{29}BN_6OS_3Zn \cdot 3CH_3OH$	$C_{84}H_{77}B_3N_{12}OZn_2 \cdot 2(CH_3)_2CO$
MW	1388.48	782.86	1457.84	2495.82	758.12	1549.98
cryst from	CH_2Cl_2/MeOH/H_2O	CH_2Cl_2	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	MeOH	acetone/water
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{3}c1$	$P2_1/c$
T (K)	247	203	245	293	217	203
Z	4	2	2	4	4	4
a (Å)	26.312(6)	11.956(2)	13.249(3)	20.566(3)	15.018(4)	24.576(4)
b (Å)	11.316(2)	13.437(2)	14.106(3)	16.961(3)	15.018(4)	14.463(2)
c (Å)	25.932(6)	13.656(2)	20.984(4)	33.994(5)	19.752(7)	22.823(4)
α (deg)	90	116.857(2)	72.788(3)	90	90	90
β (deg)	110.907(4)	103.009(2)	87.391(3)	92.157(4)	90	100.554(3)
γ (deg)	90	94.370(2)	88.649(3)	90	120	90
V (Å^3)	7213(3)	1866.7(4)	3742(1)	11849(3)	3858(2)	7975(2)
d_{calcd} (g cm^{-3})	1.28	1.45	1.29	1.40	1.28	1.29
μ(Mo Kα) (mm^{-1})	0.80	0.86	0.70	0.83	0.84	0.66
abs corrn [*SADABS*]	+	−	+	−	−	+
R1 (obsd reflns)	0.081	0.062	0.053	0.060	0.090	0.047
wR2 (all reflns)	0.235	0.180	0.169	0.211	0.300	0.1366

	10	**11**	**12**	**13**	**14**
formula	$C_{48}H_{45}B_2ClN_{12}O_{11}Zn_2$	$C_{66}H_{63}B_2ClN_{18}O_{11}Zn_2$	$C_{64}H_{65}B_2ClN_{12}O_5S_4Zn_2 \cdot 3CHCl_3$	$C_{66}H_{69}B_2ClN_{12}O_5S_6Zn_2 \cdot 3CH_3OH$	$C_{90}H_{119}B_2ClN_{12}O_5S_6Zn_2 \cdot 2CH_2Cl_2 \cdot CH_3OH$
MW	1153.76	1472.15	1756.55	1586.73	2031.17
cryst from	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	$CHCl_3$/pentane	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH
space group	$R\bar{3}$	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
T (K)	247	193	243	233	293
Z	3	8	4	4	2
a (Å)	11.786(2)	44.40(2)	17.226(3)	16.386(3)	14.465(2)
b (Å)	11.786(2)	17.703(8)	19.432(3)	19.856(4)	14.722(2)
c (Å)	31.507(2)	19.403(9)	24.621(4)	24.187(4)	14.797(2)
α (deg)	90	90	90	90	82.669(3)
β (deg)	90	110.61(1)	99.099(3)	104.803(4)	73.227(3)
γ (deg)	120	90	90	90	87.355(3)
V (Å^3)	3790(1)	14275(11)	8138(2)	7608(2)	2992(1)
d_{calcd} (g cm^{-3})	1.52	1.37	1.36	1.36	1.17
μ(Mo Kα) (mm^{-1})	1.08	0.78	0.91	0.89	0.71
abs corrn [*SADABS*]	−	+	−	−	+
R1 (obsd reflns)	0.058	0.096	0.099	0.077	0.082
wR2 (all reflns)	0.182	0.272	0.369	0.269	0.288

$Tp^{CONHtBu,Me}ZnBr$[14] in 12 mL of methanol at 0 °C with exclusion of light. After 30 min of stirring, the resulting precipitate was filtered off. The filtrate was evaporated to dryness in vacuo, leaving behind 140 mg (100%) of **3** as a colorless, very hygroscopic powder. Mp: 212 °C. IR (KBr): 3361 (s, br, H_2O), 2560 (w, BH), 1651 (s), 1608 (s, CO), 1072 (vs, ClO). ^1H NMR (CD_3OD): 1.48 [s, 27H, t-Bu], 2.46 [s, 9H, Me(pz)], 6.55 [s, 3H, H(pz)]. Anal. Calcd for $C_{27}H_{50}BClN_9O_8Zn \cdot 2H_2O$ (M_r = 740.39 + 36.04): C, 43.05; H, 6.29; N, 16.73. Found: C, 43.08; H, 6.26; N, 16.19.

