Zinc Complexes of Amino Acids and Peptides, 9[◇]

Coordination of Cysteine and Histidine Derivatives to the Pyrazolylborate-Zinc Unit

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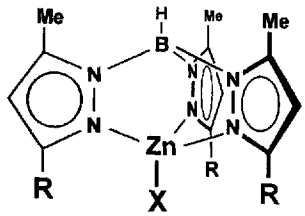
Highly substituted pyrazolylborate ligands $Tp^{R,Me}$ were used to limit the coordination number of zinc towards cysteine- and histidine-derived coligands. Monodentate thiolate attachment (→ **1a–f**) was achieved with *N*- and *C*-protected cysteine, monodentate carboxylate attachment (→ **3**) with *N*-protected histidine. *C*-protected cysteine was found to form a five-membered *N,S*-chelate ring (**2**). While imidazole coordination with *N*- and *C*-protected histidine could not be achieved, cationic pyrazolylborate-zinc-coligand complexes $[TpZn-L]^+$ (**4a, b**) were obtained for L = 2-methylimidazole. The new complexes were characterized by their spectra and three structure determinations.

Zinc exercises its biological functions in a chemical environment consisting mainly of the thiolate groups of cysteine and the imidazole groups of histidine in the protein[2]. Accordingly, the investigation of its coordination chemistry with these two amino acids as well as simple derivatives and small peptides thereof is an important aspect of the bioinorganic chemistry of zinc[3,4]. We are contributing to this by the determination of stabilities and structures of cysteine- and histidine-containing zinc complexes[5].

It is a general problem of model studies of this kind that the two amino acids are polyfunctional, even in the form of their derivatives. Therefore, in contrast to the situation in a protein, they normally occupy more than one coordination position on zinc, which often results in the formation of coordination polymers. This problem can be avoided in model compounds only in a signular case, namely by providing the most advantageous electronic situation in the form of a ZnN_2S_2 coordination. The problem does not exist in the case of the protein because the functionality of cysteine and histidine is reduced to that of their side chain donors thiolate and imidazole, and because a favorable geometrical situation is preformed.

This paper reports on our attempts to imitate the natural case by controlling the geometrical situation and by reducing the donor abilities of cysteine and histidine derivatives to monodentate coordination. Our approach was based on the use of highly substituted pyrazolylborate ligands. The target compounds were the complexes of type **A** in which the substituents R at the 3-positions of the pyrazole units encapsulate the zinc ion and its coligands. The coligands X were meant to be cysteine and histidine derivatives bound in a monodentate fashion via their thiolate or imidazole functions. The neutral complexes with X = OH were used as starting compounds, based on our experience[6,7] that the OH^- group is the most efficient leaving group in this class of complexes.



A

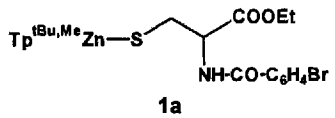
R = tert.C_4H_9: $Tp^{tBu,Me}Zn$-X

R = p-iPr-C_6H_4: $Tp^{Cum,Me}Zn$-X

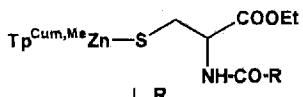
R = C_6H_5: $Tp^{Ph,Me}Zn$-X

Cysteine Derivatives

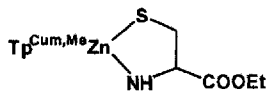
Various attempts were made to combine the TpZn–OH complexes with *N*- and *C*-protected cysteines. Some of these yielded analytically and spectroscopically pure products. In all these cases the reagent was a cysteine ethyl ester bearing an aromatic acyl group at the N terminus. Complex **1a** was obtained from $Tp^{tBu,Me}Zn-OH$, complexes **1b–f** were prepared from $Tp^{Cum,Me}Zn-OH$ and the corresponding cysteine derivative. When cysteine ethyl ester, i.e. a derivative which is unprotected at the N terminus, was used, the reaction with $Tp^{Cum,Me}Zn-OH$ yielded complex **2**.



1a



	R
1b	phenyl
1c	p-tolyl
1d	p-nitrophenyl
1e	p-bromophenyl
1f	2-pyridyl



2

[◇] Part 8: Ref.[1].

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The composition of all complexes **1** and **2** could easily be deduced from the NMR spectra (see Experimental). In **1a–e** the cysteine ligand is monofunctional, using only its thiolate group for coordination just like other thiolates[8]. In **1f** the pyridyl group offers itself as an additional donor. The ^{1}H-NMR resonances of the pyridyl group in complex **1f** are, however, very close to those in the free ligand, which makes us assume that the cysteinate in **1f** is monodentate as well. In the case of **2** the NMR evidence is inconclusive because the relevant NMR probe, the SCH_2 unit, would be in a similar environment for *S*-monodentate or *N,S*-bidentate coordination. Our previous experience[9] with *N*-unprotected cysteine derivatives, however, allowed the possibility of *N,S*-chelating cysteinate coordination.

The monodentate cysteinate coordination was proved for the case of **1e** by a structure determination, the result of which is displayed in Figure 1. **1e** can be classified as a TpZn-thiolate complex with a somewhat complicated thiolate ligand. The ZnN_3S coordination pattern is close to ideally trigonal with rather constant Zn–N bond lengths and N–Zn–N bond angles. Only one N–Zn–S angle (N3–Zn–S) indicates that the Zn–S bond is slightly bent with respect to the threefold central axis. Bond lengths and angles at the zinc and sulfur atoms are very close to those of $Tp^{Ph}Zn$–SEt[8]. The shape and electronic nature of the cysteinate ligand are responsible for two unusual features of the crystalline substance. One of them is the presence of several solvent molecules (1 water, 1 dichloromethane, 1 1/2 methanol) per formula unit, which in part are linked to each other by hydrogen bonds. The other is the fact that both terminal groups of the amino acid extend out of the encapsulating pocket of the $Tp^{Cum,Me}$ ligand, thereby making visible the limits of its encapsulating ability.

