

New Bis(mercaptoimidazolyl)(pyrazolyl)borate Ligands and Their Zinc Complex Chemistry

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Nine new tripodal NS₂ ligands of the bis(mercaptoimidazolyl)(pyrazolyl)borate type with varying 3-R-mercaptoimidazolyl moieties were prepared as their potassium salts. Treatment with zinc salts yielded the complex types L·Zn–Cl, L·Zn–I, L·Zn–ONO₂, L·Zn–OCIO₃ and [L·Zn(imidazole)]ClO₄. Attempts at the formation of L·Zn–OH or cationic L·Zn complexes resulted in dismutation and formation of ZnL₂ complexes. Hydrolytic destruction yielded one [OZn₄(thioimidazolate)₆] complex. The ZnS₂NO coordination which is pre-

sent in the enzyme-substrate complex of alcohol dehydrogenase could be successfully modelled by an [L·Zn(C₂H₅OH)]⁺ complex. The L·Zn–X complexes showed very low catalytic activity in the dehydrogenation of 2-propanol or the hydrogenation of *p*-nitrobenzaldehyde. The new compounds were identified by a total of 12 structure determinations.

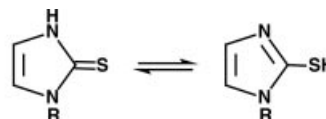
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Introduction

The importance of tris(pyrazolyl)borate ligands for coordination chemistry can only be compared with that of cyclopentadienyl ligands in organometallic chemistry. This holds specifically for the classical or bioinorganic coordination chemistry of zinc^[1,2] to which we have made contributions.^[3] The advantage of these tripodal ligands is that they quite reliably support an N₃ZnX coordination motif which has given them then name “tetrahedral enforcers” and which has made them so valuable for the bioinorganic chemistry of zinc.^[3,4]

The N₃Zn motif represents the attachment of a zinc ion to three histidine residues in a protein. Considering that cysteine is equally important for zinc binding in enzymes, one would like to have sulfur-containing tripodal ligands with qualities similar to those of the pyrazolylborates for a model complex chemistry. The accumulated experience with tripodal ligands containing thiolate functions has shown, however, that these are not suitable because the bridging tendency of the thiolates cannot be suppressed. In this context Reglinski's discovery of the tris(mercaptoimidazolyl)borates^[5] must be considered a breakthrough. As shown since by Reglinski himself^[6,7] and his competitors,^[8,9] including ourselves,^[10] these tripods are very good “tetrahedral enforcers” and allow a fruitful biomimetic zinc

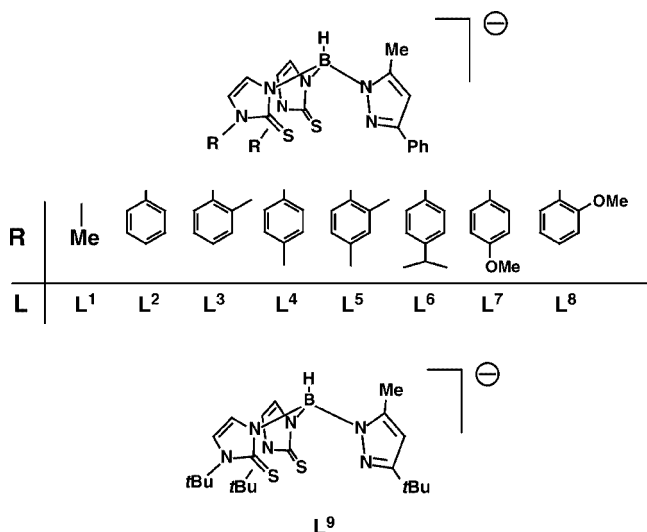
model complex chemistry. The reason for this is the fact that their sulfur donors are “tame” thiolates with a low bridging tendency due to their thiol-thione tautomerism as depicted below.



Having the easily accessible tris(pyrazolyl)- and tris(mercaptoimidazolyl)borates available as N₃ and S₃ donors, we decided to aim at their combination in the form of N₂S and NS₂ donors. Specifically, the NS₂ tripods should be valuable as they allow us to mimic the (NS₂)ZnX coordination in alcohol dehydrogenase. With this in mind both the research group of Parkin and ourselves set out to study the chemistry of the bis(mercaptoimidazolyl)(pyrazolyl)borates. Parkin has published the synthesis of one such ligand and some basic metal complex chemistry of it.^[11–13] We have communicated the first correct structural model of the enzyme-substrate complex of alcohol dehydrogenase in the form of a (NS₂)Zn(C₂H₅OH) complex.^[14]

This paper summarises our recent work on bis(mercaptoimidazolyl)(pyrazolyl)borate ligands, their basic zinc complex chemistry and attempts to apply them for the modelling of the zinc enzyme alcohol dehydrogenase. Nine new ligands **L** were prepared and their zinc complexes identified by a total of twelve structure determinations.

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Results and Discussion

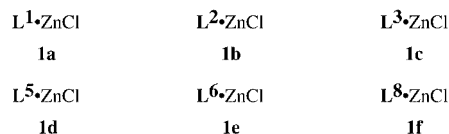
Ligand Synthesis

From our work with tris(pyrazolyl)borates we have the experience that their biomimetic zinc complex chemistry requires a good encapsulation of the metal ion. This is achieved by bulky substituents at the 3-positions of the pyrazole rings. We applied this for the new NS₂ ligands **L** by incorporating 5-methyl-3-phenylpyrazole units in **L**¹ to **L**⁸ and 3-*tert*-butyl-5-methylpyrazole in **L**⁹. Likewise, the thioimidazole units were made bulky with substituents at the outer nitrogen atoms, mostly with aromatic groups (**L**² to **L**⁸), but also with methyl (**L**¹) and *tert*-butyl (**L**⁹). Thus, all our NS₂ ligands are more bulky than the one with *N*-methylthioimidazole and unsubstituted pyrazole groups reported previously.^[13]

The synthesis of the tripodal ligands **L** from KBH_4 and the nitrogen heterocycles is favoured by the fact that the thioimidazoles react more readily with KBH_4 than the pyrazoles. Thus, lower reaction temperatures are possible which ensures better yields and which allows us to run the preparations in a one-pot procedure. Mixtures of KBH_4 , pyrazole and thioimidazole (1:1:2) were allowed to react in a melt at ca. 160 °C to form **L**¹, **L**², **L**⁵ and **L**⁹. Later it turned out that the preparations in boiling toluene gave better yields and cleaner products. Furthermore, a 10% excess of the pyrazole was found to improve the yield of ligand **L** considerably. Ligands **L**³, **L**⁴, **L**⁶, **L**⁷ and **L**⁸ were prepared this way. The isolated compounds $\text{K}[\text{L}]$ are colourless powders which are somewhat air- and light-sensitive, sparingly soluble in aromatic hydrocarbons, and which decompose upon melting between 160 and 200 °C.

Simple Zinc Complexes

Like the tris(pyrazolyl)- and tris(mercaptoimidazolyl)-borates, the mixed ligands **L** easily form stable zinc halide complexes. This was applied for the products **1a–1f** by treating the corresponding ligands with the zinc halides.



The structures of **1c** and **1d** were determined, of which the one of **1c** is displayed here (Figure 1). There is very close agreement in terms of bond lengths and angles between **1c** and **1d**, and the coordination environment of the zinc ion also resembles that in the previously reported complex L·ZnI of a related NS₂ ligand.^[11] The deviations from tetrahedral symmetry at the zinc ion are small. The largest bond angle is N–Zn–Cl, reflecting the steric hindrance between the phenyl substituent on the pyrazole and the Zn–Cl unit.

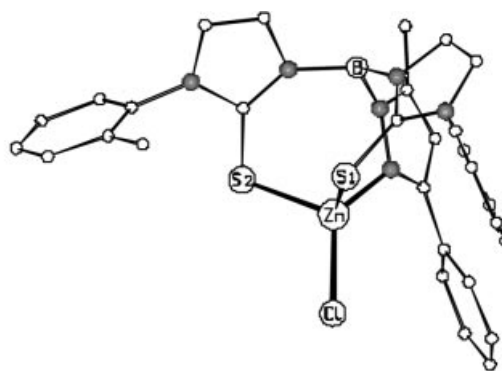
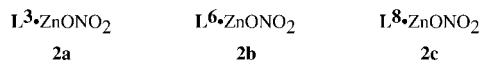


Figure 1. Molecular structure of complex **1c**; selected bond lengths [Å] and angles [°]: Zn–Cl 2.201(1), Zn–S1 2.335(1), Zn–S2 2.329(1), Zn–N 2.041(2); Cl–Zn–S1 110.91(3), Cl–Zn–S2 109.11(3), Cl–Zn–N 120.09(6), S1–Zn–S2 107.60(3), S1–Zn–N 108.24(6), S2–Zn–N 99.82(6)

Other than the zinc halide and the zinc thiolate species,^[15] the simple **L**-Zn complexes with anions of oxo acids turned out to be quite labile. Attempts to prepare acetates invariably led to the formation of ZnL₂ complexes (see below). The same was observed when trying to prepare nitrates. Only those ligands **L** with sterically demanding substituents, typically in the *ortho* positions of the aromatic rings, yielded nitrate complexes, of which **2a–2c** were isolated.