4. A total of 9 mg (0.01 mmol) of **1** was dissolved in 2 mL of dichloromethane/methanol (1:1) and subjected to very slow evaporation through a rubber stopper. The first few crystals forming after about 2 weeks were taken for structure determination, which revealed the identity of **4**. The remaining solution, according to ^1H NMR, still consisted of **1** together with some decomposition products.

5. A solution of 128 mg (0.34 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 5 mL of water was added dropwise to a solution of 165 mg (0.31 mmol) of $KTp^{4-Py,Me}$ in 20 mL of dichloromethane/methanol (1:1). After 2 h of stirring, the precipitate was filtered off. The filtrate was cooled in an ice bath and treated with a solution of 35 mg (0.62 mmol) of KOH in 10 mL of dichloromethane/methanol (1:1). After another 2 h of stirring and filtration, the filtrate was concentrated in vacuo until a precipitate started to form. Keeping this mixture at 5 °C for 2 days resulted in the precipitation of 142 mg (73%) of **5** as a colorless, very hygroscopic powder. Mp: 296 °C (dec). IR (KBr): 3633 (w, OH), 3394 (m, br, H_2O), 2551 (w, BH), 1605 (s, Py). ^1H NMR (DMSO-d_6, 40 °C): 2.01 [s, 6H, Me(pz)], 2.55 [s, 3H, Me(pz)], 6.44 [s, 2H, H(pz)], 6.62 [s, 1H, H(pz)], 7.56 [m, 6H, Py], 8.41 [d, J = 5.6 Hz, 4H, Py], 8.73 [d, J = 5.3 Hz, 2H, Py]. Anal. Calcd for $C_{27}H_{26}BN_9OZn \cdot 2H_2O$ (M_r = 568.76 + 36.04): C, 53.62; H, 5.00; N, 20.84. Found: C, 53.68; H, 4.81; N, 21.07.

5a. When the synthesis of **5** described above was carried out at room temperature, the final solution remaining after the last filtration developed a cloudy precipitate, presumed to be $Zn(OH)_2$, which was removed twice by filtration during the process of slow evaporation. Upon further evaporation, 20 mg (10%) of **5a** had formed as colorless crystals (mp 176 °C), which were analyzed without drying in vacuo. IR (KBr): 3407 (s, br, H_2O), 2555 (w, BH), 1606 (vs, Py). ^1H NMR (DMSO-d_6, 40 °C): 2.02 [s, 14H, Me(pz)], 2.08 [s, 4H,Me(pz)], 2.16 [s, 4H, Me(pz)], 2.55 [s, 14H, Me(pz)], 5.74 [s, 4H, H(pz)], 6.44 [s, 5H, H(pz)], 6.55 [s, 1H, H(pz)], 6.62 [s, 5H, H(pz)], 6.70 [s, 1H, H(pz)], 7.56 [m, 20H, Py], 7.63 [d, J = 6.2 Hz, 2H, Py], 7.74 [d, J = 6.2 Hz, 2H, Py], 8.41 [d, J = 5.9 Hz, 10H, Py], 8.48 [d, J = 6.2 Hz, 2H, Py], 8.59 [d, J = 6.2 Hz, 2H, Py], 8.73 [d, J = 4.9 Hz, 10H, Py]. Anal. Calcd for $C_{108}H_{102}B_4N_{36}O_2Zn_3 \cdot 2H_2O \cdot 2CH_2Cl_2$ (M_r = 2175.65 + 36.04 + 171.88): C, 55.43; H, 4.74; N, 21.15. Found: C, 55.12; H, 5.28; N, 20.75.