Figure 1. Molecular structure of **1e**. Pertinent bond lengths: Zn–N1 2.05(1), Zn–N2 2.05(1), Zn–N3 2.04(1), Zn–S 2.244(3), S–C40 1.82(1) A. Bond angles: N1–Zn–N2 92.9(4), N1–Zn–N3 92.3(4), N2–Zn–N3 92.6(3), N1–Zn–S 121.4(2), N2–Zn–S 121.4(3), N3–Zn–S 127.3(2), Zn–S–C40 96.8(4)°

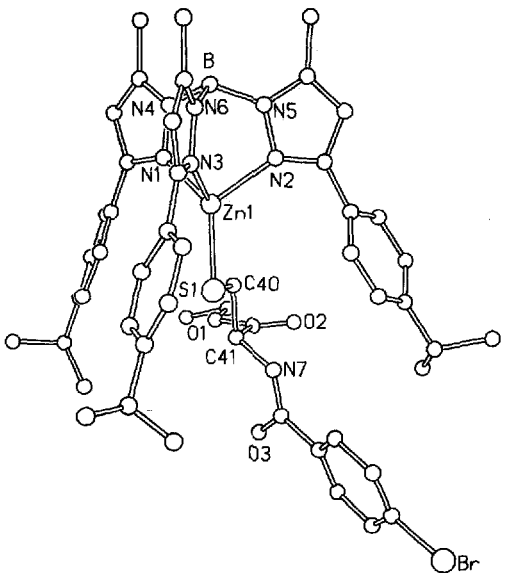


Figure 2. Molecular structure of one of the two independent molecules of **2** in the crystal

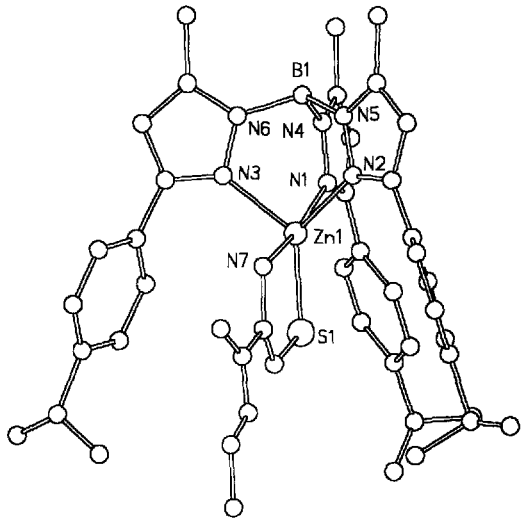


Table 1. Pertinent bond lengths [Å] and angles [°] for both molecules of complex **2**

	molecule 1	molecule 2
Zn-N1	2.260(7)	2.358(6)
Zn-N2	2.076(7)	2.075(7)
Zn-N3	2.068(6)	2.055(6)
Zn-N7	2.368(8)	2.319(7)
Zn-S	2.257(2)	2.276(3)
S-C40	1.772(12)	1.812(11)
C40-C41	1.368(14)	1.460(14)
C41-N7	1.404(12)	1.463(12)
N1-Zn-N2	83.2(3)	81.8(2)
N1-Zn-N3	85.9(2)	85.2(2)
N1-Zn-N7	167.9(3)	167.7(2)
N1-Zn-S	108.2(2)	107.9(2)
N2-Zn-N3	95.6(3)	96.1(3)
N2-Zn-N7	87.0(3)	87.4(2)
N2-Zn-S	132.2(2)	136.1(2)
N3-Zn-N7	88.0(3)	90.1(3)
N3-Zn-S	130.6(2)	126.8(2)
N7-Zn-S	83.7(2)	83.9(2)

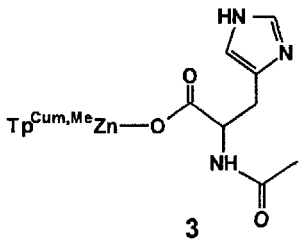
The structure determination of **2** confirmed the attachment of the cysteine as an *N,S*-chelating ligand (Figure 2). The crystals of **2** contain two independent molecules per asymmetric unit. These differ significantly only in the orientations of the *O*-ethyl groups while being close to be superimposable otherwise (Table 1). The space group is centrosymmetrical which should not be possible considering that the amino acid starting material was L-cysteine. A subsequent test revealed that **2** is not optically active which means that racemization has occurred in one of the reaction steps.

To our knowledge **2** is the first structurally characterized complex with a ZnN_4S coordination. The coordination geometry is best described as trigonal-bipyramidal. This is unusual for (pyrazolylborate)zinc complexes with high

steric hindrance, but not without precedence[6,10]. The increase of the coordination number to five causes a quite unsymmetrical attachment of the Tp ligand (cf. Zn–N distances). The two axial Zn–N distances are longer than the Zn–S distance, which indicates weak coordination on the axial positions. Otherwise, the Zn–N and Zn–S bond lengths are in the usual range for TpZn complexes. All zinc complexes of cysteine derivatives which have been structurally characterized so far[9,11] show cysteine attachment as an *N,S*-chelating ligand with bond lengths and angles comparable to those in **2**.

Histidine Derivatives

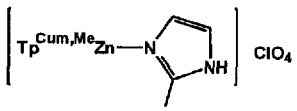
In analogy to the zinc-histidine coordination in proteins it can be envisaged that *C*- and *N*-protected histidine can be attached to the (pyrazolylborate)zinc unit via the imidazole donor in a cationic complex, e.g. $[TpZn(N-Ac-His-OEt)]^+$. Our attempts to achieve this mode of coordination with doubly protected histidine have, however, not been successful until now. Only the increase of the histidine functionality by leaving the C terminus unprotected produced an isolable complex: $Tp^{Cum,Me}Zn-OH$, and *N*-acetylhistidine yielded the neutral compound **3**.



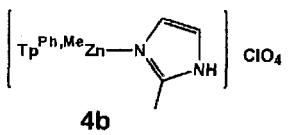
3

The composition of **3** is again evident from its spectra (see Experimental). Its molecular nature is obvious from its good solubility in nonplanar solvents. This means that the histidine ligand is carboxylate-coordinated. This can also be derived from the carboxylate IR bands at 1650 and 1399 cm^{-1} which also underline the relation of **3** to the structurally characterized complex histidinium trichlorozincate[12] with respect to the monodentate carboxylate coordination. It seems unlikely that there is an additional coordination of the imidazole group leading to a seven-membered chelate ring as previously observed in the case of simpler complexes[12,13]. The main evidence against this comes from the ^{1}H-NMR data again. The resonances of the histidine ligand are only insignificantly shifted compared to those of free *N*-acetylhistidine. If the imidazole group were coordinated to zinc it should be exposed to the ring-current effects of the three cumenyl substituents resulting in high-field shifts of up to 2 ppm[6,7,10]. Unfortunately, complex **3** shares the reluctance of many zinc-amino acid and zinc-peptide complexes to form good crystals.