The structure determination of **2a** (Figure 2) proved the composition of the nitrate complexes and the semibidentate nature of the nitrate ligand. Again, the tetrahedral ligand environment is not seriously distorted, and again the N–Zn–O angle is unusually large due to steric hindrance. The semibidentate attachment of the nitrate coupled with its orientation with respect to the two sulfur donors makes the S1–Zn–O1 angle rather large and the S2–Zn–O1 angle rather small. In all these respects **2a** resembles the Zn–NO₃ complex of a related tris(mercaptoimidazolyl)borate ligand.^[10]

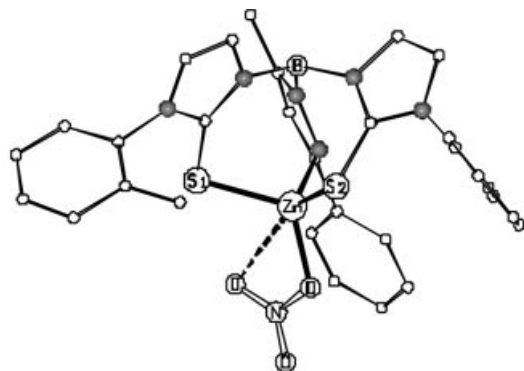


Figure 2. Molecular structure of complex **2a**; selected bond lengths [Å] and angles [°]: Zn–O1 1.965(5), Zn–O2 2.782(6), Zn–S1 2.307(2), Zn–S2 2.315(2), Zn–N 2.017(6); O1–Zn–S1 117.8(2), O1–Zn–S2 105.0(2), O1–Zn–N 115.3(2), S1–Zn–S2 108.6(1), S1–Zn–N 99.8(2), S2–Zn–N 110.2(2)

ZnL₂ Complexes

It has already been observed that the $L \cdot ZnX$ complexes of these NS₂ ligands are amenable to dismutation, with formation of the corresponding ZnL₂ complexes.^[13] Our investigations were also plagued frequently by this tendency. Many attempts to prepare $L \cdot Zn$ complexes with hard coligands did not yield the desired $L \cdot ZnX$ species, but instead ZnL₂ and, presumably, ZnX₂. The reason for this is the highly preferred ZnS₄ coordination in the uncharged ZnL₂ molecules. In the following we describe those reactions that led to ZnL₂ species, even though we performed no designed (viz. trivial) synthesis of a ZnL₂ complex.

According to one of the goals of this work, namely the modelling of zinc enzymes, we intended to prepare $[L \cdot Zn-OH_2]^+$ or $L \cdot Zn-OH$ complexes. The most straightforward way to do this^[3] is the reaction between a tripodal ligand **L** and hydrated zinc perchlorate, either directly or in combination with KOH. This was done here with **L**¹, **L**⁵ and **L**⁹. Although some evidence could be gathered for the formation of $L \cdot Zn-OH$ species (see below), they could not

be isolated in a pure form, and the final products of the reactions were the ZnL₂ complexes **3a**, **3d** and **3f**. Also, as mentioned above, the $L \cdot Zn-OAc$ complexes were not stable enough to be isolated, and in the case of **L**³ a clean dismutation yielded **3b**. Furthermore, the $L \cdot Zn-NO_3$ complexes of those ligands **L** that are sterically less hindered, evaded their isolation by dismutation. In case of **L**⁴ and **L**⁷ this resulted in the isolation of pure **3c** and **3e**.

ZnL ¹ ₂	ZnL ³ ₂	ZnL ⁴ ₂
3a	3b	3c
ZnL ⁵ ₂	ZnL ⁷ ₂	ZnL ⁹ ₂
3d	3e	3f

Structure determinations of **3a**, **3b**, **3c**, **3d** and **3f** revealed that in all cases the ligands **L** act as bidentate sulfur donors, i.e. the pyrazolyl arm of the tripod is uncoordinated. This corresponds to the observations made previously for similar ZnL₂ complexes^[13] and for those derived from the tris(mercaptoimidazolyl)borates.^[10] The molecular structures of **3a** and **3f** are shown as representative examples in Figures 3 and 4, respectively. In all complexes **3** the Zn–S bond lengths are in the range 2.33–2.40 Å, which is rather long but typical for this kind of ZnS₄ species.^[10,13] The bond angles at the zinc ion show quite a range around the tetrahedral angle, the extremes being 89° in **3a** and 125° in **3c**.

Hydrolysis Products

During our attempts to prepare $L \cdot Zn-OH$ or $[L \cdot Zn]^+$ species by treating **L** with Zn(ClO₄)₂ it also became obvious that the (mercaptoimidazolyl)borates are not only more easily formed than the pyrazolylborates but also more easily hydrolysed. Thus, the acidic conditions brought about by dissolving hydrated zinc perchlorate in alcohols frequently led to the partial destruction of the ligands **L**, and free mercaptoimidazoles were found in the solutions. In three cases zinc complexes of the mercaptoimidazoles were the result of such hydrolytic cleavages.

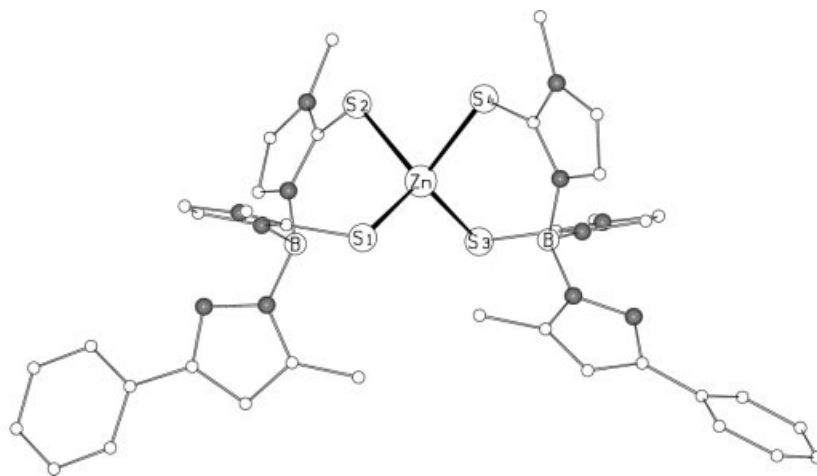


Figure 3. Molecular structure of **3a**; selected bond lengths [Å] and angles [°]: Zn–S1 2.336(2), Zn–S2 2.382(2), Zn–S3 2.346(2), Zn–S4 2.401(2); S1–Zn–S2 110.77(8), S1–Zn–S3 115.68(8), S1–Zn–S4 114.64(8), S2–Zn–S3 112.93(7), S2–Zn–S4 89.28(6), S3–Zn–S4 110.70(7)

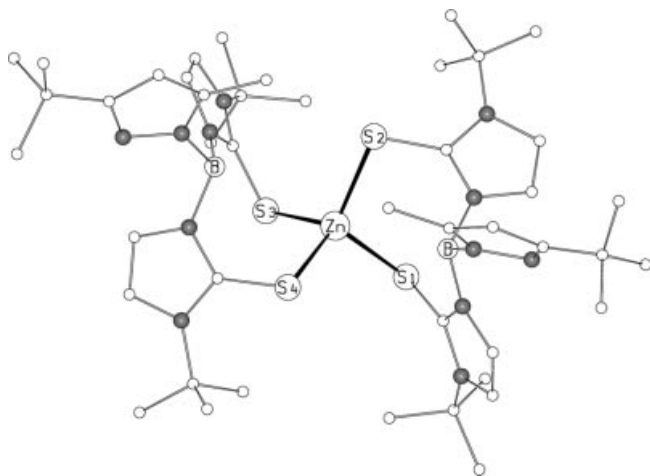


Figure 4. Molecular structure of **3f**; selected bond lengths [Å] and angles [°]: Zn–S1 2.359(2), Zn–S2 2.371(2), Zn–S3 2.368(2), Zn–S4 2.403(2); S1–Zn–S2 109.35(6), S1–Zn–S3 100.35(5), S1–Zn–S4 111.09(5), S2–Zn–S3 110.72(5), S2–Zn–S4 118.99(5), S3–Zn–S4 104.65(5)

In two of these cases the free mercaptoimidazole was incorporated as a coligand in the intended $L \cdot Zn$ complexes: $Zn(ClO_4)_2 \cdot 6H_2O$ and L^3 yielded complex **4a**, and with L^6 complex **4b** was formed. Both **4a** and **4b** were characterised by structure determinations. The structure of **4a** is shown in Figure 5. In **4a** and **4b** the tripod ligand is bound to the zinc ion in the normal fashion; the mercaptoimidazole is attached as a neutral molecule. Its bonding situation is that of a thioimidazoline, i.e. of a thiourea derivative. This is a very common situation in zinc complex chemistry, and the Zn–S bond length (2.33 Å in **4a**, 2.31 Å in **4b**) corresponds to expectation.^[16] The deviations from tetrahedral symmetry at the zinc ion (smallest angle 99°, largest angle 123°) are in the same range as observed above.

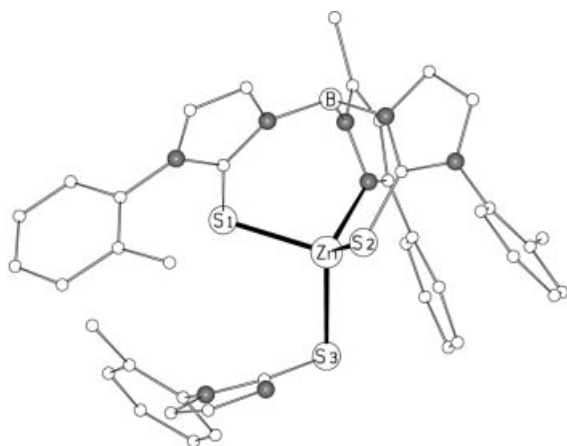
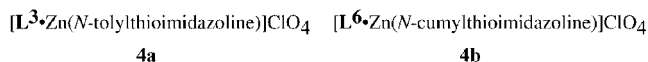


Figure 5. Molecular structure of **4a**; selected bond lengths [Å] and angles [°]: Zn–S1 2.323(2), Zn–S2 2.332(2), Zn–S3 2.326(2), Zn–N 2.027(5); N–Zn–S1 98.6(1), N–Zn–S2 105.6(1), N–Zn–S3 122.6(1), S1–Zn–S2 112.9(1), S1–Zn–S3 104.0(1), S2–Zn–S3 112.5(1)