6. A solution of 0.11 g (0.31 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 2 mL of methanol was dropped into a solution of 0.18 g (0.28 mmol) of KTp^{CONHPh} in 10 mL of dichloromethane/methanol (1:1) while cooling with ice. After 10 min of stirring, a solution of 28 mg (0.50 mmol) of KOH in 1 mL of water was added. After 1 h of stirring while cooling with ice, the precipitate was filtered off. The filtrate was evaporated to dryness and the residue recrystallized from dichloromethane/methanol (4:1) by very slow evaporation, yielding 24 mg (12%) of **6** as a colorless powder. Mp: 258 °C (dec). IR (KBr): 3281 (m, br, H_2O), 2561 (w, BH), 1655 (s), 1600 (vs, CO). ^1H NMR (DMSO-d_6): 2.41 [s, 9H, Me(pz)], 6.80 [s, 3H, H(pz)], 7.14 [m, 3H, Ph], 7.37 [t, J = 7.4 Hz, 6H, Ph], 7.74 [m, 6H, Ph], 10.18 [s, 3H, NH]. Anal. Calcd for $C_{33}H_{32}BN_9O_4Zn \cdot H_2O$ (M_r = 694.86 + 18.02): C, 55.60; H, 4.81; N, 17.68. Found: C, 54.60; H, 4.54; N, 18.05.

7. A solution of 81 mg (0.22 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 12 mL of methanol was added dropwise with stirring to a solution of 136 mg (0.22 mmol) of $KHB(Tim^{tBu2Ph})_2(Pz^{Ph,Me})$ in 12 mL of methanol. After stirring for 2 h, the mixture was filtered and the filtrate evaporated in vacuo to 5 mL. Then a solution of 13 mg (0.23 mmol) of KOH in 3 mL of methanol was added. After stirring for another 20 h and filtering, the filtrate was evaporated to dryness. The residue was extracted with 10 mL of dichloromethane, which was filtered and evaporated to dryness again, leaving behind 98 mg (71%) of **7** as a colorless powder. Mp: 198 °C. IR (KBr): 3426 (m, br, OH), 2513 (w, BH). ^1H NMR ($CDCl_3$): 1.11 [s, 18H, t-Bu], 1.23 [s, 18H, t-Bu], 2.46 [s, 3H, Me(pz)], 6.30 [s, 1H, H(pz)], 6.68 [d, J = 2.0 Hz, 2H, H(im)], 6.90 [d, J = 2.0 Hz, 2H, H(im)], 6.96−7.89 [m, 11H, Ph]. Anal. Calcd for $C_{36}H_{40}BN_6OS_2Zn$ (M_r = 713.08): C, 60.64; H, 5.65; N, 11.79; S, 8.99. Found: C, 61.22; H, 5.82; N, 11.78; S, 9.07.

8. A total of 3.5 mL (0.88 mmol) of a 0.25 M solution of NaOMe in methanol was diluted with methanol to 40 mL. A solution of 144 mg (0.48 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ in 20 mL of methanol was added slowly with stirring, followed by a solution of 300 mg (0.48 mmol) of KTm^{p-Tol} in 30 mL of methanol. After about 1 h of stirring, a precipitate appeared, which was filtered off, washed with a small amount of methanol, and dried in vacuo, leaving behind 140 mg (42%) of **8** as a colorless powder (mp 215 °C). The filtrate, upon cooling in a refrigerator, precipitated another 171 mg (53%) of crystalline **8**. IR (KBr): 3160 (m, br, OH), 2463 (m, BH). ^1H NMR ($CDCl_3$): 2.36 [s, 9H, Me(p-Tol)], 4.80 [s, 6H, CH_3OH], 6.79 [d, J = 2.0 Hz, 3H, H(im)], 7.15 [d, J = 2.0 Hz, 3H, H(im)], 7.19 [d, J = 9.0 Hz, 6H, C_6H_4], 7.24 [d, J = 9.0 Hz, 6H, C_6H_4]. Anal. Calcd for $C_{30}H_{29}BN_6OS_3Zn \cdot 2CH_3OH$ (M_r = 662.00 + 64.08): C, 52.94; H, 5.14; N, 11.57; S, 13.25. Found: C, 53.69; H, 5.46; N, 11.92; S, 12.91.