We could obtain isolable complexes with a TpZn-imidazole composition only by sacrificing the histidine functionality and using simple imidazoles as ligands. Thus, it was no problem to incorporate 2-methylimidazole in complexes **4a** and **b** by reacting it with $Tp^{Cum,Me}Zn-OH$ and $Tp^{Ph,Me}Zn-OH$, respectively, in the presence of one half equivalent of zinc perchlorate (i.e. one equivalent of perchlorate ions).



4a



4b

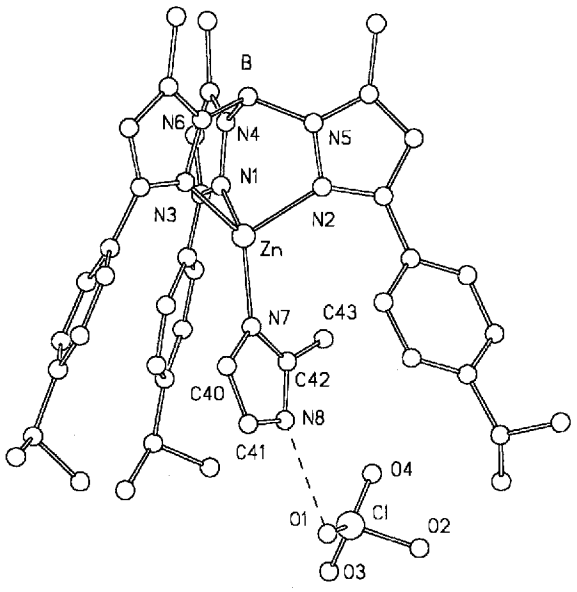
The constitutions of **4a** and **b** are evident from their ^{1}H-NMR spectra (see Experimental). The H atoms at the 4- and 5-positions of the imidazole are in different chemical environments due to the attachment of the zinc ion to one of the nitrogen atoms. Their ^{1}H-NMR resonances are 1.6 ppm apart, and the resonance for the 2-methyl group is shifted 1.8 ppm to higher field compared to free 2-methylimidazole. The perchlorate absorptions in the IR spectra of **4a** and **b** are split into several bands which reflects the attachment of the perchlorate to the imidazole via a hydrogen bond (see below).

Crystals suitable for a structure determination could be obtained from **4a**. Figure 3 shows a view of the complex. The zinc ion is coordinated in a distorted tetrahedral fashion. While the Zn–N distances to the Tp ligand indicate its symmetrical attachment, the disk-like shape of the imidazole coligand produces a 2:1 discrimination for both sets of 3 N–Zn–N angles. The Zn–N(imidazole) distance is 0.1 Å shorter than the Zn–N(Tp) distances. This is a phenomenon which we observed several times for the Zn–O distances in TpZn–OX complexes[6–8]. In comparison with simple tetrahedral complexes with Zn–N(imidazole) coordination whose Z–N distances lie in the range 1.99 ± 0.03 Å[12,14,15], the Zn–N(Tp) distances in **4a** are too long, and the Zn–N(imidazole) distance is too short. The oxygen atom of the perchlorate counterion is 2.94 Å distant from the uncoordinated nitrogen atom of the imidazole which corresponds to a weak hydrogen bond.

Discussion

The aim of this work was the synthesis of zinc complexes which bear cysteine and histidine derivatives as monodentate thiolate- or imidazole-bound ligands in an enzyme-like environment. It turned out that this could not be achieved with histidine derivatives. *N*- and *C*-protected cysteine derivatives whose functionality is only located in their thiolate side chain could, however, be coupled with TpZn units to yield tetrahedral complexes with a ZnN_3S coordination. This reflects the highly affinity between zinc and cysteine thiolate[13]. On the other hand, the non-formation of imidazole-bound TpZn–His complexes reflects an affinity between zinc and the histidine-imidazole donor which, contrary to the common opinion, is very low[1,12,16]. Only if the functionality of histidine is reduced to the bare presence of imidazole, the latter can be incorporated as a coligand. The resulting TpZnL complexes are cationic which is a rarity in the chemistry of pyrazolylborate complexes[17,18].

Figure 3. Structure of complex **4a**. Pertinent bond lengths: Zn–N1 2.025(2), Zn–N2 2.030(3), Zn–N3 2.025(3), Zn–N7 1.934(2), N8···O1 2.94(1) Å. Bond angles: N1–Zn–N2 95.2(1), N1–Zn–N3 89.8(1), N2–Zn–N3 96.3(1), N1–Zn–N7 126.6(1), N2–Zn–N7 115.1(1), N3–Zn–N7 126.1(1)°



Cysteine and histidine derivatives containing unprotected N or C termini are non-physiological bonding partners for metal ions, but better ligands. This is borne out by the formation of complexes **2** and **3**. As observed previously[9,11,13], cysteine realizes the favorable *N,S* coordination as a five-membered chelate ring. Histidine, being left with the choice between several less favorable options[1,12,16], realizes the monodentate carboxylate coordination. The pyrazolylborate ligands support the various bonding modes by encapsulating the amino acid ligands but also by allowing the unusual coordination number five despite the large steric hindrance.

The work reported here has shown the usability of the Tp–Zn–amino acid combination and the possibility of overcoming the problem of crystallization of amino acid and peptide complexes. The structure determinations have provided some material for comparative discussions. A possible outlook is indicated by the structure of the $Tp^{Cum,Me}Zn$ complex of the tripeptide mimetic ZINCOV[16] in which the Tp ligand protects the head group of the peptide-like coligand and at the same time exposes its tail to the environment.

This work was supported by the *Deutsche Forschungsgemeischaft*. We thank *B. Müller* for help with the structure determinations.

Experimental

General experimental techniques and measuring methods: see ref.[12]. The starting complexes $Tp^{tBu,Me}Zn–OH$[8], $Tp^{Cum,Me}Zn–OH$[7] and the $Tp^{Ph,Me}$ ligand[19] were prepared as described before. Cystine diethyl ester ditosylate and *N*-acetylhistidine were obtained commercially. The following abbreviations are used: NMM: *N*-methylmorpholine, DTE: dithioerythritol, HTFA: trifluoroacetic acid.