In the case of L^1 the hydrolytic destruction resulted in a zinc complex that bears only mercaptoimidazolate ligands. After addition of KOH to the reaction mixture, $[OZn_4(\text{methimazolate})_6]$ (**5**) was obtained, another crystalline form of which has already been described.^[17] Complex **5** is an analogue of $OZn_4(OAc)_6$,^[18] i.e. a variant of the classical basic beryllium acetate structure with the six chelating N,S li-

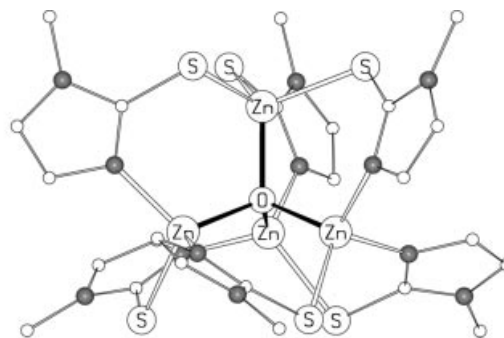


Figure 6. Molecular structure of **5**; selected bond lengths [Å]: Zn–O 1.955(2), Zn–N 2.000(4), Zn–S 2.325(1) and 2.340(1)

gands spanning the edges of the Zn_4 tetrahedron. Figure 6 shows the structure of **5**, all details of which have already been discussed.^[17]

Attempts at Enzyme Modelling

With the intention to prepare $L \cdot Zn-OH$, $L \cdot Zn(H_2O)$ or $[L \cdot Zn]^+$ complexes, i.e. functional models for the resting state of zinc enzymes, we performed a number of reactions between the ligands L and zinc salts of noncoordinating anions under varying pH conditions. So far, however, none of the intended species, which would be the starting point for modelling alcohol dehydrogenase chemistry, could be obtained in a pure form. However, in two cases evidence for the existence of a $L \cdot Zn-OH$ species could be gathered. Treatment of zinc perchlorate with L^1 and KOH allowed the precipitation of a compound whose elemental analyses and spectra may be in agreement with its formulation as **6a**. Likewise, a species which may be formulated as **6b** was obtained with L^2 . Both compounds, however, show considerable amounts of impurities in their NMR spectra, and both could not be purified due to their lability toward hydrolysis or dismutation as described above.



Only with one ligand L , namely the *o*-methoxy-substituted L^8 , could stable complexes be prepared, which come close to containing naked $[L \cdot Zn]^+$. Treatment with zinc perchlorate in methanol yielded **7**, and under the same conditions in ethanol **8** was obtained. The identification of **7** rests on its spectra. The presence of zinc-bound perchlorate is evident from the sharp and intense IR band at 1093

cm^{-1} , in analogy to the structurally characterised [tris(mercaptoimidazolyl)borate]zinc perchlorate complex.^[10] The ethanol complex **8** is a relative of two [tris(mercaptoimidazolyl)borate]zinc–alcohol complexes.^[10,19]



The structure of **8** is shown in Figure 7. The ethanol ligand occupies the fourth coordination site of the zinc ion, the coordination geometry of which is tetrahedral to a good approximation. The Zn–O bond length is very similar to that in the nitrate complexes (see above), indicating a strong Zn–O(ethanol) bond. The ethanol ligand in the crystalline compound is connected by a hydrogen bond to a second ethanol molecule, which explains the absence of characteristic OH bands in the 3300–3700 cm^{-1} region in the IR spectrum. The molecular shape of **8** does not offer a convincing clue why it is just ligand **L**⁸ that makes complexes like **7** and **8** stable. Yet it is evident that the *o*-methoxy substituents enforce an orientation of the three phenyl groups that creates a bowl-like shape of the whole ligand, which may provide just enough stabilization of the Zn–EtOH unit in its interior.

Complex **8** is the first zinc complex in which an alcohol molecule is bound to a zinc ion with NS₂ ligation, creating a tetrahedral ZnONS₂ system. This bonding pattern reproduces the attachment of ethanol to the active centre of alcohol dehydrogenase.^[20] In our preliminary communication on **8**^[14] we have elaborated the close geometrical relation between the ZnONS₂ cores of **8** and of the enzyme structure of highest resolution. Hence, in terms of bioinorganic chemistry, the formation and structure of **8** are the most relevant result of this paper (Figure 7).

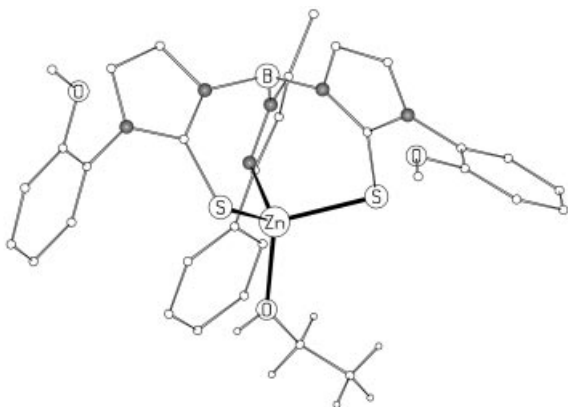
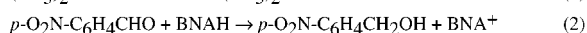


Figure 7. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: Zn–O 1.970(3), Zn–S1 2.282(1), Zn–S2 2.314(1), Zn–N 2.012(3); O–Zn–S1 105.4(1), O–Zn–S2 109.8(1), O–Zn–N 116.9(1), S1–Zn–S2 113.2(1), S1–Zn–N 111.7(1), S2–Zn–N 100.2(1).

Having achieved structural modelling of alcohol dehydrogenase we also attempted functional modelling. As done before,^[10,21,22] we used (benzyl)nicotinamide chloride ([BNA]Cl) as a mimic of NAD⁺ and (dihydrobenzyl)nicotinamide (BNAH) as a mimic of NADH. For attempts at

oxidation we used 2-propanol as an electron-rich alcohol and for attempts at reduction *p*-nitrobenzaldehyde as an electron-poor aldehyde. Thus, the model reactions were:



It is known that reaction (1) does not proceed in the absence of a catalyst, but reaction (2) proceeds very slowly. Trying some of the **L**·Zn–X complexes described here we found that they show no or very low catalytic efficiency for both processes. The best results, obtained with complex **2a**, consisted in a 2–3% yield of acetone and traces of *p*-nitrobenzyl alcohol after 24 h of heating. These are the poorest results in our studies on the functional modelling of alcohol dehydrogenase, although the applied “catalysts” are the closest structural models of the enzyme. Conversely, the best catalytic results were obtained by us with zinc complexes whose structure has no resemblance at all with that of the enzyme.^[22]

Conclusions

This work has shown that the tripodal NS₂ ligands **L** are easily accessible. They fill half of the gap between the analogous N₃ (i.e. pyrazolylborate) and S₃ (i.e. mercaptoimidazolylborate) ligands. Provided that the as-yet-unknown tripodal N₂S ligands of this type are also accessible, the door would be open for a complete set of comparative investigations of metal complexes with homologous tripodal N₃, N₂S, NS₂, and S₃ ligands. We intend to undertake this investigation with **L**·ZnX complexes, putting emphasis on enzyme model compounds.

The preliminary **L**·ZnX chemistry in this paper has revealed that the resulting complexes are not as inert as their tris(pyrazolylborate)·ZnX counterparts. One reason for this seems to be the high stability of the dismutation products ZnL₂ which comes from their ZnS₄ coordination in an uncharged complex. The other reason seems to be the geometrical disposition of the mercaptoimidazolyl moieties, which provides less encapsulation for the ZnX units than that of the pyrazolyl moieties, because their aromatic substituents point away from rather than enclosing the centre of the complexes. The relative stabilities of the **L**·ZnX complexes, however, give a clue on how to improve this situation: it seems that *ortho* substituents on the phenyl groups induce an orientation of them that creates a bowl-shaped environment around the ZnX units and hence the desired encapsulation.

The perchlorate complex **7** and the ethanol complex **8** are the best examples for this kind of stabilization. Complex **7** is as close as possible to being “naked” [**L**·Zn]⁺, and **8** is the best model so far for the enzyme-substrate complex of alcohol dehydrogenase. Both **7** and **8** also demonstrate the subtle stability differences in these complexes of weakly bound ligands: perchlorate is a better ligand than methanol (**7** crystallises from methanol) but a weaker ligand than

ethanol (**8** crystallises from ethanol). Thus **7** and **8** on one side show the way to improve the ligand design for making more stable **L**·Zn complexes of this type, on the other side they offer themselves as starting materials for a functional and possibly catalytic **L**·Zn chemistry.

