New Tris(thioimidazolyl)borate Ligands and Some Zinc Complexes Thereof

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Keywords: Alcohol ligands / Alkoxide ligands / S ligands / Tripodal ligands / Zinc

In order to improve the encapsulation of metal ions coordinated by tris(thioimidazolyl)borate ligands, four new such ligands with *o*-substituted phenyl substituents were synthesised as well as ones with *p*-tolyl and cyclohexyl substituents. In order to provide a basis for their bioinorganic zinc complex chemistry, they were converted to some zinc-halide, -carboxylate, -nitrate, -phenolate and -benzylate complexes. They form zinc-perchlorate complexes which are productive starting materials for the attachment of alcohols and alkoxides at zinc, thereby yielding new structural models for the zinc enzyme alcohol dehydrogenase.

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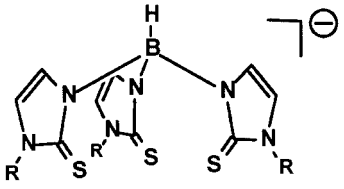
Introduction

Among the zinc enzymes the alcohol dehydrogenases[1] and the thiolate alkylating enzymes[2] have an unusually (cysteine-)sulfur-rich ligand environment of the zinc ion. We[3,4] and others[5–9] have tried to model the structure and function of these enzymes by applying tripodal scorpionate[10] ligands bearing one to three sulfur donors. During these studies Parkin's[5,8,11,12] and our own research group[3,13] have found that the sulfur-rich environment of the tris(thioimidazolyl)borate ligands (Tti^R) enables the attachment of quite unusual and biologically relevant co-ligands X at the zinc ion in an S_3ZnX environment.

During these studies it also became evident that the substituted tris(thioimidazolyl)borates (Tti^R) have one disadvantage in comparison to the widely used tris(pyrazolyl)borates (Tp^R). While the R substituents at the 3-positions of the pyrazolylborates provide an ideal encapsulation of the metal ions bound to the three pyrazole nitrogens due to their orientation, the corresponding R substituents at the 1-nitrogens of the thioimidazolylborates are less efficient in this respect because they point away from the core of the ligands. As encapsulation of the metals is a key feature in the development of ligands for a viable bioinorganic model complex chemistry, there arose the necessity to use Tti^R ligands with sterically more demanding substituents R.

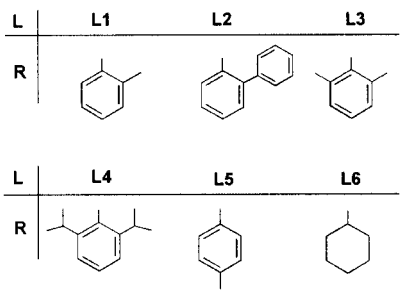
The Tti ligands, which should bear as much potential as the Tp ligands, were introduced by Reglinski in 1996.[14] Remarkably little metal complex chemistry has been done with them in the eight years since, either by Reglinski himself[15–20] or by other research groups.[3,5,8,11–16,21–25] So far only methyl,[14] *tert*-butyl,[3] benzyl,[22] phenyl,[5] *p*-tolyl,[22] mesityl[5] and *p*-cumenyl substituents[3] have been attached at the N^1 nitrogens of the thioimidazolyl moieties, of which only *tert*-butyl and mesityl can be considered as sterically demanding.

Having enjoyed the bioinorganic zinc chemistry of the Tp^R ligands for many years,[26] we trusted the zinc chemistry of the Tti^R ligands to be equally fertile. We therefore set out to lay a basis for it by obtaining Tti^R ligands with improved encapsulation abilities. In order to achieve this we chose *o*-substituted phenyl groups as the substituents R. We prepared two ligands with one *o*-substituent each (**L1**, **L2**), two with two *o*-substituents each (**L3**, **L4**), and we also de-



Tti^R

$K[Tti^R]$



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 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **DOI: 10.1002/ejic.200400994**

scribe a variation of the synthesis of *p*-substituted **L5**[22] and the synthesis of cyclohexyl-substituted **L6**. This paper reports the ligand syntheses, some simple zinc complexes, and some alcohol and alkoxide derivatives relevant to the zinc enzyme alcohol dehydrogenase.

Results and Discussion

Ligand Synthesis

While the preparation of tris(pyrazolyl)borates requires high-temperature reactions between KBH_4 and the pyrazoles in a melt, the thioimidazoles react with KBH_4 under milder conditions, typically in boiling toluene. This made the synthesis of ligands **L1**–**L6** an easy, high-yield process, the most time-consuming part of which is actually the two-step synthesis of the substituted thioimidazoles, whose overall yields rarely exceed 50%.

Except for **L2** (ca. 60%) the potassium salts of the ligands **L** were obtained in yields of around 90%. K[**L1**] and K[**L5**] were obtained analytically pure from the reaction solution, K[**L2**] needed a chromatographic purification, and the other K[**L**] complexes were crystallised from methanol. Their characteristic spectral features are the weak ν(BH) band at around 2500 cm^{-1} and a pair of doublets due to the two imidazole protons in the ^1H NMR spectra.

Complexes of Simple Anions

It was already known[3,5,11] that zinc in the sulfur-rich ligand environment of the tris(thioimidazolyl)borate ligands is complemented favourably by oxygen-containing coligands and by the halides. This was verified here for ligands **L1**, **L3** and **L5** in combination with zinc and simple anionic coligands. In order to obtain complexes **1**–**9** the potassium salts of **L** were either treated directly with $ZnCl_2$, ZnI_2, $Zn(NO_3)_2$ or $Zn(CH_3COO)_2$, or they were reacted first with zinc perchlorate and then with the deprotonated forms of thioacetic acid or *p*-nitrothiophenol. The latter was included with the anionic ligands due to its typical UV/Vis absorption, which we intend to exploit for kinetic studies of the alkylation of Zn–OR species in comparison to Zn–SR species.[8,27] Products **1**–**9** were isolated in very good yields as colourless (**1**–**5**) or yellow (**6**–**9**) powders. Except for **1**, **2** and **3** the characteristic ^1H NMR features of the anionic coligands complement the typical spectral characteristics (see above) of their ligands **L**.

L3•Zn-Cl	**L3**•Zn-I	**L3**•Zn-ONO_2
1	**2**	**3**
L1•Zn-$OCOCH_3$	**L3**•Zn-$OCOCH_3$	**L3**•Zn-$SCOCH_3$
4	**5**	**6**
L1•Zn-$OC_6H_4NO_2$	**L3**•Zn-$OC_6H_4NO_2$	**L5**•Zn-$OC_6H_4NO_2$
7	**8**	**9**

The structure determinations of **1**, **3**, **4**, **5** and **9** confirmed the identities of the ligands, the characteristic structural features of the **L**·Zn units and the coligand attachment. Figure 1 displays the complete molecule of **1** as an example; Table 1 lists the important bonding features. There is a quite uniform array of the four donors around the zinc ions. The attachment of the tripod ligands **L** nicely defines a tetrahedral geometry with remarkably constant bond lengths and angles. The coligands' donor atoms (Cl and O), however, are never positioned correctly on the trigonal axis of the complexes, as defined by the B–Zn line. Table 1 displays this in terms of the X–Zn···B angles. These deviate most from 180° in the case of the nitrate and acetate complexes **3**, **4** and **5**, thus reflecting the semi-bidentate nature of their coligands. As a consequence, the X–Zn–S angles in all complexes described in this paper show a considerable spread, typically between 100° and 120°.

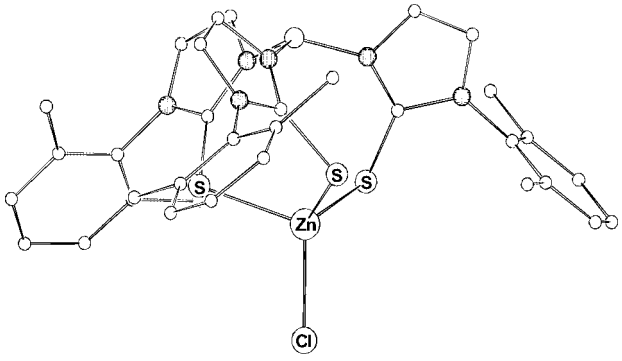

Figure 1. Molecular structure of **1**.

Table 1. Bond lengths [Å] and angles [°] around the zinc ions in complexes **1**, **3**, **4**, **5**, and **9**.