Starting Material $Tp^{Ph,Me}Zn–OH$: A solution of 1.00 g (1.91 mmol) of $KTp^{Ph,Me}$ in 50 ml of dichloromethane was treated with stirring with 0.71 g (1.91 mmol) of $Zn(ClO_4)_2 \cdot 6\,H_2O$ in 10 ml of methanol, affording a colorless precipitate. After 15 min, 0.13 g (2.2 mmol) of powdered KOH was added, and stirring was continued for 15 h. After filtration the solution was reduced to half its volume in vacuo and dropped slowly into 30 ml of pentane. The colorless precipitate which was filtered off and dried in vacuo consisted of 346 mg (37%) of $Tp^{Ph,Me}Zn–OH$, m.p. 180 °C. The purity of the compound could not be improved by repeated crystallization. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3649 w (OH), 2552 m (BH). – ^1H NMR ($CDCl_3$): δ = 2.45 [s, 9H, Me (pz)], 6.18 [s, 3H, H (pz)], 7.76 [d, J = 7.4 Hz, 6H, Ph(2,6)], 7.21–7.38 [m, 9H, Ph(3,4,5)]. – $C_{30}H_{29}BN_6OZn$ (565.8): calcd. C 63.69, H 5.17, N 14.85; found C 59.68, H 4.97, N 13.42.

Cysteine Derivatives: These were obtained by first preparing the corresponding cystine derivatives and then reducing them: *[PhCO-Cys-OEt]$_2$:* 6.41 g (10.00 mmol) of cystine diethyl ester ditosylate was suspended in 100 ml of THF. The suspension was cooled to –12 °C and treated with 4.4 ml (4.10 g, 40.00 mmol) of NMM followed by a solution of 2.32 ml (2.81 g, 20.00 mmol) of benzoyl chloride in 50 ml of THF. Stirring was continued for 24 h at room temp. After filtration the solvent was removed in vacuo and the residue dissolved in 100 ml of ethyl acetate. The solution was washed 3 times with 50 ml of water each, 3 times with 50 ml of an acetate buffer solution (pH 4.0) each, 3 times with 50 ml of water each, 3 times with 50 ml of a 4% $NaHCO_3$ solution each, and 4 to 5 times with 50 ml of water (until the filtrate had neutral pH) each. Then the organic solution was dried with Na_2SO_4 and evaporated to dryness in vacuo. The remaining solid was dried in vacuo to yield 4.60 g (91%) of $[PhCO-Cys-OEt]_2$ as a colorless powder, m.p. 156 °C.

[p-MeC$_6$H$_4$CO-Cys-OEt]$_2$: Prepared as before from 6.404 g (10.00 mmol) of cystine diethyl ester ditosylate and 2.67 ml (3.10 g, 20.00 mmol) of 4-methylbenzoyl chloride. Yield 4.92 g (92%), colorless powder, m.p. 167 °C.

[p-NO$_2$C$_6$H$_4$CO-Cys-OEt]$_2$: Prepared as before from 6.41 g (10.00 mmol) of cystine diethyl ester ditosylate and 3.71 g (20.00 mmol) of 4-nitrobenzoyl chloride. Yield 5.47 g (92%), yellow powder, m.p. 171 °C.

[p-BrC$_6$H$_4$CO-Cys-OEt]$_2$: Prepared as before from 6.41 g (10.00 mmol) of cystine diethyl ester ditosylate and 4.39 g (20.00 mmol) of 4-bromobenzoyl chloride. Yield 5.90 g (89%), colorless powder, m.p. 165 °C.

[2-PyCO-Cys-OEt]$_2$: 1.92 g (15.60 mmol) of pyridine-2-carboxylic acid was dissolved in 50 ml of THF. The solution was cooled to –12 °C and treated with 1.71 ml (1.58 g, 15.60 mmol) of NMM followed by 2.02 ml (2.12 g, 15.60 mmol) isobutyl chloroformate. After 5 min this solution was combined with 80 ml of a cooled (–12 °C) dimethylformamide/THF (1:1) solution containing 5.00 g (7.80 mmol) of cystine diethyl ester ditosylate and 1.71 ml (1.58 g, 15.60 mmol) of NMM. Stirring was continued for 14 h at room temp., the mixture was filtered, the solvent removed in vacuo and the residue dissolved in 100 ml of ethyl acetate. The obtained solution was washed 3 times with 50 ml of water each, 3 times with 50 ml of a 4% $NaHCO_3$ solution each, and 4 to 5 times with water (until the filtrate had neutral pH) each. Then the ethyl acetate phase was dried with Na_2SO_4 and evaporated to dryness in vacuo. After recrystallization of the remaining solid from 30 ml of methanol 2.76 g (70%) of $[2-PyCO-Cys-OEt]_2$ was obtained as yellow needles, m.p. 138 °C.

PhCO-Cys-OEt: A solution of 3.50 g (6.94 mmol) of [PhCO-Cys-OEt]$_2$ in 60 ml of methanol was treated with 1.39 g (9.00 mmol) of DTE. The pH was adjusted to 8 with 0.2 M NaOH, and the mixture was stirred for 4 h at room temp. It was then acidified with HTFA to pH 2 and the solvent removed in vacuo. The remaining solid was thoroughly washed 4 times with 70 ml of water each. Recrystallization from diethyl ether/methanol (8:1) yielded 2.53 g (72%) of PhCO-Cys-OEt[20] as white needles of m.p. 87°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3325 s (NH), 2563 m (SH), 1748 s, 1638 s, 1525 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.33 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.38 (t, J = 8.4 Hz, 1H, SH), 3.02–3.21 [m, 2H, SCH_2 (Cys)], 4.27 (q, J = 7.2 Hz, 2H, OCH_2), 5.01 (dd, J = 4.3 and 9.1 Hz, 1H, $C_\alpha H$), 7.03 (s, br., 1H, NH), 7.42 [m, 3H, Ph(3,4,5)], 7.71 [d, J = 6.8 Hz, 2H, Ph(2,6)].

p-MeC_6H_4CO-Cys-OEt: Prepared as before from 3.50 g (6.54 mmol) of [*p*-MeC_6H_4CO-Cys-OEt]$_2$ and 1.31 g (8.50 mmol) of DTE. Yield 2.73 g (78%), colorless powder, m.p. 98°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3325 s (NH), 2583 w (SH), 1753 s, 1633 s, 1525 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.29 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.33 (t, J = 8.6 Hz, 1H, SH), 3.06–3.18 [m, 2H, SCH_2 (Cys)], 4.28 (q, J = 7.2 Hz, 2H, OCH_2), 4.99 (dd, J = 4.8 and 9.5 Hz, 1H, $C_\alpha H$), 7.03 (s, br., 1H, NH), 7.22 [d, J = 6.9 Hz, 2H, Ph(3,5)], 7.71 [d, J = 6.9 Hz, 2H, Ph(2.6)]. – $C_{13}H_{17}NO_3S$ (267.4): calcd. C 58.40, H 6.41, N 5.24; found C 57.53, H 6.17, N 5.12.