Experimental Section

General: For general working and measuring procedures, see ref.^[23] All procedures for the ligand syntheses were performed under an inert gas. 5-Methy-3-phenylpyrazole^[24] and 3-*tert*-butyl-5-methylpyrazole^[25] were prepared according to the published procedures. All *N*-substituted mercaptoimidazoles were prepared from the corresponding amino acetals RNHCH₂CH(OEt)₂ and HSCN according to an established procedure.^[26,27] They were characterised by ¹H NMR spectroscopy in CDCl₃ as follows:

R = methyl: ¹H NMR (CHCl₃): δ = 3.66 ppm (s, 3 H, NMe), 6.59 (d, *J* = 2.0 Hz, 1 H, 4-H), 6.78 (d, *J* = 2.2 Hz, 1 H, 5-H). **R = phenyl:** ¹H NMR (CHCl₃): δ = 6.75 ppm (m, 2 H, 4-H, 5-H), 7.31–7.56 (m, 5 H, Ph). **R = *o*-tolyl:** ¹H NMR (CHCl₃): δ = 2.19 ppm (s, 3 H, Me), 6.66 (d, *J* = 2.4 Hz, 1 H, 4-H), 6.86 (d, *J* = 2.4 Hz, 1 H, 5-H), 7.00–7.43 (m, Ar). **R = *p*-tolyl:** ¹H NMR (CHCl₃): δ = 2.41 ppm (s, 3 H, Me), 6.80 (d, *J* = 1.6 Hz, 1 H, 4-H), 6.84 (d, *J* = 1.6 Hz, 1 H, 5-H), 7.28 (m, 2 H, Ar), 7.45 (m, 2 H, Ar). **R = 2,4-xylyl:** ¹H NMR (CHCl₃): δ = 2.16 ppm (s, 3 H, Me), 2.38 (s, 3 H, Me), 6.69 (d, *J* = 2.4 Hz, 1 H, 4-H), 6.81 (d, *J* = 2.4 Hz, 1 H, 5-H), 7.15 (m, 3 H, Ar), 7.26 (s, 1 H, Ar). **R = *p*-cumyl:** ¹H NMR (CHCl₃): δ = 1.28 ppm (d, *J* = 6.8 Hz, 6 H, Me), 2.97 (sept, *J* = 6.8 Hz, 1 H, CH), 6.80 (d, *J* = 2.4 Hz, 1 H, 4-H), 6.84 (d, *J* = 2.4 Hz, 1 H, 5-H), 7.34 (d, *J* = 6.6 Hz, 2 H, Ar), 7.50 (d, *J* = 6.6 Hz, 2 H, Ar). **R = *p*-anisyl:** ¹H NMR (CHCl₃): δ = 3.85 ppm (s, 3 H, OMe), 6.80 (d, *J* = 2.4 Hz, 1 H, 4-H), 6.98 (d, *J* = 2.2 Hz, 1 H, 5-H), 7.00 (d, *J* = 6.8 Hz, 2 H, Ar), 7.47 (d, *J* = 6.8 Hz, 2 H, Ar). **R = *o*-anisyl:** ¹H NMR (CHCl₃): δ = 3.74 ppm (s, 3 H, OMe), 6.81 (d, *J* = 2.1 Hz, 1 H, 4-H), 6.88 (d, *J* = 2.1 Hz, 1 H, 5-H), 6.98 (m, 2 H, Ar), 7.39 (m, 2 H, Ar). **R = *tert*-butyl:** ¹H NMR (CHCl₃): δ = 1.81 ppm (s, 9 H, *t*Bu), 6.67 (d, *J* = 2.4 Hz, 1 H, 4-H), 6.84 (d, *J* = 2.4 Hz, 1 H, 5-H).

Ligand Synthesis: All ligands **L** were prepared by thermal reaction between KBH₄, the pyrazole and the imidazole. Initially, the reactions were performed by melting the reagents (procedure A) which resulted in low yields and unsatisfactory purity of the products. Then it was found that the ligands **L** also form in boiling toluene (procedure B) which is the preferred procedure.

Procedure A: A 1:1 mixture of KBH₄ and the pyrazole was heated to 120 °C (thermometer immersed into the melt). The melt was stirred for 30 min. Then, 2 mol-equiv. of the mercaptoimidazole was added and the temperature raised slowly to 140 °C and kept at this temperature (30–60 min) until hydrogen evolution stopped. After cooling to room temp., the resulting solid was powdered and the raw product crystallised from ethanol at –30 °C.

Procedure B: A 1:1:1:2 mixture of KBH₄, the pyrazole and the imidazole was dried in vacuo at 60 °C for 2 h. 125 mL of dry toluene was added and the mixture refluxed for 4 days by heating with an oil bath (150 °C). Then, the volume of the solution was reduced in vacuo to 50 mL, and the mixture was poured into 200 mL of petroleum ether (boiling range 60–70 °C). The resulting precipitate was washed with a small amount of benzene and then with petroleum ether and dried in vacuo.

L¹: By procedure A from KBH₄ (1.70 g, 31.6 mmol), pyrazole (5.00 g, 31.6 mmol) and the imidazole (7.21 g, 63.2 mmol). Yield 4.10 g (30%); m.p. 200 °C (dec.). C₁₈H₂₀BKN₆S₂ (434.44): calcd. C 49.77, H 4.64, N 19.34; found C 48.59, H 4.90, N 17.60. ¹H NMR (CDCl₃): δ = 2.33 [s, 3 H, Me (pz)], 3.58 (s, 6 H, NMe), 6.30 [s, 1 H, H (pz)], 6.45 [d, *J* = 2.0 Hz, 2 H, H (im)], 6.63 [d, *J* = 2.0 Hz, 2 H, H (im)], 7.31 (m, 3 H, Ph), 7.51 (d, *J* = 7.4 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2392 m (BH) cm^{–1}.

L²: By procedure A from KBH₄ (920 mg, 17.1 mmol), the pyrazole (2.70 g, 17.1 mmol) and the imidazole (6.03 g, 34.2 mmol). Yield 4.9 g (50%); m.p. 180 °C (dec.). C₂₈H₂₄BKN₆S₂ (558.58): calcd. C 60.21, H 4.33, N 15.05; found C 56.50, H 4.83, N 13.69. ¹H NMR (CDCl₃): δ = 2.29 [s, 3 H, Me (pz)], 6.29 [s, 2 H, H (pz)], 6.72 (d, *J* = 2.4 Hz, 2 H, H (im)], 6.75 [d, *J* = 2.4 Hz, 2 H, H (im)], 7.30–7.51 (m, 13 H, Ar), 7.53 (d, *J* = 7.4 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2483 m (BH) cm^{–1}.

L³: By procedure B from KBH₄ (1.08 g, 20.0 mmol), the pyrazole (3.47 g, 22.0 mmol) and the imidazole (7.60 g, 40.0 mmol). Yield 10.1 g (86%); m.p. 205 °C (dec.). C₃₀H₂₈BKN₆S₂ (586.63): calcd. C 61.42, H 4.81, N 14.33, S 10.93; found C 61.36, H 5.12, N 14.23, S 10.47. ¹H NMR (CD₃OD): δ = 2.16 [s, 6 H, Me (tol)], 2.43 [s, 3 H, Me (pz)], 6.31 [s, 1 H, H (pz)], 6.59 [d, *J* = 2.2 Hz, 2 H, H (im)], 6.79 [d, *J* = 2.2 Hz, 2 H, H (im)], 7.27 (m, 8 H, Ar), 7.75 (d, *J* = 7.0 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2451 m (BH) cm^{–1}.

L⁴: By procedure B from KBH₄ (1.08 g, 20.0 mmol), the pyrazole (3.47 g, 22.0 mmol) and the imidazole (7.60 g, 40.0 mmol). Yield 9.86 g (84%); m.p. 165 °C (dec.). C₃₀H₂₈BKN₆S₂ (586.63): calcd. C 61.42, H 4.81, N 14.33, S 10.93; found C 61.29, H 5.25, N 14.25, S 9.91. ¹H NMR (CD₃OD): δ = 2.37 [s, 6 H, Me (tol)], 2.42 [s, 3 H, Me (pz)], 6.30 [s, 1 H, H (pz)], 6.57 [d, *J* = 2.2 Hz, 2 H, H (im)], 6.92 [d, *J* = 2.2 Hz, 2 H, H (im)], 7.28 (m, 8 H, Ar), 7.45 [d, *J* = 8.2 Hz, 4 H, H (tol)], 7.74 (d, *J* = 7.0 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2482 m (BH) cm^{–1}.

L⁵: By procedure A from KBH₄ (0.54 g, 10.0 mmol), the pyrazole (3.16 g, 20.0 mmol) and the imidazole (8.16 g, 40.0 mmol). Yield 0.74 g (12%); m.p. 185 °C (dec.). C₃₂H₃₂BKN₆S₂ (614.69): calcd. C 62.53, H 5.25, N 13.67; found C 58.72, H 5.31, N 12.33. ¹H NMR (CDCl₃): δ = 2.12 [s, 6 H, Me (xyl)], 2.34 [s, 6 H, Me (xyl)], 2.75 [s, 3 H, Me (pz)], 6.36 [s, 1 H, H (pz)], 6.54 [d, *J* = 2.0 Hz, 2 H, H (im)], 6.68 [d, *J* = 2.0 Hz, 2 H, H (im)], 7.04–7.15 (m, 6 H, xyl), 7.40–7.43 (m, 3 H, Ph), 7.69–7.75 (m, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2487 m (BH) cm^{–1}.

L⁶: By procedure B from KBH₄ (1.08 g, 20.0 mmol), the pyrazole (3.47 g, 22.0 mmol) and the imidazole (8.72 g, 40.0 mmol). Yield 4.63 g (36%); m.p. 165 °C (dec.). C₃₄H₃₆BKN₆S₂ (642.74): calcd. C 63.54, H 5.65, N 13.08, S 9.98; found C 63.21, H 5.91, N 13.07, S 10.08. ¹H NMR (CD₃OD): δ = 1.22 [d, *J* = 6.8 Hz, 18 H, Me (*i*Pr)], 2.08 [s, 3 H, Me (pz)], 2.89 [sept, *J* = 6.8 Hz, 2 H, CH (*i*Pr)], 6.26 [s, 1 H, H (pz)], 6.37 [d, *J* = 2.2 Hz, 2 H, H (im)], 6.75 [d, *J* = 2.2 Hz, 2 H, H (im)], 7.24 (m, 8 H, Ar), 7.42 (d, *J* = 8.3 Hz, 4 H, Cum), 7.68 (d, *J* = 7.0 Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2476 m (BH) cm^{–1}.

L⁷: By procedure B from KBH₄ (0.54 g, 10.0 mmol), the pyrazole (1.74 g, 11.0 mmol) and the imidazole (4.12 g, 20.0 mmol). Yield 5.57 g (90%); m.p. 175 °C (dec.). C₃₀H₂₈BKN₆O₂S₂ (618.63): calcd. C 58.25, H 4.56, N 13.58, S 10.37; found C 57.68, H 4.42, N 13.20, S 10.13. ¹H NMR (CD₃OD): δ = 2.44 [s, 3 H, Me (pz)], 3.82 (s, 6 H, OMe), 6.29 [s, 1 H, H (pz)], 6.57 [d, *J* = 2.2 Hz, 2 H, H (im)], 6.90 [d, *J* = 2.2 Hz, 2 H, H (im)], 7.00 (d, *J* = 8.4 Hz, 4 H, C₆H₄),

7.31 (m, 3 H, Ph), 7.44 (d, $J = 8.3$ Hz, 4 H, C₆H₄), 7.72 (d, $J = 7.0$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2486$ m (BH) cm⁻¹.