	X	Zn–X	Zn–S(av)	S–Zn–S(av)	X–Zn···B
1	Cl	2.252(2)	2.34(1)	108(2)	175
3	O	2.007(6)	2.33(1)	109(2)	171
4	O	2.005(11)	2.37(1)	107(1)	161
5	O	1.954(5)	2.34(2)	108(1)	172
9	O	1.926(5)	2.33(1)	106(3)	174

The voluminous nature of the tripod ligands **L** somewhat obscures their essential bonding characteristics. Therefore, two views of molecular fragments were chosen to make them visible. One of them is the view along the B···Zn axis (Figure 2), which shows the chiral, screw-like array of the three thioimidazolyl moieties between the boron and zinc atoms that is the most characteristic feature distinguishing the tris(thioimidazolyl)borates from the tris(pyrazolyl)borates. The other is the orientation of the external aromatic substituents (Figure 3). Following the trigonal symmetry of the **L**·Zn units, all three of them are always tilted in the same direction with respect to the thioimidazole rings. The amount of this tilting varies within each complex and between complexes. It places the "down" parts of the aromatic rings in the vicinity of the zinc-bound coligands, thereby providing the encapsulation of the Zn–X units, though in a much less efficient way than in related tris(pyrazolyl)borates. Yet, as Figure 3 shows, the best way to improve this encapsulation should be the attachment of *ortho*-substitu-

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ents at the aromatic rings, which, due to the tilting, are most likely to be located in the vicinity of the Zn–X units.

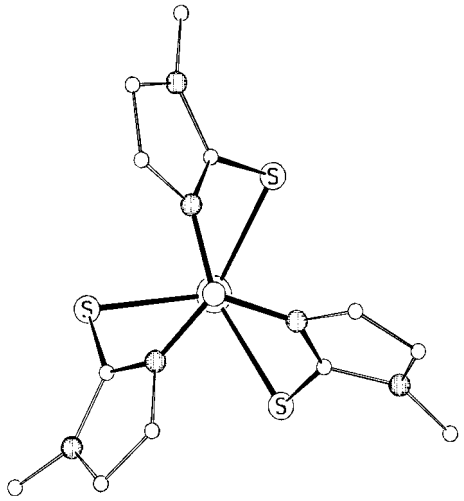

Figure 2. A view of complex **1** down the B···Zn line (aromatic substituents omitted for clarity).

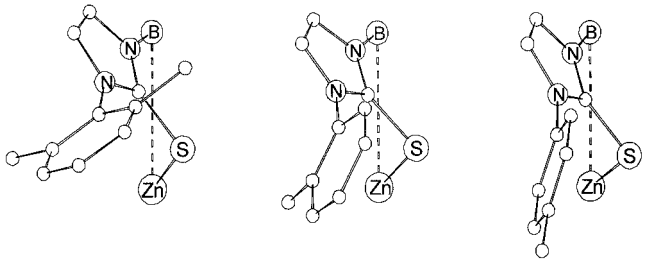

Figure 3. One substituted thioimidazolyl fragment each of complexes **1**, **4** and **21**, viewed perpendicular to the B···Zn line.

Perchlorate Complexes

Quite a number of the complexes described in this paper were prepared by combining a ligand **L** with zinc perchlorate first. This implies that in the intermediate species either perchlorate or the solvent used is coordinated to zinc. Probing this we realized that the **L**·Zn-perchlorate complexes are easily formed and that they can be used as precursors of **L**·Zn complexes with other unusual coligands X. The solvent of choice for this purpose is methanol, which obviously binds less well to zinc than perchlorate. Accordingly, complexes **10**–**14** were obtained from K[**L**] and $Zn(ClO_4)_2$ in methanol.

L1•Zn-$OClO_3$ **10** **L2**•Zn-$OClO_3$ **11** **L3**•Zn-$OClO_3$ **12**

L4•Zn-$OClO_3$ **13** **L6**•Zn-$OClO_3$ **14**

The characteristic feature of **10**–**14**, apart from the weak ν(BH) band, is the very strong perchlorate band in the infrared spectra in the region of 1090 cm^{-1}. The existence of a Zn–$OClO_3$ connection has already been proved by us by the structure determination of tris(*N*-*tert*-butylthioimidazolyl)boratozinc perchlorate.[3] The ease of isolation of **10**–**14** has made it clear now that these complexes are much less labile than originally assumed.

Alkoxide Complexes

In our previous studies of zinc complexes of tris(thioimidazolyl)borate ligands, which were aimed predominantly at modelling alcohol dehydrogenase,[3] alkoxide complexes had evaded us. We now found that they are accessible with the new ligands **L**. In trying to make mononuclear **L**·Zn–OR complexes we learnt that these are still inaccessible with aliphatic alkoxides or with benzylate, but the more electronegative *p*-nitrobenzylate and *p*-(trifluoromethyl)benzylate could be introduced as terminal ligands in complexes **15** and **16**. The procedure which led to them is the reverse of the procedure used for all other complexes: zinc perchlorate and the benzylate are combined first, and only after that is the tripod **L3** attached.

L3•Zn-$OCH_2C_6H_4NO_2$ **15** **L3**•Zn-$OCH_2C_6H_4CF_3$ **16**

The mononuclear nature of **15** and **16** is evident from their solubility in non-polar solvents and from their ^1H NMR spectra, which correspond for the **L3**·Zn unit to those of the other mononuclear **L3**·Zn complexes. In addition the ^1H and ^{19}F NMR spectroscopic data confirm the presence of the benzylate ligands. Unfortunately, complexes **15** and **16** did not yield crystals suitable for a structure determination.

Aliphatic alkoxides could be incorporated using the standard procedure, i.e. first making the intermediate **L**·Zn perchlorate complex and then treating it with the alkoxide. Methoxide, ethoxide and trifluoroethoxide could be combined with **L3**·Zn, but the structure determinations showed that the resulting complexes **17**–**19** are dinuclear and contain bridging alkoxide ligands. The ionic nature of **17**–**19** is reflected by their solubility only in polar solvents. Their ^1H NMR spectra show small but significant shifts compared to those of the mononuclear **L3**·Zn complexes.

[**L3**•Zn-OR-Zn**L3**]ClO_4

17: R = CH_3, **18**: R = C_2H_5, **19**: R = CH_2CF_3

Figure 4 shows the structure of **17** as an example; that of **18** is very similar. In both **17** and **18** the alkoxide bridge is nicely symmetrical with two virtually identical Zn–O distances and Zn–O–C angles each (see Table 2). The Zn–O bond lengths (near 1.95 Å) resemble those for the **L**·Zn nitrophenolates (see above and ref.[3]). We could not find a structurally characterised dizinc complex with a single unsupported alkoxide bridge in the literature, but there are some related complexes with single hydroxide bridges.[28–32] Their Zn–O bond lengths (1.87–2.00 Å) and Zn–O–Zn angles (132–141°) closely resemble those of **17** and **18**. With

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respect to the **L3**·Zn units, specifically the displacement of the bridging oxygen off the B···Zn line, complexes **17** and **18** are completely analogous to the other **L**·Zn–X complexes reported here.

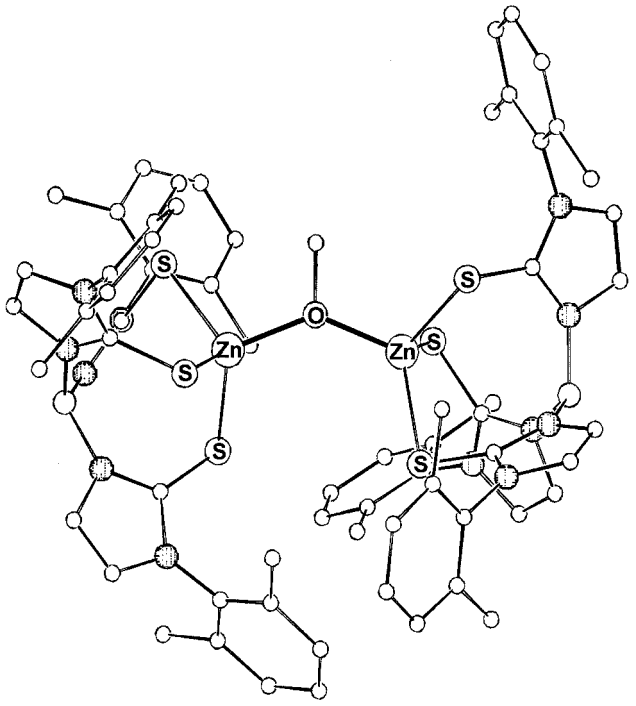

Figure 4. Structure of the dinuclear cation of **17**. See Table 2 for details.

Table 2. Relevant distances [Å] and angles [°] araound the zinc ions in the alkoxide-bridged complexes.

	17	**18**
Zn–O	1.957(5)/1.941(5)	1.959(3)/1.967(3)
Zn···Zn	3.63	3.64
Zn–S(av)	2.35 ± 2	2.36 ± 2
Zn–O–Zn	137.0(3)	136.0(2)
S–Zn–S(av)	108.5 ± 1	107.5 ± 1
O–Zn–S	105–118	107–118
Zn–O–C	109.8(7)/110.2(7)	110.7(3)/111.7(3)

Complexes with Alcohol and Aldehyde Ligands

We have already shown[3] that the electron-rich nature of the **L**·Zn unit and its favourable combination with oxygen donors allows the attachment of ethanol as a coligand. We could now show that with the ligands **L** used in this paper even the weaker oxygen donor 2-propanol can be attached. The 2-propanol complexes **20** and **21** crystallised when **L3** or **L5** were combined with zinc perchlorate in 2-propanol.