p-$NO_2C_6H_4$CO-Cys-OEt: Prepared as before from 3.50 g (5.88 mmol) of [*p*-$NO_2C_6N_4$CO-Cys-OEt]$_2$ and 1.18 g (7.65 mmol) of DTE. Yield 2.84 g (81%), colorless powder, m.p. 122°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3322 s (NH), 2553 w (SH), 1740 s, 1639 s (CO), 1532 vs (NO). – ^{1}H NMR ($CDCl_3$): δ = 1.28 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.31 [t, J = 8.6 Hz, 1H, SH], 3.04–3.12 [m, 2H, SCH_2 (Cys)], 4.22 (q, J = 7.2 Hz, 2H, OCH_2), 5.02 (dd, J = 4.5 and 9.8 Hz, 1H, $C_\alpha H$), 7.05 (s, br., 1H, NH), 7.92 [d, J = 8.9 Hz, 2H, Ph(2,6)], 8.22 [d, J = 8.9 Hz, 2H, Ph(3,5)]. – $C_{12}H_{14}N_2O_5S$ (298.3): calcd. C 48.32, H 4.73, N 9.39; found C 47.93, H 4.40, N 9.13.

p-BrC_6H_4CO-Cys-OEt: Prepared as before from 3.50 g (5.28 mmol) of [*p*-BrC_6H_4CO-Cys-OEt]$_2$ and 1.06 g (6.86 mmol) of DTE. Yield 2.66 g (76%), colorless powder, m.p. 118°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3322 s (NH), 2536 w (SH), 1737 s, 1635 s, 1525 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.34 [t, J = 7.1 Hz, 3H, CH_3 (OEt)], 1.38 (t, J = 8.4 Hz, 1H, SH), 3.06–3.18 [m, 2H, SCH_2 (Cys)], 4.31 (q, J = 7.1 Hz, 2H, OCH_2), 5.03 (dd, J = 4.3 and 9.1 Hz, 1H, $C_\alpha H$), 7.03 (s, br., 1H, NH), 7.61 [d, J = 6.8 Hz, 2H, Ph(2,6)], 7.74 [d, J = 6.8 Hz, 2H, Ph(3,5)]. – $C_{12}H_{14}BrNO_3S$ (332.2): calcd. C 43.38, H 4.25, N 4.22; found C 43.40, H 4.17, N 4.23.

2-PyCO-Cys-OEt: A solution of 2.76 g (5.45 mmol) [2-PyCO-Cys-OEt]$_2$ in 60 ml of methanol was treated with 1.09 g (6.98 mmol) of DTE. The pH was adjusted to 8 with 0.2 M NaOH, and the mixture was stirred for 4 h at room temp. It was then acidified with HTFA to pH 2 and the solvent removed in vacuo. The remaining oil was washed 3 times with 50 ml of a 4% $NaHCO_3$ solution each and 4 to 5 times with water. Then the oil was dissolved in 150 ml of diethyl ether. The obtained solution was washed again 3 times with 50 ml of water each, 3 times with 50 ml of a 4% $NaHCO_3$ solution each, and 4 to 5 times with water (until the filtrate had neutral pH). After drying of the solution with Na_2SO_4, evaporation of the solvent in vacuo yielded 2.55 g (91%) of 2-PyCO-Cys-OEt as a colorless oil. – IR (film, cm^{-1}): $\tilde{\nu}$ = 3378 m (NH), 2566 w (SH), 1740 s, 1678 s, 1592 w, 1515 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.27 [t, J = 6.9 Hz, 3H, CH_3 (OEt)], 1.43 [t, J = 9.1 Hz, 1H, SH], 3.02–3.18 [m, 2H, SCH_2 (Cys)], 4.23 (q, J = 6.9 Hz, 2H, OCH_2), 4.98 (dd, J = 5.7 and 8.5 Hz, 1H, $C_\alpha H$), 7.39 [m, 1H, Pyr(3)], 7.79 [dt, J = 1.1 and 7.4 Hz, 1H, Pyr(2)], 8.11 [d, J = 7.4 Hz, 1H, Pyr(1)], 8.54 [d, J = 5.1 Hz, 1H, Pyr(4)], 8.73 (s, br., 1H, NH). – $C_{11}H_{14}N_2O_3S$ (254.3): calcd. C 51.95, H 5.55, N 11.02; found C 52.18, H 5.52, N 11.04.

Complexes: **1a**: A solution of 200 mg (0.395 mmol) of $Tp^{tBu,Me}$-Zn–OH in 20 ml of dichloromethane was treated with 131 mg (0.395 mmol) of *p*-BrC_6H_4CO-Cys-OEt, and the mixture was stirred for 15 h. The solvent was removed in vacuo and the residue taken up in boiling *n*-pentane, the solution was filtered and left to crystallize at –25°C to afford 180 mg (55%) of **1a**, m.p. 183°C, colorless crystals. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3135 w (NH), 2554 m (BH), 1733 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.31 [t, J = 7.1 Hz, 3H, CH_3 (OEt)], 1.38 (s, 27H, *t*Bu), 2.38 [s, 9H, Me (pz)], 3.30 (dd, J = 4.3 and 11.9 Hz, 1H, $C_\beta H_1$), 3.49 (dd, J = 4.5 and 11.9 Hz, 1H, $C_\beta H_2$), 4.27 [d, J = 7.1 Hz, 2H, CH_2 (OEt)], 5.08 (ddd, J = 4.3, 4.5, 7.1 Hz, 1H, $C_\alpha H$), 5.83 [s, 3H, H (pz)], 7.52 (d, J = 7.1 Hz, 1H, NH), 7.57 [d, J = 8.6 Hz, 2H, Ph(3,5)], 7.77 [d, J = 8.6 Hz, 2H, Ph(2,6)]. – $C_{36}H_{53}BBrN_7O_3SZn$ (820.0): calcd. C 52.73, H 6.51, N 11.96; found C 53.20, H 6.66, N 11.99.