L⁸: By procedure B from KBH₄ (0.70 g, 13.0 mmol), the pyrazole (2.26 g, 14.3 mmol) and the imidazole (5.35 g, 26.0 mmol). Yield 6.79 g (85%); m.p. 185 °C (dec.). C₃₀H₂₈BKN₆O₅S₂ (618.63): calcd. C 58.25, H 4.56, N 13.58, S 10.37; found C 57.99, H 4.60, N 13.54, S 10.43. ¹H NMR ([D₆]DMSO): $\delta = 2.43$ [s, 3 H, Me (pz)], 3.73 (s, 6 H, OMe), 6.24 [s, 1 H, H (pz)], 6.76 [d, $J = 2.1$ Hz, 2 H, H (im)], 6.82 [d, $J = 2.1$ Hz, 2 H, H (im)], 6.85–7.49 (m, 1 H, Ar), 7.74 (d, $J = 7.1$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2441$ w (BH) cm⁻¹.

L⁹: By procedure A from (0.54 g, 10.0 mmol) of KBH₄, (3.00 g, 20.0 mmol) of the pyrazole and (6.24 g, 40.0 mmol) of the imidazole. Yield 0.51 g (10%), m.p. 160 °C (dec.). The product contained considerable amounts of impurities. ¹H NMR ([D₆]DMSO): $\delta = 1.18$ [s, 9 H, *t*Bu (pz)], 1.73 [s, 18 H, *t*Bu (im)], 2.15 [s, 3 H, Me (pz)], 5.59 [s, 1 H, H (pz)], 6.26 [d, $J = 2.0$ Hz, 2 H, H (im)], 6.79 [d, $J = 2.0$ Hz, 2 H, H (im)] ppm. IR (KBr): $\tilde{\nu} = 2496$ m (BH) cm⁻¹.

Zinc Halide Complexes. General Procedure: A solution of the zinc halide in 10 mL of methanol was added dropwise, with stirring, to a solution of the ligand in 50 mL of dichloromethane. After 2 h of stirring, the solution was filtered, the filtrate reduced to half of its volume in vacuo and then cooled to –30 °C overnight. The resulting precipitate of the raw product was filtered off, washed with 1–2 mL of methanol and dried in vacuo. If necessary it was recrystallised from CH₂Cl₂/CH₃OH or CH₂Cl₂/CH₃CN. All L·ZnHal complexes were obtained as colourless powders.

1a: From L¹ (200 mg, 0.46 mmol) and ZnCl₂ (63 mg, 0.46 mmol). Yield 57 mg (25%); m.p. 225 °C (dec.). C₁₈H₂₀BCIN₆S₂Zn (496.20): calcd. C 43.57, H 4.06, N 16.94; found C 42.86, H 4.13, N 16.32. ¹H NMR (CDCl₃): $\delta = 2.42$ [s, 3 H, Me (pz)], 3.57 [s, 6 H, Me (im)], 6.22 [s, 1 H, H (pz)], 6.60 [d, $J = 2.0$ Hz, 2 H, H (im)], 7.15 [d, $J = 2.0$ Hz, 2 H, H (im)], 7.28 (m, 3 H, Ph), 7.74 (d, $J = 7.4$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2503$ m (BH) cm⁻¹.

1b: From L² (300 mg, 0.52 mmol) and ZnCl₂ (71 mg, 0.52 mmol). Yield 156 mg (48%); m.p. 215 °C (dec.). C₂₈H₂₄BCIN₆S₂Zn (620.33): calcd. C 54.21, H 3.90, N 13.55; found C 54.68, H 4.05, N 13.57. ¹H NMR (CDCl₃): $\delta = 2.29$ [s, 3 H, Me (pz)], 6.29 [s, 1 H, H (pz)], 6.75 [d, $J = 2.4$ Hz, 2 H, H (im)], 6.81 [d, $J = 2.4$ Hz, 2 H, H (im)], 7.30–7.51 (m, 13 H, Ar), 7.53 (d, $J = 7.4$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2507$ m (BH) cm⁻¹.

1c: From L³ (196 mg, 0.33 mmol) and ZnCl₂ (46 mg, 0.34 mmol). Yield 180 mg (84%); m.p. 270 °C (dec.). C₃₀H₂₈BCIN₆S₂Zn (648.38): calcd. C 55.57, H 4.35, N 12.96, S 9.89; found C 55.23, H 4.58, N 13.33, S 9.34. ¹H NMR (CDCl₃): $\delta = 2.06$ [s, 3 H, Me¹ (tol)], 2.28 [s, 3 H, Me² (tol)], 2.49 [s, 3 H, Me (pz)], 6.39 [s, 1 H, H (pz)], 6.88 [s, 2 H, H (im)], 7.05 [s, 2 H, H (im)], 7.25–7.37 (m, 11 H, Ar), 7.53 (d, $J = 7.2$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2559$ w (BH) cm⁻¹.

1d: From L⁵ (614 mg, 1.00 mmol) and ZnCl₂ (136 mg, 1.00 mmol). Yield 0.25 mg (37%), m.p. 220 °C (dec.). C₃₂H₃₂BCIN₆S₂Zn (676.43): calcd. C 56.82, H 4.77, N 12.42; found C 56.99, H 4.70, N 12.36. ¹H NMR (CDCl₃): $\delta = 2.14$ [s, 6 H, Me (xyl)], 2.37 [s, 6 H, Me (xyl)], 2.48 [s, 3 H, Me (pz)], 6.38 [s, 1 H, H (pz)], 6.83 [d, $J = 2.0$ Hz, 2 H, H (im)], 6.99 [d, $J = 2.0$ Hz, 2 H, H (im)], 7.00–7.17 (m, 6 H, xyl), 7.31–7.37 (m, 3 H, Ph), 7.53–7.58 (m, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2505$ m (BH) cm⁻¹.

1e: From L⁶ (206 mg, 0.33 mmol) and ZnCl₂ (46 mg, 0.34 mmol). Yield 169 mg (67%), m.p. 240 °C (dec.). C₃₆H₄₀BCIN₆S₃Zn

(764.60): calcd. C 56.55, H 5.27, N 10.99, S 12.58; found C 56.31, H 5.60, N 11.02, S 12.25. ¹H NMR (CDCl₃): $\delta = 1.26$ [d, $J = 7.0$ Hz, 12 H, Me (*i*Pr)], 2.93 [sept, $J = 7.0$ Hz, 2 H, CH (*i*Pr)], 6.38 [s, 1 H, H (pz)], 7.01 [d, $J = 2.0$ Hz, 2 H, H (im)], 7.07 [d, $J = 2.0$ Hz, 2 H, H (im)], 7.28 (m, 8 H, Ar), 7.45 (m, 3 H, Ar), 7.62 (d, $J = 7.4$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2512$ w (BH) cm⁻¹.

1f: From L⁸ (301 mg, 0.49 mmol) and ZnI₂ (155 mg, 0.49 mmol). Yield 257 mg (69%), m.p. 230 °C (dec.). C₃₀H₂₈BIN₆O₅S₂Zn·0.5(CH₂Cl₂) (771.83 + 42.47): calcd. C 44.99, H 3.59, N 10.32, S 7.88; found C 45.79, H 3.95, N 10.75, S 8.25. ¹H NMR (CDCl₃): $\delta = 2.49$ [s, 3 H, Me (pz)], 3.85 (s, 6 H, OMe), 5.32 (s, 1 H, CH₂Cl₂), 6.15 [s, 1 H, H (pz)], 6.91–7.95 [m, 15 H, H (im) + Ar] ppm. IR (KBr): $\tilde{\nu} = 2511$ w (BH) cm⁻¹.

Zinc Nitrate Complexes

2a: A solution of L₃ (196 mg, 0.33 mmol) in 5 mL of dichloromethane was added dropwise with stirring to a solution of Zn(NO₃)₂·6H₂O (95 mg, 0.34 mmol) in 10 mL of methanol. After 4 h of stirring, the precipitate was filtered off. Recrystallisation from dichloromethane/acetonitrile yielded 158 mg (71%) of **2a**, m.p. 220 °C (dec.). C₃₀H₂₈BN₇O₅S₂Zn (674.93): calcd. C 53.39, H 4.18, N 14.53, S 9.50; found C 53.29, H 4.29, N 14.42, S 9.30. ¹H NMR (CD₂Cl₂): $\delta = 1.96$ [s, 3 H, Me¹ (tol)], 2.25 [s, 3 H, Me² (tol)], 2.53 [s, 3 H, Me (pz)], 6.46 [s, 1 H, H (pz)], 6.96 [d, $J = 2.2$ Hz, 2 H, H (im)], 7.08 [d, $J = 2.2$ Hz, 2 H, H (im)], 7.37 (m, 11 H, Ar), 7.52 (d, $J = 6.0$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2479$ w (BH), 1382 vs (NO₃), 1294 vs (NO₃) cm⁻¹.

2b: Like **2a** from L⁶ (214 mg, 0.33 mmol) and Zn(NO₃)₂·6H₂O (95 mg, 0.34 mmol). Yield 169 mg (73%); m.p. 180 °C (dec.). C₃₄H₃₆BN₇O₅S₂Zn (731.04): calcd. C 55.86, H 4.96, N 13.41, S 8.77; found C 56.26, H 5.46, N 12.87, S 8.01. ¹H NMR (CDCl₃): $\delta = 1.27$ [d, $J = 6.9$ Hz, 12 H, Me (*i*Pr)], 2.96 [sept, $J = 6.9$ Hz, 2 H, CH (*i*Pr)], 6.40 [s, 1 H, H (pz)], 7.00 [s, 4 H, H (im)], 7.36 (s, 8 H, Cum), 7.38 (m, 3 H, Ph), 7.56 (d, $J = 5.4$ Hz, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2486$ w (BH), 1373 s (NO₃), 1292 s (NO₃) cm⁻¹.