[**L3**•Zn(*i*-C_3H_7OH)]ClO_4 **20**

[**L5**•Zn(*i*-C_3H_7OH)]ClO_4 **21**

Complex **21** was chosen for a structure determination (see Figure 5). There are two formula units of **21** in the asymmetric unit. In one of them the 2-propanol ligand is linked through a hydrogen bond (2.67 Å) to another 2-propanol molecule, and in the other it is linked by a hydrogen bond (2.84 Å) to a perchlorate anion. This attachment of an external hydrogen-bond acceptor seems to be a common feature of all zinc–alcohol complexes with tripodal ligands.[3–5] Likewise, the Zn–O bond lengths in both complex units of **21** (av. 1.98 Å) lie within the small range of such bond lengths observed before (1.97–2.01 Å),[3–5] and they are nearly identical to the one in the pentafluorobenzyl alcohol adduct of alcohol dehydrogenase (ADH).[33] This adds complex **21** to the list of structural models of ADH.

The idea of modelling ADH was also the reason for attaching the two functional phenols salicylic alcohol and salicylic aldehyde as phenolates to the **L3**·Zn unit. The *o*-hydroxymethylphenolate complex **22** and the *o*-formylphenolate complex **23** were obtained by treating the deprotonated phenols first with zinc perchlorate and then with K[**L3**]. It was hoped that the chelate effect would enable a coordination of the alcoholic function in **22** and the aldehydic function in **23** to zinc, thereby generating a pair of complexes that mimic the binding of substrate and product in the active centre of ADH, as we had achieved before with $Zn(SR)_2$ systems.[34]

L3•Zn-OC_6H_4-*o*-CH_2OH **22**

L3•Zn-OC_6H_4-*o*-CHO **23**

While the spectroscopic data of **22** are inconclusive, those of **23** indicate coordination of the aldehyde oxygen to zinc: both the ν(CO) IR band (1671 → 1659 cm^{-1}) and the ^1H NMR formyl signal (δ = 9.99 → 11.03 ppm) undergo shifts in the expected direction relative to those of formylphenolate. The structure determination of **23**, however, disproved this assumption. As Figure 6 shows, the formyl oxygen is

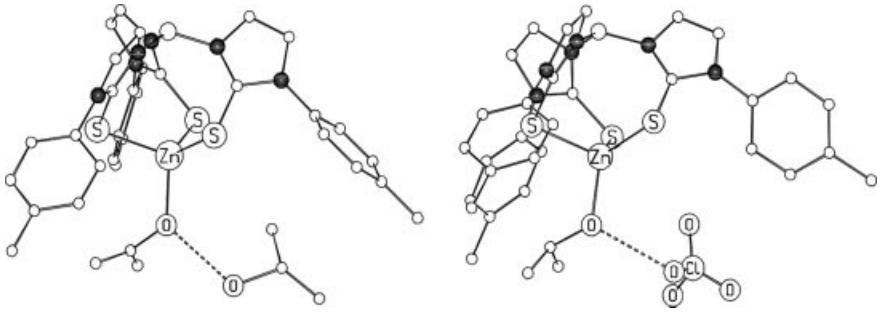

Figure 5. The two crystallographically independent complex cations of **21**. Left (linked to a molecule of 2-propanol): Zn–O 1.979(4), Zn–S 2.307(2), 2.317(2) and 2.332(2) Å. Right (linked to a perchlorate anion): Zn–O 1.984(4), Zn–S 2.309(2), 2.315(2) and 2.332(2) Å.

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oriented away from the zinc ion, thus making **23** a normal phenolate complex comparable to **7**–**9**. Based on this observation, and on the similar non-coordination of the hydroxymethyl group in **24** (see below), it must be concluded that the hydroxymethyl function in **22** is also not coordinated to zinc.

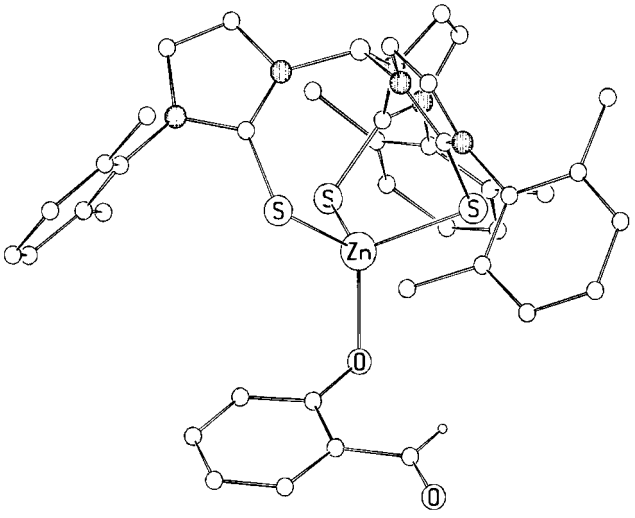

Figure 6. Molecular structure of complex **23**. Zn–O 1.937(2), Zn–S 2.338(1), 2.363(1), and 2.319(1) Å.

The same reasoning as above, together with the knowledge that the **L**·Zn units, unlike the TpZn units, easily bind uncharged nitrogen ligands,[3,5,12,13] led us to the application of 1-methyl-2-hydroxymethylimidazole. It was hoped that the coordination of both its 3-nitrogen and the hydroxymethyl oxygen to zinc would be favoured by the formation of a five-membered chelate ring. The desired complex **24** was formed by treating the intermediate **L5**·Zn perchlorate with the imidazole.

[**L5**•Zn(1-methyl-2-hydroxymethylimidazole)]ClO_4

24

The structure determination of **24** again eliminated the assumption of Zn–OH coordination. Just as observed for $Zn(SR)_2$ complexes of 1-methyl-2-hydroxymethylimidazole and 1-methyl-2-formylimidazole,[34] only the imidazole nitrogen is coordinated to zinc. As Figure 7 shows, complex **24** is essentially an imidazole adduct of [**L5**·Zn]$^+$ with a nicely symmetrical arrangement of the NS_3donor set.

Conclusions

This paper has about doubled the number of available tris(thioimidazolyl)borate ligands and underlined their suitability for a biomimetic zinc complex chemistry. Although they still lack the major advantage of the tris(pyrazolyl)borates, i.e. the ease of encapsulating the metal ion by properly placed substituents, an approach seems to be emerging to achieve this. As the structural dispositions exemplified by Figures 2 and 3 show, voluminous substituents at the *ortho*-positions of phenyl rings at the thioimidazole's N3 nitro-

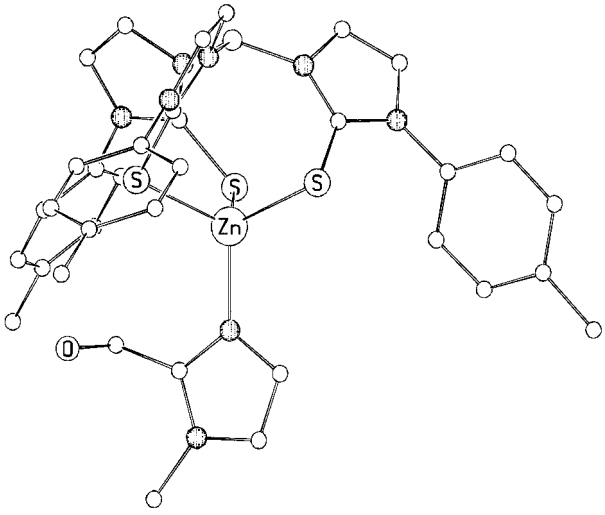

Figure 7. Structure of the complex cation of **24**. Zn–N 1.991(4), Zn–S 2.315(2), 2.325(2), and 2.333(2) Å. S–Zn–S 105.6–109.8(1)°, S–Zn–N 108.0–113.1(1)°.

gens should be oriented towards the neighbourhood of the metal ions and thereby create the desired cavity for them.

We have already observed[3] that the very soft environment of the zinc ion provided by these S_3 tripods results in a reluctance of zinc to bind a fourth soft donor, for instance an alkanethiolate. Conversely, hard oxygen donors are bound very well, as exemplified here by acetate, nitrate and *p*-nitrophenolate. Particularly noteworthy in this respect is the ease of formation of perchlorate complexes, which promise to be good starting materials for further labile **L**·Zn complexes of ligands **L1**–**L6**.

The latter was exemplified by the formation of the 2-propanol complexes **20** and **21**. Thus, 2-propanol is preferred over perchlorate as a donor here. In contrast, methanol is not, as all the perchlorate complexes described here were prepared in methanol. There seems to be a delicate balance of stabilities which is controlled by the substituents on the thioimidazole rings: with R = mesityl Parkin isolated a methanol complex,[5] with R = *tert*-butyl we obtained an ethanol complex,[3] and now with R = 2,6-xylyl and *p*-tolyl the 2-propanol complexes were obtained. We consider it likely that equilibrium mixtures of alcohol and perchlorate complexes exist in solution.