9. A total of 9 mg (0.01 mmol) of **1** was dissolved in 2 mL of acetone/water (3:1) and subjected to very slow evaporation through a rubber stopper. The first few crystals forming after about 2 weeks were taken for structure determination, which revealed the identity of **9**. The remaining solution, according to ^1H NMR, still consisted of **1** together with some decomposition products.

10. A solution of 74 mg (0.20 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 20 mL of methanol was dropped with stirring into a solution of 100 mg (0.20 mmol) of $KTp^{Fu,Me}$ in 20 mL of dichloromethane over a period of 2 h. After filtration, the filtrate was evaporated to dryness in vacuo. The residue was suspended in 10 mL of methanol and the solvent filtered off. The remaining solid was recrystallized from dichloromethane/methanol (1:1) by slow evaporation, yielding 100 mg (87%) of **10** as colorless crystals. Mp: 216 °C. IR (KBr): 3531 (w, OH), 2543 (m, BH), 1107 (s, ClO). ^1H NMR ($CDCl_3$): 2.59 [s, 18H, Me(pz)], 5.91 [dd, J = 3.4 and 1.8 Hz, 6H, Fu], 6.31 [s, 6H, H(pz)], 6.50 [d, J = 3.4 Hz, 6H, Fu], 6.63 [d, J = 1.7 Hz, 6H, Fu]. Anal. Calcd for $C_{48}H_{45}B_2ClN_{12}O_{11}Zn_2$ (M_r = 1153.82): C, 49.97; H, 3.93; N, 14.47. Found: C, 49.51; H, 4.07; N, 14.17.

11. A solution of 84 mg (0.22 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 2 mL of methanol was added dropwise to a solution of 133 mg (0.20 mmol) of $KTp^{CONHPh,Me}$ in 10 mL of methanol/dichloromethane (1:1). After 3 h of stirring, the precipitated $KClO_4$ was removed by filtration and the clear filtrate was slowly evaporated at room temperature to yield 111 mg (74%) of **11** as colorless crystals. Mp: 218 °C. IR (KBr): 3298 (m, br, OH), 2565 (w, BH), 1107 (s, ClO). ^1H NMR ($CDCl_3$): 1.55 [s, br, 2H, H_2O], 2.43 [s, 18H, Me(pz)], 6.54 [s, 6H, H(pz)], 6.78 [m, 18H, Ph], 7.07 [m, 12H, Ph], 9.29 [s, br, 6H, NH]. Anal. Calcd for $C_{66}H_{63}B_2ClN_{18}O_{11}Zn_2 \cdot H_2O$ (M_r =

1472.19 + 18.02): C, 53.20; H, 4.40; N, 16.92. Found: C, 52.84; H, 4.67; N, 16.34.

12. A solution of 123 mg (0.20 mmol) of $KHB(Tim^{Xyl})_2(Pz^{Ph,Me})$ in 50 mL of methanol was added dropwise with stirring to a solution of 74 mg (0.20 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ in 20 mL of methanol. After stirring for 12 h and filtration, the solvent was removed in vacuo. The residue was picked up in 10 mL of dichloromethane, washed twice with 5 mL of water, filtered through a layer of Celite, and then evaporated to dryness again. Recrystallization by diffusion of pentane into a solution in 5 mL of chloroform yielded 38 mg (27%) of **12** as colorless crystals. Mp: 229 °C. IR (KBr): 3437 (m, OH), 2462 (m, BH), 1090 (vs, ClO). ^{1}H NMR ($CDCl_3$): 1.89 [s, 6H, Me(Xyl)], 1.93 [s, 6H, Me(Xyl)], 2.43 [s, 3H, Me(pz)], 6.36 [s, 1H, H(pz)], 6.77 [d, J = 2.1 Hz, 2H, H(im)], 7.01 [d, J = 2.1 Hz, 2H, H(im)], 7.04−7.31 [m, 4H, Ar], 7.44−7.75 [m, 7H, Ar]. Anal. Calcd for $C_{64}H_{65}B_2ClN_{12}O_5S_4Zn_2$ (M_r = 1398.41): C, 54.97; H, 4.68; N, 12.02; S, 9.17. Found: C, 53.38; H, 4.62; N, 11.65; S, 8.75.