1b: A solution of 73 mg (0.29 mmol) of PhCO-Cys-OEt in 25 ml of methanol was added with stirring to a solution of 200 mg (0.29 mmol) of $Tp^{Cum,Me}$Zn–OH in 30 ml of dichloromethane. After stirring for 4 h, the solution was reduced to half its volume in vacuo. Another fourth of the volume was allowed to effuse in the course of several days in a desiccator. 148 mg (55%) of **1b** precipitated as colorless crystals, m.p. 128°C, which were filtered off, washed with little methanol and dried in vacuo. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3414 w (NH), 2546 m (BH), 1741 s, 1668 s, 1517 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.12 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.20 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 1.57–1.76 [m, 2H, SCH_2 (Cys)], 2.54 [s, 9H, Me (pz)], 2.84 [sept, J = 6.9 Hz, 3H, CH (*i*Pr)], 3.51 (dd, J = 4.1 and 8.9 Hz, 1H, $C_\alpha H$), 3.94 (q, J = 7.2 Hz, 2H, OCH_2), 6.14 [s, 3H, H (pz)], 6.25 (s, br., 1H, NH), 7.21 [d, J = 8.2 Hz, 6H, Ph′(3,5)], 7.42 [m, 3H, Ph(3,4,5)], 7.61 [d, J = 8.2 Hz, 6H, Ph′(2,6)], 7.78 [d, J = 6.8 Hz, 2H, Ph(2,6)]. – $C_{51}H_{60}BN_7O_3SZn$ (927.4): calcd. C 66.05, H 6.52, N 10.57; found C 65.47, H 6.51, N 10.48.

1c: Prepared as described for **1b** from 78 mg (0.29 mmol) of *p*-MeC_6H_4CO-Cys-OEt and 200 mg (0.29 mmol) of $Tp^{Cum,Me}$-Zn–OH. After stirring for 4 h the volume of the solution was reduced in vacuo to ca. 10 ml. Cooling to –30°C resulted in the precipitation of 138 mg (49%) of **1c** which was filtered off, washed with 2 ml of cold methanol and dried in vacuo. Colorless powder, m.p. 131°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3408 w (NH), 2547 m (BH), 1741 s, 1665 s, 1519 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.12 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.20 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 1.53–1.77 [m, 2H, SCH_2 (Cys)], 2.54 [s, 9H, Me (pz)], 2.84 [sept, J = 6.9 Hz, 3H, CH (*i*Pr)], 3.52 (dd, J = 4.5 and 9.5 Hz, 1H, $C_\alpha H$), 3.94 (q, J = 7.2 Hz, 2H, OCH_2), 6.14 [s, 3H, H (pz)], 6.25 (s, br., 1H, NH), 7.21 [d, J = 8.2 Hz, 6H, Ph′(3,5)], 7.23 [d, J = 6.9 Hz, 2H, Ph(3,5)], 7.61 [d, J = 8.2 Hz, 6H, Ph′(2,6)], 7.63 [d, J = 6.9 Hz, 2H, Ph(2,6)]. – $C_{52}H_{62}BN_7O_3SZn$ (941.4): calcd. C 66.34, H 6.64, N 10.42; found C 65.79, H 6.50, N 10.24.

1d: Prepared as described for **1b** from 87 mg (0.29 mmol) of *p*-$NO_2C_6H_4$CO-Cys-OEt and 200 mg (0.29 mmol) of $Tp^{Cum,Me}$-Zn–OH. Yield 180 mg (64%) of **1d**, yellow crystals, m.p. 142°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3416 w (NH), 2545 m (BH), 1745 s, 1666 s, 1524 s (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.12 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.20 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 1.58–1.85 [m, 2H, SCH_2 (Cys)], 2.54 [s, 9H, Me (pz)], 2.84 [sept, J = 6.9 Hz, 3H, CH (*i*Pr)], 3.49 (dd, J = 4.5 and 9.8 Hz, 1H, $C_\alpha H$), 3.94 (q, J = 7.2 Hz, 2H, OCH_2), 6.14 [s, 3H, H (pz)], 6.25 (s, br., 1H, NH),

7.21 [d, J = 8.2 Hz, 6H, Ph′(3,5)], 7.61 [d, J = 8.2 Hz, 6H, Ph′(2,6)], 7.77 [d, J = 8.9 Hz, 2H, Ph(2,6)], 8.25 [d, J = 8.9 Hz, 2H, Ph(3,5)]. – $C_{51}H_{59}BN_8O_5SZn$ (972.4): calcd. C 63.00, H 6.12, N 11.53; found C 62.28, H 6.08, N 11.39.

1e: Prepared as described for **1b** from 96 mg (0.29 mmol) of *p*-BrC_6H_4CO-Cys-OEt and 200 mg (0.29 mmol) of $Tp^{Cum,Me}$-Zn–OH. Yield 196 mg (67%) of **1e**, colorless crystals, m.p. 138°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3411 w (NH), 2546 m (BH), 1741 s, 1671 s, 1518 s (CO). – ^1H NMR ($CDCl_3$): δ = 1.12 [t, J = 7.2 Hz, 3H, CH_3 (OEt)], 1.20 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 1.57–1.75 [m, 2H, SCH_2 (Cys)], 2.54 [s, 9H, Me (pz)], 2.84 [sept., J = 6.9 Hz, 3H, CH (*i*Pr)], 3.48 (dd, J = 4.2 and 9.2 Hz, 1H, $C_\alpha H$), 3.94 (q, J = 7.2 Hz, 2H, OCH_2), 6.14 [s, 3H, H (pz)], 6.25 (s, br., 1H, NH), 7.21 [d, J = 8.2 Hz, 6H, Ph′(3.5)], 7.55 [s, br., 4H, Ph(2,3,5,6)], 7.61 [d, J = 8.2 Hz, 6H, Ph′(2,6)]. – $C_{51}H_{59}BBrN_7O_3SZn$ (1006.3): calcd. C 60.87, H 5.91, N 9.75; found C 60.44, H 5.85, N 9.61.