With respect to the modelling of alcohol dehydrogenase some new insights are provided by this work too. One of them is the accessibility of the alcohol complexes. Another is the accessibility of alkoxide complexes. Although the latter could only be obtained with a singly bridging alkoxide for methanol and ethanol, they resulted as monomers with terminal alkoxide ligands for *para*-substituted benzyl alcohol. As before[3] our attempts failed to induce alcohol or aldehyde coordination by the chelate effect: the hydroxymethyl and formyl side-arms of the coligands in complexes **22**–**24** remain uncoordinated. Nevertheless, complexes **20/21** and **15/16** represent the first chemical reproduction of the enzymatic situation where first the alcohol and then the alkoxide are bound to the same **L**·Zn unit.

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Experimental Section

For general working and measuring procedures, see ref.[35] All procedures for the ligand synthesis were performed under an inert gas. The isolation procedures described below yielded the new complexes spectroscopically pure. Samples for elemental analyses were recrystallised from methanol and/or dichloromethane. All *N*-substituted mercaptoimidazoles were prepared from bromoacetaldehyde diethylacetal, the amine RNH_2 and HSCN according to the established procedure.[36,37] They were characterised by ^{1}H NMR spectroscopy in $CDCl_3$ as follows:

R = *o*-tolyl: δ = 2.21 (s, 3 H, Me), 6.72 (d, *J* = 2.3 Hz, 1 H, Im), 6.84 (d, *J* = 2.3 Hz, 1 H, Im), 7.26–7.44 (m, 4 H, Ph), 10.94 (br. s, 1 H, NH) ppm.

R = *o*-biphenylyl: δ = 6.40 (d, *J* = 2.1 Hz, 1 H, Im), 6.62 (d, *J* = 2.1 Hz, 1 H, Im), 7.29–7.43 (m, 4 H, Ph), 7.45–7.65 (m, 5 H, Ar), 12.15 (s, 1 H, NH) ppm.

R = 2,6-xylyl: δ = 2.12 (s, 6 H, Me), 6.72 (d, *J* = 2.2 Hz, 1 H, Im), 6.98 (d, *J* = 2.2 Hz, 1 H, Im), 7.20 [d, *J* = 6.4 Hz, 2 H, Ph(3,5)], 7.29 [t, *J* = 5.6 Hz,, 1 H, Ph(4)], 12.34 (s, 1 H, NH) ppm.

R = 2,6-di(isopropyl)phenyl: δ = 1.12 (d, *J* = 6.9 Hz, 6 H, Me), 1.30 (d, *J* = 6.9 Hz, 6 H, Me), 2.61 (m, *J* = 6.7 Hz, 2 H, CH), 6.64 (d, *J* = 2.2 Hz, 1 H, Im), 6.85 (d, *J* = 2.2 Hz, 1 H, Im), 7.28 [d, *J* = 7.8 Hz, 2 H, Ph(3,5)], 7.43 [t, *J* = 7.3 Hz, 1 H, Ph(4)], 12.20 (s, 1 H, NH) ppm.

R = *p*-tolyl: 2.41 (s, 3 H, Me), 6.80 (d, *J* = 1.6 Hz, 1 H, Im), 6.84 (d, *J* = 1.6 Hz, 1 H, Im), 7.28 (m, 2 H, Ph), 7.45 (m, 2 H, Ph) ppm.

R = cyclohexyl: δ = 1.17–1.56 [p, *J* = 9.8 Hz, 4 H, CH_2(3,5-cyclohexyl)], 1.73–1.85 [q, *J* = 10.8 Hz, 4 H, CH_2(2,6-cyclohexyl)], 1.91 [m, 2 H, CH_2(4-cyclohexyl)], 4.66 (m, *J* = 4.00 Hz, 1 H, CH), 6.71 (d, *J* = 2.3 Hz, 1 H, Im), 6.73 (d, *J* = 2.3 Hz, 1 H, Im), 10.75 (s, 1 H, NH) ppm.

Ligand Synthesis. General Procedure: The *N*-substituted thioimidazole and KBH_4 were ground very finely. Toluene (100 mL) was added and the mixture refluxed for one week. After cooling to room temperature the precipitate was filtered off, washed with toluene and dried in vacuo.

L1: From 11.4 g (60.0 mmol) of *N*-(*o*-tolyl)thioimidazole and 1.08 g (20.0 mmol) of KBH_4. The precipitate was analytically pure. Yield 11.5 g (93%) of **L1** as a colourless powder, m.p. 200 °C (dec.). $C_{30}H_{28}BKN_6S_3$ (618.70): calcd. C 58.24, H 4.56, N 13.58, S 15.55; found C 59.10, H 5.08, N 13.87, S 15.80. ^{1}H NMR ($CDCl_3$): δ = 2.10 (s, 9 H, Me), 6.47 (d, *J* = 2.2 Hz, 3 H, Im), 6.70 (d, *J* = 2.2 Hz, 3 H, Im), 7.29 (m, 12 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2520 w (BH) cm^{-1}.

L2: From 4.92 g (19.50 mmol) of *N*-(*o*-biphenylyl)thioimidazole and 0.35 g (6.50 mmol) of KBH_4. Purification of the ligand required column chromatography over silica gel with methanol/dichloromethane (1:10). Yield 3.26 g (62%) of **L2** as a colourless powder, m.p. 215 °C (dec.). $C_{45}H_{34}BKN_6S_3$ (804.91): calcd. C 67.15, H 4.26, N 10.44, S 11.95; found C 64.73, H 4.49, N 10.02, S 11.73. ^{1}H NMR ($CDCl_3$): δ = 5.77 (d, *J* = 2.0 Hz, 3 H, Im), 6.37 (d, *J* = 2.0 Hz, 3 H, Im), 7.09–7.20 (m, 12 H, Ph), 7.31–7.46 (m, 15 H, Ar) ppm. IR (KBr): $\tilde{\nu}$ = 2482 w (BH) cm^{-1}.

L3: From 4.80 g (23.5 mmol) of *N*-(2,6-xylyl)thioimidazole and 0.42 g (7.8 mmol) of KBH_4. Recrystallisation from methanol yielded 4.57 g (88%) of **L3** as a colourless powder, m.p. 220 °C (dec.). $C_{33}H_{34}BKN_6S_3{\cdot}H_2O$ (660.78 + 18.01): calcd. C 58.39, H 5.35, N 12.38, S 14.17; found C 57.87, H 5.38, N 12.25, S 14.00. ^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 18 H, Me), 6.59 (d, *J* = 2.2 Hz, 3 H, Im), 6.63 (d, *J* = 2.2 Hz, 3 H, Im), 7.15 [d, *J* = 7.4 Hz, 6 H, Ph(3,5)], 7.26 [t, *J* = 6.3 Hz,, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2555 w (BH) cm^{-1}.

L4: From 8.38 g (32.2 mmol) of *N*-(2,6-diisopropylphenyl)thioimidazole and 0.58 g (10.7 mmol) of KBH_4. Recrystallisation from methanol yielded 7.45 g (84%) of **L4** as a colourless powder, m.p. 255 °C (dec.). $C_{45}H_{58}BKN_6S_3$ (829.10): calcd. C 65.19, H 7.05, N 10.14, S 11.60; found C 65.22, H 7.41, N 9.46, S 10.81. ^{1}H NMR ($CDCl_3$): δ = 1.12 (d, *J* = 6.8 Hz, 18 H, Me), 1.30 (d, *J* = 6.8 Hz, 18 H, Me), 2.58 (m, *J* = 6.7 Hz, 6 H, CH), 6.64 (d, *J* = 2.29 Hz, 3 H, Im), 6.85 (d, *J* = 2.3 Hz, 3 H, Im), 7.28 [d, *J* = 7.8 Hz, 6 H, Ph(3,5)], 7.46 [m, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2533 w (BH) cm^{-1}.

L5: From 9.12 g (0.48 mmol) of *N*-(*p*-tolyl)thioimidazole and 0.86 g (0.16 mmol) of KBH_4. The precipitate was analytically pure. Yield 8.61 g (87%) of **L5** as a colourless powder, m.p. 215 °C (dec.). $C_{30}H_{28}BKN_6S_3$ (618.70): calcd. C 58.24, H 4.56, N 13.58, S 15.55; found C 57.55, H 4.80, N 13.57, S 15.37. ^{1}H NMR (CD_3OD): δ = 2.38 (s, 9 H, Me), 6.70 (d, *J* = 2.2 Hz, 3 H, Im), 6.98 (d, *J* = 2.2 Hz, 3 H, Im), 7.26 (d, *J* = 8.2 Hz, 6 H, Ph), 7.45 (d, *J* = 8.2 Hz, 6 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2495 w (BH) cm^{-1}.