2c: Like **2a** from L⁸ (307 mg, 0.52 mmol) and Zn(NO₃)₂·4H₂O (137 mg, 0.52 mmol). Yield 115 mg (31%), m.p. 215 °C (dec.). C₃₀H₂₈BN₇O₅S₂Zn (706.93): calcd. C 50.97, H 3.99, N 13.87, S 9.07; found C 50.43, H 4.28, N 13.51, S 8.93. ¹H NMR (CDCl₃): $\delta = 2.44$ [s, 3 H, Me (pz)], 3.75 (s, 6 H, OMe), 6.32 [s, 1 H, H (pz)], 6.86 [d, $J = 2.2$ Hz, 2 H, H (im)], 6.96 [d, $J = 2.2$ Hz, 2 H, H (im)], 7.10–7.48 (m, 11 H, Ar), 7.54–7.60 (m, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2489$ w (BH), 1384 vs (NO₃), 1294 vs (NO₃) cm⁻¹.

ZnL₂ Complexes

3a: A solution of (171 mg, 0.46 mmol) of Zn(ClO₄)₂·6H₂O in 20 mL of methanol was added with stirring to a solution of (200 mg, 0.46 mmol) of L¹ in 50 mL of dichloromethane. After 30 min, powdered KOH (29 mg, 0.50 mmol) was added. After 20 h of stirring and filtration, the volume of the solution was reduced to one half in vacuo. Cooling to –4 °C overnight produced a colourless precipitate of **6a** (characterisation see below). Attempts to purify this product by dissolution in dichloromethane and slow concentration yielded, after 4 weeks, 18 mg (4%) of colourless crystalline **3a**; m.p. 230 °C (dec.). C₃₆H₄₀B₂N₁₂S₄Zn·3H₂O (856.14 + 54.02): calcd. C 47.51, H 5.09, N 18.47; found C 46.40, H 5.03, N 19.25. ¹H NMR (CDCl₃): $\delta = 1.49$ (s, 6 H, H₂O), 2.38 [s, 6 H, Me (pz)], 3.43 [s, 12 H, Me (im)], 6.22 [s, 2 H, H (pz)], 6.67 [d, $J = 2.0$ Hz, 4 H, H (im)], 7.17 [d, $J = 2.0$ Hz, 4 H, H (im)], 7.31 (m, 6 H, Ph), 7.75 (d, $J = 7.4$ Hz, 4 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2500$ m (BH) cm⁻¹.

3b: A solution of **L**³ (196 mg, 0.33 mmol) in methanol (5 mL) was added dropwise with stirring to a solution of Zn(CH₃COO)₂ (62 mg, 0.34 mmol) in methanol (10 mL). After 4 h of stirring, the precipitate of raw **3b** was filtered off. Crystallisation from methanol/dichloromethane by slow concentration yielded 146 mg (76%) of **3b** as colourless crystals; m.p. 250 °C (dec.). C₆₀H₅₆B₂N₁₂S₄Zn (1160.46): calcd. C 62.10, H 4.86, N 14.48, S 11.05; found C 61.90, H 4.90, N 14.56, S 11.27. ¹H NMR (CDCl₃): δ = 1.97 [s, 3 H, Me (tol)], 2.04 [s, 3 H, Me (tol)], 2.53 [s, 3 H, Me (pz)], 6.33 [s, 1 H, H (pz)], 6.59 [d, *J* = 2.0 Hz, 2 H, H (im)], 6.68 [d, *J* = 2.0 Hz, 2 H, H (im)], 7.18–7.41 (m, 11 H, Ar), 7.89 (d, *J* = 7.2 Hz, 2 H, Ph) ppm. IR (KBr): ν̃ = 2521 m (BH) cm⁻¹.

3c: Like **3b** from **L**⁴ (196 mg, 0.33 mmol) and Zn(NO₃)₂·6H₂O (95 mg, 0.34 mmol). Yield 159 mg (83%) of **3c** as colourless crystals; m.p. 240 °C (dec.). C₆₀H₅₆B₂N₁₂S₄Zn (1160.46): calcd. C 62.10, H 4.86, N 14.48, S 11.05; found C 61.10, H 4.74, N 14.24, S 10.56. ¹H NMR (CDCl₃): δ = 2.43 [s, 6 H, Me (tol)], 2.75 [s, 3 H, Me (pz)], 6.38 [s, 1 H, H (pz)], 6.84 [d, *J* = 2.2 Hz, 2 H, H (im)], 6.94 [d, *J* = 2.2 Hz, 2 H, H (im)], 7.10–7.45 (m, 11 H, Ar), 7.74 (d, *J* = 7.2 Hz, 2 H, Ph) ppm. IR (KBr): ν̃ = 2477 w (BH) cm⁻¹.

3d: A solution of Zn(ClO₄)₂·6H₂O (372 mg, 1.00 mmol) in methanol (10 mL) was slowly added dropwise with stirring to a solution of **L**⁵ (614 mg, 1.00 mmol) in dichloromethane (10 mL). After 2 h of stirring, all volatiles were removed in vacuo. The residue was extracted with four 5-mL portions of dichloromethane. The combined extracts were concentrated to dryness and the residue dissolved in a minimum amount of benzene. Slow concentration produced a precipitate of crystalline solvated **3d**. Filtration and drying for 3 h in vacuo yielded 200 mg (32%) of **3d** as a colourless powder; m.p. 230 °C (dec.). C₆₄H₆₄B₂N₁₂S₄Zn (1216.58): calcd. C 63.19, H 5.30, N 13.82; found C 63.26, H 5.66, N 12.80. ¹H NMR (CDCl₃): δ = 2.00 [s, 6 H, Me (xyl)], 2.21 [s, 6 H, Me (xyl)], 2.94 [s, 3 H, Me (pz)], 6.15 [s, 1 H, H (pz)], 6.25 [d, *J* = 2.0 Hz, 2 H, H (im)], 6.55 [d, *J* = 2.0 Hz, 2 H, H (im)], 6.79–7.00 (m, 6 H, xyl), 7.45–7.53 (m, 3 H, Ph), 8.32–8.35 (m, 2 H, Ph) ppm. IR (KBr): ν̃ = 2513 m (BH) cm⁻¹.

3e: Like **3b** from **L**⁷ (206 mg, 0.33 mmol) and Zn(NO₃)₂·6H₂O (95 mg, 0.34 mmol). Yield 127 mg (63%) of **3e** as colourless crystals; m.p. 245 °C (dec.). C₆₀H₅₆B₂N₁₂O₄S₄Zn (1224.46): calcd. C 58.86, H 4.61, N 13.73, S 10.48; found C 58.54, H 4.83, N 13.52, S 10.12. ¹H NMR (CD₂Cl₂): δ = 2.75 [s, 3 H, Me (pz)], 3.83 (s, 6 H, OMe), 6.38 [s, 1 H, H (pz)], 6.83 [s, 2 H, H (im)], 6.96 (d, *J* = 8.4 Hz, 4 H, anisyl), 7.44 (d, *J* = 8.4 Hz, 4 H, anisyl), 7.46 (m, 3 H, Ph), 7.74 (d, *J* = 7.4 Hz, 2 H, Ph) ppm. IR (KBr): ν̃ = 2488 m (BH) cm⁻¹.

3f: Like **3d** from Zn(ClO₄)₂·6H₂O (372 mg, 1.00 mmol) and **L**⁹ (500 mg, 1.00 mmol). Recrystallisation from acetonitrile yielded 120 mg (24%) of **3f** as colourless crystals; m.p. 180 °C (dec.). C₄₄H₇₂B₂N₁₂S₄Zn (984.40): calcd. C 53.69, H 7.37, N 17.07, S 13.03; found C 52.61, H 6.84, N 16.98, S 12.56. ¹H NMR (CD₂Cl₂): δ = 1.28 [s, 9 H, *t*Bu (pz)], 1.70 [s, 18 H, *t*Bu (im)], 2.44 [s, 3 H, Me (pz)], 5.78 [s, 1 H, H (pz)], 6.82 [d, *J* = 2.0 Hz, 2 H, H (im)], 6.87 [d, *J* = 2.2 Hz, 2 H, H (im)] ppm. IR (KBr): ν̃ = 2520 m (BH) cm⁻¹.

Hydrolysis Products

4a: A solution of **L**³ (196 mg, 0.33 mmol) in dichloromethane (5 mL) was added dropwise, with stirring, to a solution of Zn(ClO₄)₂·6H₂O (124 mg, 0.34 mmol) in ethanol (10 mL). After stirring for 24 h, all volatiles were removed in vacuo, the residue extracted with dichloromethane, filtered and the filtrate concen-

trated to dryness again. Recrystallisation from dichloromethane/ethanol yielded 110 mg (35%) of **4a** as colourless crystals; m.p. 210 °C (dec.). C₄₀H₃₈BClN₈O₄S₃Zn (902.64): calcd. C 53.23, H 4.24, N 12.41, S 10.66; found C 51.94, H 4.36, N 11.95, S 10.02. ¹H NMR (CD₂Cl₂): δ = 1.78 [s, 3 H, Me (tol)], 1.96 [s, 3 H, Me (tol)], 2.12 [s, 3 H, Me (tol)], 2.49 [s, 3 H, Me (pz)], 6.40 [s, 1 H, H (pz)], 6.72 [s, 1 H, H (im)], 6.73 [d, *J* = 2.2 Hz, 1 H, H (im)], 6.80 [s, 1 H, H (im)], 6.84 [s, 1 H, H (im)], 7.00 [s, 2 H, H (im)], 7.10–7.39 (m, 17 H, Ar), 10.64 (s, 1 H, NH) ppm. IR (KBr): ν̃ = 2463 w (BH) cm⁻¹.