1f: Prepared as described for **1b** from 74 mg (0.29 mmol) of 2-PyCO-Cys-OEt and 200 mg (0.29 mmol) of $Tp^{Cum,Me}$Zn–OH. After stirring for 4 h, the volume of the solution was reduced in vacuo to ca. 10 ml. Cooling to –30°C resulted in the precipitation of 159 mg (59%) of **1f** which was filtered off, washed with 2 ml of cold methanol and dried in vacuo. Colorless powder, m.p. 146°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3386 w (NH), 2546 m (BH), 1739 s, 1678 s, 1517 s (CO). – ^1H NMR ($CDCl_3$): δ = 1.04 [t, J = 6.9 Hz, 3H, CH_3 (OEt)], 1.20 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 1.59–1.78 [m, 2H, SCH_2 (Cys)], 2.54 [s, 9H, Me (pz)], 2.84 [sept, J = 6.9 Hz, 3H, CH (*i*Pr)], 3.67 (dd, J = 5.7 and 8.5 Hz, 1H, $C_\alpha H$), 3.82 (q, J = 6.9 Hz, 2H, OCH_2), 6.14 [s, 3H, H (pz)], 7.21 [d, J = 8.2 Hz, 6H, Ph′(3,5)], 7.33–7.42 [m, 1H, Pyr(3)], 7.61 [d, J = 8.2 Hz, 6H, Ph′(2,6)], 7.79 [dt, J = 1.1 and 7.4 Hz, 1H, Pyr(2)], 8.04 (s, br., 1H, NH), 8.11 [d, J = 7.4 Hz, 1H, Pyr(1)], 8.62 [d, J = 5.1 Hz, 1H, Pyr(4)]. – $C_{50}H_{59}BN_8O_3SZn$ (928.4): calcd. C 64.69, H 6.41, N 12.04; found C 64.04, H 6.41, N 11.96.

2: 2.9 ml (0.29 mmol) of a 0.1 M solution of cysteine ethyl ester in chloroform was added to a solution of 200 mg (0.29 mmol) of $Tp^{Cum,Me}$Zn–OH in 30 ml of chloroform. After stirring for 30 min, 30 ml of ethanol was added with stirring. The resulting colourless precipitate was filtered off and washed with little ethanol. Recrystallization from ethanol/chloroform yielded 178 mg (75%) of **2** as colorless crystals, m.p. 144°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3371 w, 3271 m (NH), 2540 m (BH), 1731 s (CO). – ^1H NMR ($CDCl_3$): δ = 0.89–1.36 [m, 2H, SCH_2 (Cys)], 0.99 [t, J = 7.1 Hz, 3H, CH_3 (OEt)], 1.22 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 2.35 (dd, J = 3.7 and 12.2 Hz, 1H, $C_\alpha H$), 2.54 [s, 9H, Me (pz)], 2.90 [sept, J = 6.9 Hz, 3H, CH (*i*Pr)], 3.67–3.83 (m, 2H, OCH_2), 6.10 [s, 3H, H (pz)], 7.27 [d, J = 8.2 Hz, 6H, Ph(3,5)], 7.63 [d, J = 8.2 Hz, 6H, Ph(2,6)]. – $C_{44}H_{56}Bn_7O_2SZn$ (823.2): calcd. C 64.11, H 6.86, N 11.90; found C 63.71, H 6.97, N 11.40.

3: A solution of 53 mg (0.29 mmol) of *N*-acetylhistidine in 30 ml of methanol was added to a solution of 200 mg (0.29 mmol) of $Tp^{Cum,Me}$Zn–OH in 30 ml of dichloromethane. After stirring for 1 h, the volume was reduced in vacuo to ca. 5 ml. Cooling to –30°C resulted in the precipitation of 130 mg (52%) of **3** which was freed from the solvent with a syringe and washed with 1 ml of cold meth-

Table 2. Crystallographic data

Complex	**1e**	**2**	**4a**
formula	$C_{51}H_{59}BBrN_7O_3SZn \cdot H_2O \cdot 1.5CH_3OH \cdot CH_2Cl_2$	$C_{44}H_{56}BN_7O_2SZn \cdot 0.5\ CHCl_3$	$C_{43}H_{52}BN_8ZnClO_4$
mol.wt.	1157.2	882.9	856.6
cryst.size [mm]	0.5 · 0.4 · 0.4	0.8 · 0.5 · 0.3	0.5 · 0.4 · 0.4
crystal system	orthorhombic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/n$	P-1
Z	4	8	2
a [Å]	13.868(5)	20.750(4)	12.767(3)
b [Å]	15.090(4)	18.483(4)	14.263(3)
c [Å]	28.947(8)	25.881(5)	15.448(4)
α [°]	90	90	94.80(2)
β [°]	90	103.81(3)	113.40(2)
γ [°]	90	90	115.87(2)
V [nm^3]	6.058(3)	9.639(3)	2.2076(9)
d_{calc} [g cm^{-3}]	1.26	1.22	1.29
d_{obs} [g cm^{-3}]	1.23	1.20	1.25
μ(MoKα) [mm^{-1}]	1.237	0.678	0.667
Θ-range [°]	3.1-26.0	2.4-22.8	2.6-25.0
hkl-range	$-17 \le h \le 0$ $0 \le k \le 18$ $-35 \le l \le 0$	$-21 \le h \le 21$ $0 \le k \le 18$ $-26 \le l \le 0$	$-15 \le h \le 13$ $-16 \le k \le 16$ $0 \le l \le 18$
refl.measd.	6502	11506	8044
indep.refl.	6502	11212(R-int=0.06)	7732(R-int=0.01)
obs.refl,I>2σ(I)	4844	6778	6493
parameters	696	1035	513
R (obs.refl.)	0.088	0.067	0.050
wR2 (all.refl.)	0.280	0.233	0.165
res.el.dens. [e/Å³]	+1.5 -0.8	+0.7 -0.6	+0.9 -0,7

anol. Colorless powder, m.p. 160°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3215 m, 3163 m (NH), 2548 m (BH), 1650 s, 1437 s (CO). – ^1H NMR ([D_6]DMSO): δ = 1.21 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 1.85 (s, 3H, NAc), 2.52 [s, 9H, Me (pz)], 2.86 [m, 4H, H (*i*Pr) and $C_\alpha H$ (His)], 6.37 [s, 1H, CH (Im)], 6.44 [s, 3H, H (pz)], 7.23 [s, 1H, CH (Im)], 7.27 [d, J = 8.2 Hz, 6H, Ph(3,5)], 7.52 [d, J = 8.2 Hz, 6H, Ph(2,6)], 7.63 [s, 1H, NH (Im)]. – $C_{47}H_{56}BN_9O_3Zn$ (872.2): calcd. C 64.80, H 6.48, N 14.47; found C 64.38, H 6.60, N 13.47.