L6: From 7.25 g (40.0 mmol) of *N*-cyclohexylthioimidazole and 0.72 g (13.3 mmol) of KBH_4. Recrystallisation from methanol yielded 7.15 g (91%) of **L6** as a colourless powder, m.p. 220 °C (dec.). $C_{27}H_{37}BKN_6S_3{\cdot}2H_2O$ (591.74 + 36.03): calcd. C 51.65, H 6.58, N 13.39, S 15.32; found C 51.74, H 6.98, N 13.35, S 15.39. ^{1}H NMR (CD_3OD): δ = δ = 1.27–1.49 [p, *J* = 12.3, 12 H, CH_2(3,5-cyclohexyl)], 1.49–1.78 [q, *J* = 5.3, 12 H, CH_2(2,6-cyclohexyl)], 1.86 [m, 6 H, CH_2(4-cyclohexyl)], 4.64 (m, *J* = 3.5 Hz, 3 H, CH-cyclohexyl), 6.31 (d, *J* = 2.2 Hz, 3 H, Im), 6.79 (d, *J* = 2.2 Hz, 3 H, Im) ppm. IR (KBr): $\tilde{\nu}$ = 2514 w (BH) cm^{-1}.

Simple Zinc Complexes

1: A solution of 264 mg (0.40 mmol) of **L3** in 10 mL of absolute methanol was added dropwise with stirring to a solution of 55 mg (0.40 mmol) of anhydrous $ZnCl_2$ in 10 mL of absolute methanol. After stirring for 4 h the volume of the solution was reduced to 10 mL in vacuo. The precipitate was filtered off and the filtrate evaporated to dryness. The residue was taken up in 10 mL of dichloromethane, filtered and the solvents evaporated to dryness again, to give 276 mg (96%) of **1** as a colourless powder, m.p. 265 °C (dec.). $C_{33}H_{34}BClN_6S_3Zn$ (722.52): calcd. C 54.86, H 4.74, N 11.63, S 13.31, Zn 9.05; found C 54.07, H 4.97, N 11.29, S 12.89, Zn 8.76. ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 9 H, Me), 2.10 (s, 9 H, Me), 6.83 (d, *J* = 2.0 Hz, 3 H, Im), 7.08 (d, *J* = 2.0 Hz, 3 H, Im), 7.11 [d, *J* = 4.6 Hz, 6 H, Ph(3,5)], 7.26 [t, *J* = 3.8 Hz, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2438 w (BH) cm^{-1}.

2: Like **1** from 200 mg (0.30 mmol) of **L3** and 97 mg (0.30 mmol) of ZnI_2. Yield 232 mg (94%) of **2** as a colourless powder, m.p. 300 °C (dec.). $C_{33}H_{34}BIN_6S_3Zn$ (813.97): calcd. C 48.69, H 4.21, N 10.32, S 11.82, Zn 8.03; found C 47.77, H, 4.27, N 10.09, S 11.64, Zn 7.91. ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 9 H, Me), 2.08 (s, 9 H, Me), 6.84 (d, *J* = 2.1 Hz, 3 H, Im), 7.14 (d, *J* = 2.1 Hz, 3 H, Im), 7.16 [d, *J* = 7.6 Hz, 6 H, Ph(3,5)], 7.25 [t, *J* = 7.5 Hz, 3 H, Ph(4)] ppm. IR (KBr): = $\tilde{\nu}$ = 2437 w (BH) cm^{-1}.

3: Like **1** from 200 mg (0.30 mmol) of **L3** and 80 mg (0.30 mmol) of $Zn(NO_3)_2{\cdot}4H_2O$. Yield 194 mg (85%) of **3** as a colourless powder, m.p. 235 °C (dec.). $C_{33}H_{34}BN_7O_3S_3Zn$ (749.08): calcd. C 52.91, H 4.57, N 13.09, S 12.84, Zn 8.72; found C 52.53, H 4.70, N 12.96, S 12.63, Zn 8.58. ^{1}H NMR ($CDCl_3$): δ = 1.95 (s, 9 H, Me), 2.17 (s, 9 H, Me), 6.86 (d, *J* = 2.1 Hz, 3 H, Im), 7.09 (d, *J* = 2.1 Hz, 3

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H, Im), 7.14 [d, J = 7.2 Hz, 6 H, Ph(3,5)], 7.25 [t, J = 7.4 Hz, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2426 w (BH) cm^{-1}.

4: Like **1** from 206 mg (0.33 mmol) of **L1** and 62 mg (0.34 mmol) of $Zn(CH_3COO)_2 \cdot 2H_2O$. Yield 156 mg (67%) of **4** as a colourless crystals, m.p. 265 °C (dec.). $C_{32}H_{31}BN_6O_2S_3Zn$ (704.03): calcd. C 54.59, H 4.4, N 11.94, S 13.66, Zn 9.29; found C 54.48, H 4.34, N 12.00, S 13.59, Zn 9.14. ^1H NMR ($CDCl_3$): δ = 1.76 [s, 3 H, Me(acetate)], 2.1 (s, 9 H, Me), 6.96 (d, J = 2.0 Hz, 3 H, Im), 7.16 (d, J = 2.0 Hz, 3 H, Im), 7.28 (m, 12 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2412 w (BH) cm^{-1}.

5: Like **1** from 264 mg (0.40 mmol) of **L3** and 88 mg (0.40 mmol) of $Zn(CH_3COO)_2 \cdot 2H_2O$. Yield 250 mg (84%) of **4** as a colourless powder, m.p. 235 °C (dec.). $C_{35}H_{37}BN_6O_2S_3Zn$ (746.12): calcd. C 56.34, H 5.00, N 11.27, S 12.89, Zn 8.76; found C 55.40, H 5.30, N 11.85, S 11.85, Zn 8.73. ^1H NMR ($CDCl_3$): δ = 1.82 [s, 3 H, Me(acetate)], 1.99 (s, 9 H, Me), 2.17 (s, 9 H, Me), 6.82 (d, J = 2.2 Hz, 3 H, Im), 7.11 (d, J = 2.2 Hz, 3 H, Im), 7.17 [d, J = 7.6 Hz, 6 H, Ph(3,5)], 7.22 [t, J = 7.4 Hz, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2412 w (BH), 1598 s ($OCOCH_3$) cm^{-1}.

6: A solution of 200 mg (0.30 mmol) of **L3** 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 the resulting $KClO_4$ was filtered off. In a separate flask a solution of 33 mg (0.30 mmol) of CH_3COSH was deprotonated with 0.30 mmol of a 0.5 M solution of sodium methoxide in methanol. The two solutions were combined and stirred for 15 h. Then, all volatiles were removed in vacuo, the residue taken up in 15 mL of dichloromethane and filtered again. The filtrate was evaporated to dryness to give 161 mg (70%) of **6** as a yellow powder, m.p. 225 °C (dec.). $C_{35}H_{37}BN_6OS_4Zn$ (762.19): calcd. C 55.19, H 4.89, N 11.03, S 16.83, Zn 8.58; found C 54.76, H 4.96, N 10.87, S 15.72, Zn 8.46. ^1H NMR ($CDCl_3$): δ = 1.75 [s, 3 H, Me(thioacetate)], 1.92 (s, 9 H, Me), 2.04 (s, 9 H, Me), 6.74 (d, J = 2.1 Hz, 3 H, Im), 7.02 (d, J = 2.1 Hz, 3 H, Im), 7.03 [d, J = 7.6 Hz, 6 H, Ph(3,5)], 7.18 [t, J = 7.4 Hz, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2430 w (BH) cm^{-1}.

7: Like **6** from 200 mg (0.32 mmol) of **L1** and 45 mg (0.32 mmol) of *p*-nitrophenol. Yield 197 mg (78%) of **7** as a yellow powder, m.p. 225 °C (dec.). $C_{36}H_{32}BN_7O_3S_3Zn$ (783.09): calcd. C 55.22, H 4.12, N 12.52, S 12.88, Zn 8.35; found C 54.92, H 4.11, N 12.47, S 12.59, Zn 8.56. ^1H NMR ($CDCl_3$): δ = 2.11 (s, 9 H, Me), 6.44 [d, J = 9.1 Hz, 2 H, nitro(2,6)], 6.97 (d, J = 2.2 Hz, 3 H, Im), 7.16 (d, J = 2.2 Hz, 3 H, Im), 7.29–7.42 (m, 12 H, Ph), 7.81 [d, J = 9.1 Hz, 2 H, nitro(3,5)] ppm. IR (KBr): $\tilde{\nu}$ = 2442 w (BH).

8: Like **6** from 213 mg (0.32 mmol) of **L3** and 45 mg (0.32 mmol) of *p*-nitrophenol. Yield 236 mg (89%) of **8** as a yellow powder, m.p. 200 °C (dec.). $C_{39}H_{38}BN_7O_3S_3Zn$ (825.17): calcd. C 56.77, H 4.64, N 11.88, S 11.66, Zn 7.92; found C 55.41, H 4.65, N 12.68, S 11.38, Zn 7.74. ^1H NMR ($CDCl_3$): δ = 2.02 (s, 18 H, Me), 6.51 [d, J = 8.9 Hz, 2 H, nitro(2,6)], 6.89 (d, J = 2.2 Hz, 3 H, Im), 7.13 [d, J = 7.2 Hz, 6 H, Ph(3,5)], 7.17 (d, J = 2.2 Hz, 3 H, Im), 7.27 [t, J = 7.4 Hz, 3 H, Ph(4)], 7.83 [d, J = 8.9 Hz, 2 H, nitro(3,5)] ppm. IR (KBr): $\tilde{\nu}$ = 2440 w (BH).