4b: Like **4a** from **L**⁶ (214 mg, 0.33 mmol) and Zn(ClO₄)₂·6H₂O (124 mg, 0.34 mmol). Yield 88 mg (27%) of **4b** as colourless crystals; m.p. 180 °C (dec.). C₄₆H₅₀BClN₈O₄S₃Zn (986.80): calcd. C 55.99, H 5.11, N 11.36, S 9.75; found C 55.27, H 5.52, N 11.10, S 9.07. ¹H NMR (CDCl₃): δ = 1.28 [d, *J* = 7.0 Hz, 18 H, Me(*i*Pr)], 2.52 [s, 3 H, Me (pz)], 2.97 [sept, *J* = 7.0 Hz, 3 H, CH(*i*Pr)], 6.39 [s, 1 H, H (pz)], 6.83 [s, 1 H, H (im)], 6.94 [s, 1 H, H (im)], 6.99 [s, 2 H, H (im)], 7.14 [s, 2 H, H (im)], 7.29 (d, *J* = 8.0 Hz, 6 H, C₆H₄), 7.39 (m, 3 H, Ph), 7.43 (d, *J* = 8.0 Hz, 6 H, C₆H₄), 7.47 (d, *J* = 7.8 Hz, 2 H, Ph), 10.92 (s, 1 H, NH) ppm. IR (KBr): ν̃ = 2468 w (BH) cm⁻¹.

5: A solution of **L**¹ (350 mg, 0.80 mmol) in dichloromethane (50 mL) was added dropwise, with stirring, to a solution of Zn(ClO₄)₂·6H₂O (300 mg, 0.18 mmol) in methanol (100 mL). After 2 h of stirring, powdered KOH (46 mg, 0.80 mmol) was added and the mixture stirred for another 20 h. After filtration, the filtrate was concentrated to half its volume. Within a few weeks 74 mg (9%) of colourless crystalline **5**, m.p. 167 °C, was obtained. C₂₄H₃₀N₁₂OS₆Zn₄·6H₂O (956.50 + 108.06): calcd. C 27.08, H 3.98, N 15.79; found C 27.03, H 3.26, N 16.59. ¹H NMR (CDCl₃): δ = 1.51 (s, 2 H, H₂O), 3.49–3.69 (m, 3 H, Me), 6.78–7.10 (m, 2 H, H (im)) ppm.

Enzyme Models

6a: The precipitate of **6a**, which is an intermediate in the formation of **3a** (see above), was dried in vacuo. 46 mg (21%) of raw **6a** remained as a colourless powder; m.p. 220 °C (dec.). C₁₈H₂₁BN₆OS₂Zn (477.74): calcd. C 45.25, H 4.43, N 17.59, S 13.42; found C 43.44, H 4.16, N 17.56, S 12.66. ¹H NMR (CDCl₃): δ = 2.36 [s, 3 H, Me (pz)], 3.50 [s, 6 H, Me (im)], 6.22 [s, 1 H, H (pz)], 6.61 [d, *J* = 2.0 Hz, 2 H, H (im)], 7.14 [d, *J* = 2.0 Hz, 2 H, H (im)], 7.28 (m, 3 H, Ph), 7.77 (d, *J* = 7.4 Hz, 2 H, Ph) ppm. IR (KBr): ν̃ = 3630 vw (OH), 2503 m (BH) cm⁻¹.

6b: A solution of Zn(ClO₄)₂·6H₂O (130 mg, 0.35 mmol) in methanol (20 mL) was added with stirring to a solution of **L**² (200 mg, 0.35 mmol) in dichloromethane (100 mL). After 30 min, powdered KOH (22 mg, 0.39 mmol) was added. After stirring for 20 h, the mixture was filtered and the filtrate reduced in vacuo to half its volume. Cooling to –30 °C for 3 days precipitated 96 mg (44%) of raw **6b** as colourless powder, m.p. 220 °C (dec.) which started decomposing upon attempts of further purification. C₂₈H₂₅BN₆OS₂Zn (601.88): calcd. C 55.88, H 4.19, N 13.96, N 10.86; found C 54.68, H 4.05, N 13.57, Zn 10.71. ¹H NMR (CDCl₃): δ = 2.29 [s, 3 H, Me (pz)], 6.29 [s, 2 H, H (pz)], 6.73 [d, *J* = 2.4 Hz, 2 H, H (im)], 6.80 [d, *J* = 2.4 Hz, 2 H, H (im)], 7.30–7.51 (m, 13 H, Ar), 7.53 (d, *J* = 7.3 Hz, 2 H, Ph) ppm. IR (KBr): ν̃ = 3650 w (OH), 2499 m (BH) cm⁻¹.

7: A solution of **L**⁵ (665 mg, 1.08 mmol) and anhydrous methanol (60 mL) was slowly added dropwise, with stirring, to a solution of Zn(ClO₄)₂·6H₂O (400 mg, 1.08 mmol) in anhydrous methanol (60 mL). After stirring for 1 h, the precipitate was filtered off and the filtrate reduced to 80 mL in vacuo. The resulting precipitate

was also filtered off and the filtrate concentrated to dryness. The residue was extracted with dichloromethane (14 mL). After filtration, the extract was concentrated to dryness and the residue dried in vacuo. 438 mg (55%) of **7** remained as a colourless powder; m.p. 230 °C (dec.). $C_{30}H_{28}BClN_6O_6S_2Zn$ (744.37): calcd. C 48.41, H 3.79, N 11.29, S 8.62; found C 48.57, H 4.30, N 11.28, S 8.43. 1H NMR ($CDCl_3$): δ = 2.28 [s, 3 H, Me (pz)], 3.68 (s, 6 H, OMe), 6.49 [s, 1 H, H (pz)], 6.94–7.70 [m, 15 H, H (im), Ar], 7.93 [d, J = 7.2 Hz, 2 H, Ph] ppm. IR (KBr): $\tilde{\nu}$ = 2476 w (BH), 1179 vs, 1093 vs (ClO_4) cm^{-1} .

8: A solution of **L**⁸ (309 mg, 0.50 mmol) in anhydrous ethanol (25 mL) was slowly added dropwise, with stirring, to a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (186 mg, 0.50 mmol) in anhydrous ethanol (25 mL) and the mixture stirred for 15 h. After filtration, the volume was reduced to one half in vacuo and the resulting precipitate filtered off. Recrystallisation from anhydrous ethanol yielded 313 mg (71%) of **8** as colourless crystals, m.p. 200 °C (dec.). $C_{32}H_{34}BClN_6O_7S_2Zn \cdot C_2H_5OH$ (790.44 + 46.07): calcd. C 48.82, H 4.82, N 10.05, S 7.67; found C 47.75, H 4.87, N 9.74, S 7.33. 1H NMR ($CDCl_3$): δ = 1.18 [t, J = 7.0 Hz, 6 H, CH_3 (Et)], 2.50 [s, 3

Table 1. Crystallographic details

	1c	1d	2a	3a	3b	3c
Empirical formula	$C_{30}H_{28}BClN_6S_2Zn$	$C_{32}H_{32}BClN_6S_2Zn \cdot 2CH_3CN$	$C_{30}H_{28}BN_7O_3S_2Zn$	$C_{36}H_{40}B_2N_{12}S_4Zn \cdot 3H_2O$	$C_{60}H_{56}B_2N_{12}S_4Zn \cdot CH_3CN \cdot 2H_2O$	$C_{60}H_{56}B_2N_6S_4Zn \cdot H_2O$
Molecular mass	648.33	758.49	674.89	910.11	1237.54	1178.47
Crystal size [mm]	$0.15 \times 0.2 \times 0.35$	$0.4 \times 0.3 \times 0.3$	$0.1 \times 0.1 \times 0.2$	$0.4 \times 0.3 \times 0.2$	$0.05 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.3$
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	4	2	2	2
a [Å]	11.322(2)	10.087(2)	10.243(1)	8.98(2)	11.234(2)	10.788(1)
b [Å]	14.625(2)	11.908(2)	29.169(3)	15.07(3)	17.060(2)	15.874(1)
c [Å]	18.481(2)	17.035(3)	11.475(1)	17.55(4)	17.377(2)	19.024(2)
α [°]	90	102.41(3)	90	77.35(3)	75.297(3)	106.094(2)
β [°]	95.549(3)	95.34(3)	113.356(3)	80.10(3)	81.242(3)	104.962(2)
γ [°]	90	110.13(3)	90	78.80(3)	87.280(3)	105.176(2)
V [Å ³]	3045.9(7)	1845.0(6)	3147.8(6)	2252.4(8)	3183.7(8)	2822.5(4)
d (calcd.) [g·cm ⁻³]	1.41	1.37	1.42	1.34	1.55	1.37
μ (Mo- K_{α}) [mm ⁻¹]	1.06	0.89	0.96	0.78	1.14	0.64
hkl range	h : -15 to 9 k : -19 to 19 l : -24 to 24	h : -12 to 0 k : -13 to 14 l : -20 to 20	h : -13 to 5 k : -38 to 38 l : -15 to 14	h : -11 to 0 k : -18 to 18 l : -21 to 21	h : -14 to 14 k : -22 to 22 l : -23 to 23	h : -13 to 14 k : -20 to 21 l : -25 to 24
Measured reflections	19180	7657	20120	9427	29078	25673
Independent reflections	7362	7230	7680	8831	14881	13177
Observed refl. [$I > 2\sigma(I)$]	5294	5589	2749	5204	5199	6271
Parameters	370	448	398	523	746	712
Refined reflections	7362	7230	7680	8831	14881	13177
R_1 (obsd. refl.)	0.035	0.046	0.072	0.066	0.079	0.056
wR_2 (all refl.)	0.113	0.132	0.256	0.238	0.282	0.145
Residual electron density [e/Å ³]	+0.5/-0.4	+1.3/-0.6	+0.8/-0.8	+1.3/-0.9	+1.1/-0.6	+0.7/-0.7