13. A solution of 200 mg (0.30 mmol) of KTm^{Xyl} in 10 mL of methanol was added dropwise with stirring to a solution of 112 mg (0.30 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ in 10 mL of methanol. After stirring for 2 h and filtration, a solution of 17 mg (0.30 mmol) of KOH in 5 mL of methanol was added with stirring. Within 15 h of stirring, a precipitate was formed. This was filtered off and the filtrate evaporated to dryness. The residue was suspended in 20 mL of dichloromethane and filtered and the filtrate evaporated to dryness again. Recrystallization from dichloromethane/methanol by slow evaporation yielded 169 mg (75%) of **13** as colorless crystals. Mp: 234 °C (dec). IR (KBr): 3508 (w br, OH), 2418 (w, BH), 1100 (s, ClO). ^{1}H NMR ($CDCl_3$): 1.93 [s, 36H, Me(Xyl)], 6.51 [d, J = 2.1 Hz, 6H, H(im)], 6.75 [d, J = 2.1 Hz, 6H, H(im)], 6.80−7.03 [m, 12H, Ar], 7.05−7.13 [m, 6H, Ar]. Anal. Calcd for $C_{66}H_{69}B_2ClN_{12}O_5S_6Zn_2$ (M_r = 1490.60): C, 53.18; H, 4.67; N, 11.28; S, 12.91. Found: C, 54.54; H, 4.97; N, 11.47; S, 13.21.

14. Like **13**, **14** was produced from 200 mg (0.24 mmol) of $KTm^{i-Pr2Ph}$, 90 mg (0.24 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$, and 14 mg (0.24 mmol) of KOH. Yield: 179 mg (81%) as colorless crystals. Mp: 260 °C (dec). IR (KBr): 3442 (w, br, OH), 2442 (w, BH), 1097 (s, ClO). ^{1}H NMR ($CDCl_3$): 0.39 [d, J = 6.8 Hz, 12H, Me-(i-Pr)], 0.88 [d, J = 6.8 Hz, 12H, Me(i-Pr)], 1.03 [d, J = 6.8 Hz, 6H, Me(i-Pr)], 1.20 [d, J = 6.8 Hz, 42H, Me(i-Pr)], 2.35 [m, 10H, H(i-Pr)], 2.71 [m, 2H, H(i-Pr)], 6.85 [d, J = 2.1 Hz, 6H, H(im)], 6.99−7.16 [m, 6H, Ar], 7.18 [d, J = 2.1 Hz, 6H, H(im)], 7.23−7.39 [m, 12H, Ar]. Anal. Calcd for $C_{90}H_{119}B_2ClN_{12}O_5S_6Zn_2$ (M_r = 1829.26): C, 59.09; H, 6.56; N, 9.12; S, 10.52. Found: C, 58.70; H, 6.45; N, 9.02; S, 10.64.

Structure Determinations. All details are listed in Table 2. Diffraction data were recorded with a Bruker AXS Smart CCD diffractometer with Mo Kα radiation. The structures were solved with direct methods.[31] Parameters were refined against F^2. Drawings were produced with *SCHAKAL*.[32] In the crystal lattice of **2**, two water molecules, one methanol, and one dichloromethane molecule and, in the crystal lattice of **11**, one water molecule, one methanol, and one dichloromethane molecule per asymmetric unit were present in a severely disordered form. They were treated as a diffuse contribution using the program *SQUEEZE*.[33] Accordingly, they do not appear as individual atoms in the parameter listings.

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Supporting Information Available: Eleven crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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