9: Like **6** from 206 mg (0.38 mmol) of **L5** and 54 mg (0.38 mmol) of *p*-nitrophenol. Yield 193 mg (73%) of **9** as a yellow powder, m.p. 205 °C (dec.). $C_{36}H_{34}BN_7O_3S_3Zn$ (785.11): calcd. C 55.07, H 4.36, N 12.49, S 12.25, Zn 8.33; found C 54.84, H 4.27, N 12.59, S 11.83, Zn 8.22. ^1H NMR ($CDCl_3$): δ = 2.40 (s, 9 H, Me), 6.36 [d, J = 9.3 Hz, 2 H, nitro(2,6)], 7.04 (d, J = 2.2 Hz, 3 H, Im), 7.11 (d, J = 2.2 Hz, 3 H, Im), 7.22 (s, 12 H, Ph), 7.66 [d, J = 9.3 Hz, 2 H, nitro(3,5)] ppm. IR (KBr): $\tilde{\nu}$ = 2345 w (BH) cm^{-1}.

Perchlorate Complexes

10: A solution of 45 mg (0.07 mmol) of **L1** in 5 mL of methanol was slowly added dropwise with stirring into a solution of 27 mg (0.07 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 5 mL of methanol. After stirring for 2 h the solvent was removed in vacuo. The residue was picked up in 10 mL of dichloromethane and filtered. Evaporation to dryness gave 44 mg (81%) of **10** as a colourless powder, m.p. 220 °C (dec.). $C_{30}H_{28}BClN_6O_4S_3Zn$ (744.44): calcd. C 48.40, H 3.79, N 11.29, S 12.92, Zn 8.78; found C 48.42, H 4.12, N 10.96, S 12.48, Zn 8.48. ^1H NMR ($CDCl_3$): δ = 2.13 (s, 9 H, Me), 6.96 (br, 3 H, Im), 7.16 (br, 3 H, Im), 7.22–7.37 (m, 12 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2448 w (BH), 1105vs. (ClO_4) cm^{-1}.

11: Like **10** from 310 mg (0.38 mmol) of **L2** and 143 mg (0.38 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$. Yield 245 mg (68%) of **11** as a colourless powder, m.p. 230 °C (dec.). $C_{45}H_{34}BClN_6O_4S_3Zn$ (930.65): calcd. C 58.08, H 3.68, N 9.03, S 10.34, Zn 7.03; found C 56.67, H 4.07, N 8.74, S 10.16, Zn 6.91. ^1H NMR ($CDCl_3$): δ = 6.63 (br, 3 H, Im), 6.78 (br, 3 H, Im), 6.98–7.16 (m, 12 H, Ph), 7.32–7.41 (m, 15 H, Ar) ppm. IR (KBr): $\tilde{\nu}$ = 2437 w (BH), 1090 s (ClO_4^-) cm^{-1}.

12: Like **10** from 264 mg (0.40 mmol) of **L3** and 149 mg (0.40 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$. Yield 257 mg (82%) of **12** as a colourless powder, m.p. 245 °C (dec.). $C_{33}H_{34}BClN_6O_4S_3Zn$ (786.52): calcd. C 50.39, H 4.36, N 10.69, S 12.23, Zn 8.31; found C 49.27, H 4.51, N 11.12, S 11.79, Zn 8.03. ^1H NMR ($CDCl_3$): δ = 1.98 (s, 9 H, Me), 2.06 (s, 9 H, Me), 6.89 (d, J = 2.1 Hz, 3 H, Im), 7.10 [d, J = 7.4 Hz, 6 H, Ph(3,5)], 7.16 (d, J = 2.1 Hz, 3 H, Im), 7.25 [t, J = 7.4 Hz, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2448 w (BH), 1991 s (ClO_4^-) cm^{-1}.

13: Like **10** from 200 mg (0.24 mmol) of **L4** and 90 mg (0.24 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$. Yield 193 mg (84%) of **13** as a colourless powder, m.p. 230 °C (dec.). $C_{45}H_{58}BClN_6O_4S_3Zn$ (954.84): calcd. C 56.61, H 6.12, N 8.80, S 10.07, Zn 6.85; found C 56.29, H 6.48, N 8.73, S 10.04, Zn 6.82. ^1H NMR ($CDCl_3$): δ = 0.82 (d, J = 6.6 Hz, 3 H, Me), 0.98 (d, J = 6.6 Hz, 9 H, Me), 1.16 (d, J = 6.6 Hz, 24 H, Me), 2.28 (m, J = 6.7 Hz, 3 H, CH), 2.58 (m, J = 6.7 Hz, 3 H, CH), 6.90 (d, J = 1.6 Hz, 3 H, Im), 7.21 [d, J = 7.6 Hz, 6 H, Ph(3,5)], 7.25 (d, J = 1.6 Hz, 3 H, Im), 7.45 [m, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2449 w (BH), 1102 s (ClO_4^-) cm^{-1}.

14: Like **10** from 178 mg (0.30 mmol) of **L6** and 112 mg (0.30 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$. Yield 182 mg (84%) of **14** as a colourless powder, m.p. 230 °C (dec.). $C_{27}H_{37}BClN_6O_4S_3Zn \cdot CHCl_3$ (717.47 + 119.38): calcd. C 40.19, H 4.58, N 10.04, S 11.50, Zn 7.81; found C 41.15, H 5.19, N 10.32, S 11.63, Zn 8.27. ^1H NMR (CD_3OD): δ = 1.17–1.31 [p, J = 10.2 Hz, 12 H, CH_2(3,5-cyclohexyl)], 1.38–1.58 [q, J = 5.3 Hz, 12 H, CH_2(2,6-cyclohexyl)], 1.78 [m, 6 H, CH_2(4-cyclohexyl)], 4.53 (m, J = 3.8 Hz, 3 H, CH), 6.99 (d, J = 1.9 Hz, 3 H, Im), 7.23 (d, J = 1.9 Hz, 3 H, Im) ppm. IR (KBr): $\tilde{\nu}$ = 2435 w (BH), 1091 s (ClO_4^-) cm^{-1}.

Alkoxide Complexes

15: A solution of 46 mg (0.30 mmol) of *p*-nitrobenzyl alcohol in 5 mL of methanol was treated dropwise, with stirring, first with 0.30 mmol of a 0.5 M solution of $NaOCH_3$ in CH_3OH, then with 112 mg (0.30 mmol) of $Zn(ClO_4) \cdot 6H_2O$ in 10 mL of methanol, and finally with 200 mg (0.30 mmol) of **L3** in 10 mL of methanol. After stirring for 12 h the solvent was removed in vacuo, the residue taken up in 20 mL of dichloromethane and filtered. After evaporation to dryness, 205 mg (81%) of **15** was isolated as a yellow powder, m.p. 200 °C (dec.). $C_{40}H_{40}BN_7O_3S_3Zn$ (839.2): calcd. C 57.25, H 4.80, N 11.68, S 11.46, Zn 7.79; found C 57.72, H 5.36, N 11.71, S 11.54, Zn 7.86. ^1H NMR ($CDCl_3$): δ = 1.99 (s, 18 H, Me), 4.84

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(s, 2 H, CH_2), 6.58 (d, J = 2.1 Hz, 1 H, Im), 6.81 (d, J = 2.1 Hz, 3 H, Im), 6.84 (d, J = 2.1 Hz, 2 H, Im), 6.89 [d, J = 6.2 Hz, 6 H, Ph(3,5)], 7.19 [t, J = 7.6 Hz, 3 H, Ph(4)], 7.53 [d, J = 8.7 Hz, 2 H, nitro(2,6)], 8.22 [d, J = 8.7 Hz, 2 H, Nitro(3,5)] ppm. IR (KBr): $\tilde{\nu}$ = 2444 w (BH) cm^{-1}.

16: Like **15** from 53 mg (0.30 mmol) of *p*-(trifluoromethyl)benzyl alcohol, 112 mg (0.30 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ and 200 mg (0.30 mmol) of **L3**. Yield 214 mg (82%) of **16** as a colourless powder, m.p. 180 °C. $C_{41}H_{40}BF_3N_6OS_3Zn \cdot 0.25CH_2Cl_2$ (862.20 + 21.23): calcd. C 56.08, H 4.62, N 9.52, S 10.88, Zn 7.40; found C 56.43, H 4.88, N 9.42, S 10.13, Zn 6.89. ^{1}H NMR ($CDCl_3$): δ = 2.00 (s, 18 H, Me), 4.78 (d, J = 2.8 Hz, 2 H, CH_2), 5.29 (s, 0.5 H, CH_2Cl_2), 6.58 (d, J = 2.1 Hz, 1 H, Im), 6.81 (d, J = 2.1 Hz, 3 H, Im), 6.89 (d, J = 2.1 Hz, 2 H, Im), 7.01 [d, J = 6.6 Hz, 6 H, Ph(3,5)], 7.19 [t, J = 7.4 Hz, 3 H, Ph(4)], 7.48 [d, J = 8.2 Hz, 2 H, trifluoromethyl(2,6)], 7.61 [d, J = 8.2 Hz, 2 H, trifluoromethyl(3,5)] ppm. ^{19}F NMR ($CDCl_3$): δ = 61.21 ppm. IR (KBr): $\tilde{\nu}$ = 2441 w (BH) cm^{-1}.