	3d	3f	4a	4b	5	8
Empirical formula	$C_{64}H_{64}B_2N_{12}S_4Zn \cdot 8C_6H_6$	$C_{44}H_{72}B_2N_{12}S_4Zn$	$C_{40}H_{38}BClN_8O_4S_3Zn \cdot CH_2Cl_2$	$C_{46}H_{50}BClN_8O_4S_3Zn \cdot CH_2Cl_2$	$C_{24}H_{30}N_{12}OS_6Zn_4 \cdot 6H_2O$	$C_{32}H_{34}BClN_6O_7S_2Zn \cdot 2C_2H_5OH$
Molecular mass	1841.47	984.37	987.52	1071.68	1064.56	882.58
Crystal size [mm]	$0.2 \times 0.25 \times 0.35$	$0.5 \times 0.4 \times 0.4$	$0.15 \times 0.15 \times 0.25$	$0.1 \times 0.05 \times 0.05$	$0.2 \times 0.1 \times 0.1$	$0.25 \times 0.15 \times 0.1$
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
Z	4	2	4	2	6	2
a [Å]	26.507(3)	10.576(1)	11.399(1)	10.897(1)	15.993(2)	10.962(1)
b [Å]	20.022(2)	16.243(1)	11.133(1)	15.635(2)	15.993(2)	14.131(2)
c [Å]	20.914(3)	16.809(1)	35.651(3)	17.131(2)	33.715(5)	14.834(2)
α [°]	90	105.253(2)	90	66.431(2)	90	101.011(2)
β [°]	112.828(2)	101.468(2)	97.978(2)	74.600(2)	90	109.568(2)
γ [°]	90	104.034(2)	90	80.263(3)	120	94.234(2)
V [Å ³]	10229.9(18)	2594.2(4)	4480.6(6)	2572.6(5)	7468.0(15)	2101.6(4)
d (calcd.) [gcm ⁻³]	1.20	1.26	1.46	1.38	1.40	1.40
μ (Mo- K_{α}) [mm ⁻¹]	0.38	0.68	0.92	0.81	2.20	0.81
hkl range	h : -35 to 33 k : -26 to 19 l : -27 to 27	h : -12 to 13 k : -21 to 21 l : -22 to 22	h : -15 to 6 k : -14 to 13 l : -47 to 44	h : -14 to 14 k : -20 to 20 l : -22 to 22	h : -19 to 19 k : -19 to 19 l : -41 to 41	h : -14 to 14 k : -18 to 18 l : -19 to 19
Measured reflections	32298	23401	27857	23909	19601	19203
Independent reflections	12428	11738	10752	12173	3219	9895
Observed refl. [$I > 2\sigma(I)$]	4317	6604	5145	2730	2134	5057
Parameters	596	576	578	605	106	509
Refined reflections	12428	11738	10752	12173	3219	9895
R_1 (obsd. refl.)	0.069	0.078	0.077	0.105	0.043	0.061
wR_2 (all refl.)	0.204	0.230	0.264	0.387	0.132	0.187
Residual electron density [e/Å ³]	+1.2/-0.5	+1.2/-0.8	+1.3/-1.1	+1.1/-0.8	+1.3/-0.4	+0.8/-0.8

H, Me (pz)], 3.62 [dq, $J = 7.0/5.2$ Hz, 4 H, CH₂ (Et)], 3.82 (s, 6 H, OMe), 6.40 [s, 1 H, H (pz)], 6.94 [d, $J = 2.1$ Hz, 2 H, H (im)], 7.02 [d, $J = 2.1$ Hz, 2 H, H (im)], 7.03–7.48 (m, 11 H, Ar), 7.54–7.60 (m, 2 H, Ph) ppm. IR (KBr): $\tilde{\nu} = 2499$ w (BH), 1180 s, 1096 s, br. (ClO₄) cm⁻¹.

Catalytic Studies. Oxidation of 2-Propanol: **2a** (33.8 mg, 0.05 mmol) and [BNA]Cl (12.5 mg, 0.05 mmol) were dissolved in [D₆]DMSO (2 mL). 2-Propanol (0.2 mL, 2.6 mmol) was added and the mixture stirred for 24 h at 100 °C in the dark. The oxidation reaction was monitored by recording the ¹H NMR signals of acetone at $\delta = 2.08$ ppm and of the benzyl group of BNAH at $\delta = 4.30$ ppm.

Reduction of *p*-Nitrobenzaldehyde: **2a** (20.3 mg, 0.03 mmol), *p*-nitrobenzaldehyde (4.5 mg, 0.03 mmol) and BNAH (6.5 mg, 0.03 mmol) were dissolved in [D₆]DMSO (2 mL) and the mixture was stirred at 100 °C for 24 h. The reduction was monitored by recording the ¹H NMR signals of *p*-nitrobenzyl alcohol at $\delta = 4.25$ ppm and of the benzyl group of BNA⁺ at $\delta = 5.91$ ppm.

Structure Determinations:^[28] Crystals were obtained as described above. Diffraction data were recorded at 200 K (**2a**, **3c**, **3d**, **3f**, **4a**, **4b**, **5**, **8**) and at room temp. (**1c**, **1d**, **3a**, **3b**) with a Nonius CAD4 (**1d**, **3a**, **3d**, **5**) or a Bruker Smart CCD diffractometer (**1c**, **2a**, **3b**, **3c**, **3f**, **4a**, **4b**, **8**). Empirical absorption corrections were applied for **3b**, **3c**, **4a**, **4b** and **8**. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.^[29] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5-times those of their attached atoms. Parameters were refined against F^2 . The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]^2/\Sigma[w(F_o^2)]^2\}^{1/2}$. Drawings were produced with SCHAKAL.^[30] Table 1 lists the crystallographic data.

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[1] G. Parkin, *Adv. Inorg. Chem.* **1995**, 42, 291–393.

[2] N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, 43, 419–531.

[3] H. Vahrenkamp, *Acc. Chem. Res.* **1999**, 32, 589–596.

[4] G. Parkin, *Chem. Commun.* **2000**, 1971–1985.

[5] M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer, A. R. Kennedy, *Chem. Commun.* **1996**, 1975–1976.

[6] J. Reglinski, M. D. Spicer, M. Garner, A. R. Kennedy, *J. Am. Chem. Soc.* **2000**, 121, 2317–2318.

[7] I. Cassidy, M. Garner, A. R. Kennedy, G. B. S. Potts, J. Reglinski, P. A. Slavin, M. D. Spicer, *Eur. J. Inorg. Chem.* **2002**, 1235–1239.

[8] J. L. White, J. M. Tanski, D. Rabinovich, *J. Chem. Soc., Dalton Trans.* **2002**, 2987–2991, and references cited therein.

[9] B. M. Bridgewater, G. Parkin, *Inorg. Chem. Commun.* **2001**, 4, 126–129.

[10] M. Tesmer, M. Shu, H. Vahrenkamp, *Inorg. Chem.* **2001**, 40, 4022–4029.

[11] C. Kimblin, T. Hascall, G. Parkin, *Inorg. Chem.* **1997**, 36, 5680–5681.

[12] C. Kimblin, B. M. Bridgewater, T. Hascall, G. Parkin, *J. Chem. Soc., Dalton Trans.* **2000**, 1267–1274.

[13] C. Kimblin, B. M. Bridgewater, D. G. Churchill, T. Hascall, G. Parkin, *Inorg. Chem.* **2000**, 39, 4240–4243.

[14] J. Seebacher, M. Shu, H. Vahrenkamp, *Chem. Commun.* **2001**, 1026–1027.

[15] J. Seebacher, H. Vahrenkamp, unpublished.

[16] In 2002 the Cambridge Crystallographic Data File had 76 entries for zinc complexes of thiourea-derived ligands.

[17] R. Castro, J. A. Garcia-Vazquez, J. Romero, A. Sousa, Y. D. Chang, J. Zubietta, *Inorg. Chim. Acta* **1995**, 237, 143–146.

[18] H. Kayama, Y. Saito, *Bull. Chem. Soc. Jpn.* **1954**, 27, 12–16.

[19] C. Kimblin, B. M. Bridgewater, D. G. Churchill, G. Parkin, *Chem. Commun.* **1999**, 2301–2302.

[20] S. Ramaswamy, H. Eklund, B. V. Plapp, *Biochemistry* **1994**, 33, 5230–5237.

[21] R. Walz, H. Vahrenkamp, *Inorg. Chim. Acta* **2000**, 314, 58–62.

[22] Y. Zhang, H. Vahrenkamp, *Inorg. Chim. Acta*, in print.

[23] M. Förster, R. Burth, A. K. Powell, T. Eiche, H. Vahrenkamp, *Chem. Ber.* **1993**, 126, 2643–2648.

[24] R. Alsasser, M. Ruf, S. Trofimenko, H. Vahrenkamp, *Chem. Ber.* **1993**, 126, 703–710.

[25] J. Elguero, R. Jaquier, *Bull. Soc. Chim. Fr.* **1966**, 2832–2845.

[26] R. G. Jones, E. C. Kornfeld, K. C. McLaughlin, R. C. Anderson, *J. Am. Chem. Soc.* **1949**, 71, 4000–4002.

[27] J. Kister, G. Assef, G. Mille, J. Metzger, *Can. J. Chem.* **1979**, 57, 813–821.

[28] CCDC-203392 (**1c**), -203393 (**1d**), -203394 (**2a**), -203395 (**3a**), -203396 (**3b**), -203397 (**3c**), -203398 (**3d**), -203399 (**3f**), -203400 (**4a**), -203401 (**4b**), -203402 (**5**) and -156428 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[29] *SHELXTL*, program package of the Bruker Smart CCD diffractometer, version 5.1, **2002**.

[30] E. Keller, *SCHAKAL for Windows*, Universität Freiburg, **1999**.

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