4a: To a solution of 200 mg (0.29 mmol) of $Tp^{Cum,Me}Zn-OH$ in 30 ml of dichloromethane a solution of 24 mg (0.29 mmol) of 2-methylimidazole in 15 ml of methanol and a solution of 54 mg (0.15 mmol) of $Zn(ClO_4)_2 \cdot 6\,H_2O$ in 15 ml of methanol were added with stirring. After stirring for 1 h, the mixture was reduced to half its volume in vacuo. Another fourth of the volume was allowed to effuse in the course of several days in a desiccator. 211 mg (85%) of **4a** precipitated which was filtered off and dried in vacuo. Colorless crystals, m.p. 255°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3220 m (NH), 2546 m (BH), 1146 s, 1115 s, 1062 s (ClO). – ^1H NMR ($CDCl_3$): δ = 0.70 [s, 3H, Mc (Im)], 1.24 [d, J = 6.9 Hz, 18H, Me (*i*Pr)], 2.59 [s, 9H, Me (pz)], 2.92 [sept, J = 6.9 Hz, 3H, H (*i*Pr)], 5.16 [t, J = 1.6 Hz, 1H, H (Im)], 6.22 [s, 3H, H (pz)], 6.79 [t, J = 1.6 Hz, 1H, H (Im)], 7.07 [d, J = 8.2 Hz, 6H, Ph(3,5)], 7.15 [d, J = 8.2 Hz, 6H, Ph(2,6)], 11.15 (s, 1H, NH). – $C_{43}H_{52}BClN_8O_4Zn$ (856.6): calcd. C 60.29, H 6.12, N 13.08; found C 60.15, H 6.22, N 12.96.

4b: Prepared as described for **4a** from 200 mg (0.35 mmol) of $Tp^{Ph,Me}Zn-OH$, 67 mg (0.18 mmol) of $Zn(ClO_4)_2 \cdot 6\,H_2O$, and 24 mg (0.35 mmol) of 2-methylimidazole. After filtration the solution was reduced to half its volume in vacuo and allowed to stand overnight. 168 mg (65%) of **4b** was obtained as colorless crystals, m.p. 245°C (dec.). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3236 m (NH), 2554 m (BH), 1143 s, 1096 s, 1064 s (ClO). – ^1H NMR ($CDCl_3$): δ = 0.66 [s, 3H, Me (Im)], 2.61 [s, 9H, Me (pz)], 5.22 [t, J = 1.6 Hz, 1H, H (Im)], 6.26 [s, 3H, H (pz)], 6.82 [t, J = 1.6 Hz, 1H, H (Im)], 7.22 [d, J = 8.2 Hz, 6H, Ph(2,6)], 7.35–7.68 [m, 9H, Ph(3,4,5)], 10.97 (s, 1H, NH). – $C_{34}H_{34}BClN_8O_4Zn$ (730.3): calcd. C 55.91, H 4.69, N 15.35; found C 56.68, H 4.78, N 14.78.

Structure Determinations[21]: Crystals of **1e** · H_2O · 1.5 CH_3OH · CH_2Cl_2 were formed by slow evaporation of a methanol/dichloromethane solution, crystals of **2** · 1/2 $CHCl_3$ were obtained from chloroform by cooling to 4°C, those of **4a** from dichloromethane/methanol (1:2) by slow evaporation of the solvent. The data sets were obtained with a Nonius CAD4 diffractometer by the $\omega/2\Theta$ technique by using graphite-filtered Mo-K_α radiation. An absorption correction based on azimutal scans was applied to **1e**. The structures were solved with direct methods and refined anisotropically. H atoms were included with C–H = N–H = 0.96 Å and isotropic temperature factors 1.2 times those of their attached atoms (1.5 times in methyl groups). The perchlorate ion in **4a** was treated with twofold disorder. The loss of solvent from **1e** and disorder among the solvent molecules resulted in a mediocre quality of the structure determination. The computer programs by Sheldrick[22] and Keller[23] were used. Table 2 lists the crystallogrpahic data.

[1] P. Gockel, H. Vahrenkamp, *Chem. Ber.* **1996**, *129*, 1243–1249.
[2] *Zinc Enzymes* (Eds.: I. Bertini, C. Luchinat, W. Maret, M. Zeppezauer), Birkhäuser, Boston, **1986**.
[3] *Biocoordination Chemistry: Coordination Equilibria in Biologically Active Systems* (Ed.: K. Burger), Ellis Horwood, New York, **1990**.
[4] *Amino Acids and Derivatives as Ambivalent Ligands* (Ed.: H. Sigel), Marcel Dekker, New York, **1979**.
[5] Cf. Ref.[1] and references cited therein.
[6] U. Hartmann, H. Vahrenkamp, *Chem. Ber.* **1994**, *127*, 2381–2385.
[7] M. Ruf, H. Vahrenkamp, *Inorg. Chem.*, in print.
[8] R. Alsfasser, A. K. Powell, S. Trofimenko, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 685–694.
[9] H. Albrich, H. Vahrenkamp, *Chem. Ber.* **1994**, *127*, 1223–1233.
[10] M. Ruf, K. Weis, I. Brasack, H. Vahrenkamp, *Inorg. Chim. Acta*, in print.
[11] P. Bell, W. S. Sheldrick, *Z. Naturforsch., Part B*, **1984**, *39*, 1732–1737.
[12] M. Förster, R. Burth, A. K. Powell, T. Eiche, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 2643–2648.
[13] P. Gockel, A. D. Zuberbühler, H. Vahrenkamp, *Helv. Chim. Acta* **1993**, *76*, 511–520.
[14] C. A. Baer, K. A. Duggan, H. C. Freeman, *Acta Crystallogr.* **1963**, *16*, 748–752.
[15] R. Alsfasser, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 695–701.
[16] M. Förster, I. Brasack, A. K. Duhme, H. F. Nolting, H. Vahrenkamp, *Chem. Ber.* **1996**, *129*, 347–353.
[17] S. Trofimenko, *Prog. Inorg. Chem.* **1986**, *34*, 115–210; *Chem. Rev.* **1993**, *93*, 943–980.
[18] F. Hartmann, W. Kläui, A. Kremer-Aach, D. Mootz, A. Sterath, H. Wunderlich, *Z. Anorg. Allg. Chem.* **1993**, *619*, 2071–2076.
[19] A. Rheingold, R. L. Ostrander, B. S. Haggerty, S. Trofimenko, *Inorg. Chem.* **1994**, *33*, 3666–3676.
[20] W. Hanefeld, *Arch. Pharm. (Weinheim)* **1985**, *318*, 375–377.
[21] Further details of the structure determination may be obtained on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405189 (for **1e**), CSD-405187 (for **2**) and CSD-405188 (for **4a**), the names of the authors, and the journal citation.
[22] *SHELXL-93* and *SHELXS-86*, G. M. Sheldrick, Universität Göttingen, **1986** and **1993**.
[23] *SCHAKAL-93*, E. Keller, Universität Freiburg, **1993**.

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