17: A solution of 200 mg (0.30 mmol) of **L3** and 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 the resulting $KClO_4$ was filtered off. The filtrate was treated with 0.3 mmol of a 0.25 M solution of $NaOCH_3$ in CH_3OH. After stirring for another 8 h the solvent was removed in vacuo, the residue taken up in 20 mL of dichloromethane and filtered. After evaporation to dryness 161 mg (71%) of **17** was isolated as a colourless powder, m.p. 255 °C (dec.). $C_{67}H_{71}B_2ClN_{12}O_5S_6Zn_2$ (1504.63): calcd. C 53.48, H 4.76, N 11.17, S 12.79, Zn 8.69; found C 53.35, H 4.88, N 11.07, S 12.67, Zn 8.61. ^{1}H NMR ($CDCl_3$): δ = 1.58 (s, 18 H, Me), 1.99 (s, 18 H, Me), 2.10 (s, 3 H, OMe), 6.57 (d, J = 2.1 Hz, 3 H, Im), 6.80 (d, J = 2.1 Hz, 6 H, Im), 6.87–7.09 [d, J = 6.8 Hz, 12 H, Ph(3,5)], 7.13 (d, J = 2.1 Hz, 3 H, Im), 7.19 [t, J = 7.5 Hz, 6 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2439 w (BH), 1095 s (ClO_4^-) cm^{-1}.

18: Like **17** (all operations in absolute ethanol) from 200 mg (0.30 mmol) of **L3**, 112 mg (0.30 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ and 0.30 mmol of $NaOC_2H_5$. Yield 180 mg (78%) of **18** as a colourless powder, m.p. 250 °C (dec.). $C_{68}H_{73}B_2ClN_{12}O_5S_6Zn_2$ (1518.65): calcd. C 53.78, H 4.84, N 11.07, S 12.67, Zn 8.61; found C 52.86, H 4.80, N 11.14, S 12.87, Zn 8.75. ^{1}H NMR ($CDCl_3$): δ = 1.24 [t, J = 7.0 Hz, 3 H, Me(Ethyl)], 1.58 (s, 18 H, Me), 2.05 (s, 18 H, Me), 3.72 [q, J = 5.2 Hz, CH_2(Ethyl)], 6.82 (d, J = 2.2 Hz 3 H, Im), 6.84 (d, J = 2.2 Hz, 6 H, Im), 6.88–7.10 [d, J = 6.8 Hz, 12 H, Ph(3,5)], 7.14 (d, J = 2.2 Hz, 3 H, Im), 7.20 [t, J = 7.4 Hz, 6 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2417 w (BH), 1096 s (ClO_4^-) cm^{-1}.

19: Like **17** (all operations in absolute ethanol) from 200 mg (0.30 mmol) of **L3**, 112 mg (0.30 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ and 0.30 mmol of $NaOCH_2CF_3$. Yield 166 mg (70%) of **19** as a colourless powder, m.p. 260 °C (dec.). $C_{68}H_{70}B_2ClF_3N_{12}O_5S_6Zn_2$ (1572.62): calcd. C 51.94, H 4.49, N 10.69, S 12.23, Zn 8.32; found C 52.23, H 4.93, N 11.61, S 12.85, Zn 8.73. ^{1}H NMR ($CDCl_3$): δ = 1.58 (s, 18 H, Me), 1.99 (s, 18 H, Me), 2.07 (s, 2 H, CH_2), 6.81 (br, 6 H, Im), 6.84 (br, 3 H, Im), 6.87–7.13 [d, J = 7.2 Hz, 12 H, Ph(3,5)], 7.14 (d, J = 2.1 Hz, 3 H, Im), 7.23 [t, J = 6.0 Hz, 6 H, Ph(4)] ppm. ^{19}F NMR ($CDCl_3$): δ = 77.81 ppm. IR (KBr): $\tilde{\nu}$ = 2490 w (BH), 1097 s (ClO_4^-) cm^{-1}.

Complexes with Alcohol and Aldehyde Ligands

20: A solution of 200 mg (0.30 mmol) of **L3** in 10 mL of absolute 2-propanol 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 absolute 2-propanol. After stirring for 4 h the volume of the solution was reduced to 10 mL in vacuo, the precipitate filtered off, and the filtrate evaporated to dryness. The residue was taken up in 10 mL of dichloromethane, filtered, and the filtrate evaporated to dryness again to give 150 mg (62%) of **20** as a colourless powder, m.p. 275 °C (dec.). $C_{36}H_{42}BClN_6O_5S_3Zn$ (846.62): calcd. C 51.07, H 5.00, N 9.93, S 11.36, Zn 7.72; found C 49.28, H 4.95, N 9.89, S 11.34, Zn 7.71. ^{1}H NMR ($CDCl_3$): δ = 1.12 [d, J = 6.2 Hz, 6 H, Me(*i*Pr)], 1.91 (s, 9 H, Me), 1.97 (s, 9 H, Me), 4.02 [m, J = 6.2 Hz, 1 H, CH(*i*Pr)], 6.82 (d, J = 2.0 Hz, 3 H, Im), 7.07 [d, J = 7.6 Hz, 6 H, Ph(3,5)], 7.09 (d, J = 2.0 Hz, 3 H, Im), 7.19 [t, J = 7.4 Hz, 3 H, Ph(4)] ppm. IR (KBr): $\tilde{\nu}$ = 2448 w (BH), 1101 s (ClO_4^-) cm^{-1}.

21: Like **20** from 206 mg (0.33 mmol) of **L5** and 124 mg (0.33 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$. Yield 149 mg (56%) of **21** as a

Table 3. Crystallographic data.

	1	**3**	**4**	**5**	**9**
Empirical formula	$C_{33}H_{34}BClN_6S_3Zn \cdot CH_3OH$	$C_{33}H_{34}BN_7O_3S_3Zn \cdot CH_3OH$	$C_{32}H_{31}BN_6O_2S_3Zn$	$C_{35}H_{37}BN_6O_2S_3Zn \cdot 3.5CH_3OH$	$C_{36}H_{32}BN_7O_3S_3Zn \cdot 2CH_3CN$
Molecular mass	722.5 + 32.0	749.1 + 32.0	704.0	746.1 + 112.1	783.0 + 82.1
Crystal size [mm]	0.1×0.2×0.3	0.1×0.2×0.3	0.1×0.2×0.2	0.1×0.1×0.2	0.2×0.2×0.4
Space group	$P2_12_12_1$	$P2_12_12_1$	$R3c$	$P\bar{1}$	$P\bar{1}$
Z	4	4	6	2	4
a [Å]	10.646(2)	11.152(3)	12.776(6)	9.531(2)	13.948(3)
b [Å]	11.439(2)	11.666(3)	12.776(6)	14.915(3)	17.548(4)
c [Å]	29.061(5)	28.563(7)	35.782(2)	16.552(3)	17.681(4)
α [°]	90	90	90	73.989(4)	88.006(4)
β [°]	90	90	90	77.480(4)	89.104(4)
γ [°]	90	90	120	81.549(4)	75.700(4)
V [Å^3]	3538.8(11)	3715.8(15)	5058.2(5)	2198.4(8)	4190.9(17)
d(calcd.) [g cm^{-3}]	1.42	1.39	1.39	1.29	1.37
μ(Mo-$K\alpha$) [mm^{-1}]	0.98	0.88	0.95	0.75	0.79
hkl range	h: –13 to 10 k: –13 to 15 l: –39 to 11	h: –15 to 3 k: –13 to 14 l: –28 to 36	h: –16 to 16 k: –16 to 16 l: –46 to 46	h: –12 to 12 k: –20 to 19 l: –22 to 22	h: –18 to 18 k: –23 to 22 l: –23 to 23
Measured reflections	13 471	13 824	14 153	19 701	38 232
Independent reflections	6895	6874	2747	10 181	19 929
Obsd. reflections [$I > 2\sigma(I)$]	4712	3356	1915	3316	8975
Parameters	414	451	137	475	1031
Refined reflections	6895	6874	2747	10 181	19 929
R_1 (obs.refl.)	0.053	0.058	0.058	0.069	0.061
wR_2 (all refl.)	0.143	0.182	0.171	0.211	0.189
Res. electron density [e Å^{-3}]	+0.6/–0.5	+0.7/–0.4	+0.8/–0.5	+0.8/–0.7	+1.3/–0.7

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Table 4. Crystallographic data.

	17	**18**	**21**	**23**	**24**
Empirical formula	$C_{67}H_{71}B_2ClN_{12}S_6Zn_2$·$CH_3OH$	$C_{68}H_{73}B_2ClN_{12}O_5S_6Zn_2$·$2C_2H_5OH$	$C_{33}H_{36}BClN_6O_5S_3Zn$·$0.25CH_2Cl_2$·$0.5\,i$PrOH·$0.5H_2O$	$C_{40}H_{39}BN_6O_2S_3Zn$·CH_3OH	$C_{35}H_{36}BClN_8O_5S_3Zn$·$1.5CH_2Cl_2$
Molecular mass	1504.6 + 32.0	1518.7 + 92.1	804.5 + 21.2 + 24.0 + 9.0	808.2 + 32.0	856.6 + 127.3
Crystal size [mm]	0.1 × 0.2 × 0.2	0.1 × 0.1 × 0.3	0.3 × 0.2 × 0.1	0.1 × 0.2 × 0.3	0.2 × 0.1 × 0.1
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	8	8	4	1	2
a [Å]	16.405(3)	16.621(3)	11.014(7)	11.989(2)	13.746(3)
b [Å]	19.815(4)	20.171(4)	16.066(10)	10.775(2)	13.996(3)
c [Å]	24.003(5)	23.854(5)	23.450(15)	32.154(6)	15.878(4)
α [°]	90	90	82.184(10)	90	92.615(4)
β [°]	104.640(4)	106.549(3)	82.050(10)	91.637(4)	112.714(4)
γ [°]	90	90	81.099(10)	90	114.316(3)
V [Å^3]	7549(2)	7666(3)	4032.2(4)	4152.0(13)	2490.6(10)
d(calcd.) [g cm^{-3}]	1.35	1.39	1.42	1.34	1.31
μ(Mo-K_α) [mm^{-1}]	0.89	0.88	0.91	0.79	0.88
hkl range	h: –2 to 22 k: –26 to 26 l: –32 to 32	h: –22 to 22 k: –27 to 26 l: –32 to 31	h: –14 to 14 k: –20 to 21 l: –31 to 31	h: –15 to 16 k: –15 to 14 l: –40 to 44	h: –18 to 17 k: –18 to 17 l: –20 to 20
Measured reflections	67 044	68 310	36 905	40 134	22 054
Independent reflections	18 373	18 624	18 966	11 744	11 307
Obsd. reflections [$I > 2\sigma(I)$]	6012	10 317	8940	7069	6239
Parameters	887	900	973	496	595
Refined reflections	18 373	18 624	18 966	11 744	11 307
R_1 (obs.refl.)	0.079	0.064	0.069	0.061	0.077
wR_2 (all refl.)	0.302	0.215	0.235	0.153	0.259
Res. electron density [e Å^{-3}]	+0.9/–0.8	+1.1/–1.1	+1.5/–0.9	+0.8/–0.6	+1.2/–0.7

colourless powder, m.p. 215 °C (dec.). $C_{33}H_{36}BClN_6O_5S_3Zn$ (804.54): calcd. C 49.27, H 4.51, N 10.45, S 11.96, Zn 8.13; found C 49.45, H 4.89, N 9.97, S 11.19, Zn 7.98. ^{1}H NMR ($CDCl_3$): δ = 1.16 [d, J = 6.0 Hz, 6 H, Me(*i*Pr)], 2.38 (s, 6 H, Me), 2.41 (s, 3 H, Me), 4.03 [m, J = 6.0 Hz, 1 H, CH(*i*Pr)], 7.07 (br, 2 H, Im), 7.09 (d, J = 2.2 Hz, 2 H, Im), 7.14 (br, 2 H, Im), 7.22 (m, 12 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2452 w (BH) cm^{-1}.

22: A solution of 37 mg (0.30 mmol) of 2-hydroxybenzyl alcohol in 5 mL of methanol was treated dropwise with stirring first with 0.30 mmol of a 0.25 M solution of $NaOCH_3$ in CH_3OH, then with a solution of 112 mg (0.30 mmol) of $Zn(ClO_4)_2$·$6H_2O$ in 10 mL of methanol, and finally with a solution of 200 mg (0.30 mmol) of **L3**. After stirring for 12 h the solvent was removed in vacuo, the residue taken up in 10 mL of dichloromethane, filtered and the filtrate evaporated to dryness again to give 218 mg (89%) of **22** as a colourless powder, m.p. 180 °C (dec.). $C_{40}H_{41}BN_6O_2S_3Zn$·$0.5CH_2Cl_2$ (810.20 + 42.46): calcd. C 57.05, H 4.96, N 9.86, S 11.28, Zn 7.67; found C 57.52, H 5.11, N 9.19, S 10.54, Zn 8.07. ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 18 H, Me), 4.48 (m, 1 H, OH), 4.85 (s, 2 H, CH_2), 5.30 (s, 1 H, CH_2Cl_2), 6.82 (d, J = 2.0 Hz, 3 H, Im), 6.86 (d, J = 2.0 Hz, 3 H, Im), 7.03 [d, J = 5.0 Hz, 6 H, Ph(3,5)], 7.13 [m, 2 H, Ph(3,5-phenolate)], 7.16 [t, J = 6.6 Hz, 3 H, Ph(4)], 7.26 [m, 2 H, Ph(4,6-phenolate)] ppm. IR (KBr): $\tilde{\nu}$ = 2442 w (BH) cm^{-1}.

23: Like **22** from 38 mg (0.30 mmol) of salicylic aldehyde, 112 mg (0.30 mmol) of $Zn(ClO_4)_2$·$6H_2O$ and 200 mg (0.30 mmol) of **L3**. Yield 202 mg (83%) of **23** as a colourless powder, m.p. 180 °C (dec.). $C_{40}H_{39}BN_6O_2S_3Zn$ (808.19): calcd. C 59.45, H 4.86, N 10.40, S 11.90, Zn 8.09; found C 58.23, H 4.83, N 10.99, S 11.87, Zn 8.07. ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 18 H, Me), 6.82 (d, J = 2.0 Hz, 3 H, Im), 6.85 (d, J = 2.0 Hz, 3 H, Im), 7.02 [d, J = 8.0 Hz, 6 H, Ph(3,5)], 7.13 [m, 2 H, Ph(3,5-salicyl)], 7.20 [t, J = 4.8 Hz, 3 H, Ph(4)], 7.54 [m, 2 H, Ph(4,6-salicyl)], 9.91 [s, 1 H, CHO] ppm. IR (KBr): $\tilde{\nu}$ = 2460 w (BH), 1659 m (CO) cm^{-1}.

24: Equimolar amounts of **L5** and $Zn(ClO_4)_2$ were converted into the **L5**·Zn-$OClO_3$ complex as described above for **10**. Then, a solution of 245 mg (0.33 mmol) of this complex in 5 mL of dichloromethane was treated with a solution of 37 mg (0.33 mmol) of 2-(hydroxymethyl)-1-methylimidazole in 5 mL of dichloromethane. After stirring for 6 h the product was precipitated by addition of 30 mL of petroleum ether (60–70). Filtration and recrystallisation from dichloromethane/petroleum ether yielded 150 mg (53%) of **24** as colourless crystals, m.p. 210 °C (dec.). $C_{35}H_{36}BClN_8O_5S_3Zn$ (856.57): calcd. C 49.08, H 4.24, N 13.08, S 11.23, Zn 7.63; found C 48.10, H 4.54, N 13.18, S 10.18, Zn 7.67. ^{1}H NMR ($CDCl_3$): δ = 22.38 (s, 9 H, Me), 3.62 [s, 3 H, Me(imidazole)], 4.46 [s, 2 H, CH_2(imidazole)], 6.67 (s, 1 H, imidazole), 6.87 (s, 1 H, imidazole), 7.10 (d, J = 2.2 Hz, 6 H, Im), 7.16 (d, J = 8.6 Hz, 6 H, Ph), 7.26 (d, J = 8.6 Hz, 6 H, Ph) ppm. IR (KBr): $\tilde{\nu}$ = 2454 w (BH) cm^{-1}.

Structure Determinations:[38] Crystals of **1**, **3**, **4**, **5**, **17** and **23** were obtained by recrystallisation from methanol/dichloromethane mixtures, those of **18** from ethanol/dichloromethane, those of **9** from acetonitrile/dichloromethane, those of **21** by layering a dichloromethane/2-propanol (1:4) solution with petroleum ether, and those of **24** by layering a dichloromethane solution with petroleum ether. Diffraction data were recorded at room temperature (**10**, **12**), at –50 °C (**3**, **5**, **17**, **18**), at –80° (**1**, **23**, **24**) or at –140 °C (**4**) with a Bruker Smart CCD diffractometer. Empirical absorption corrections were applied to all data sets except those of **9** and **17**. The structures were solved by direct methods and refined anisotropically with the SHELX program suite.[39] 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.[40] Tables 3 and 4 list the crystallographic data.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are indebted to Drs. W. Deck and H. Brombacher for their help with the structure determinations.

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Received: December 01, 2004

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