New Tripodal N_3S Ligands and Some Zinc Complexes Thereof☆

Rainer Burth, Andreas Stange, Markus Schäfer, and Heinrich Vahrenkamp*

Institut für Anorganische und Analytische Chemie der Universität Freiburg,
Albertstraße 21, D-79104 Freiburg, Germany

Received May 22, 1998

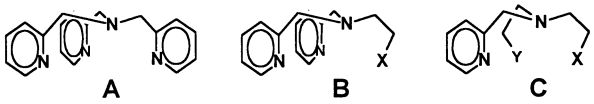
Keywords: Tripodal ligands / Nitrogen–sulfur ligands / Zinc complexes / Structure determination

Attachment of 2-pyridylmethyl units to cysteine amide and 2-mercaptobenzylamine leads to the new tripodal N_3S ligands N^{α}-(4-methylbenzoyl)-L-cysteine-bis(2-pyridylmethyl)amide (**CBPA-H**) and 2-mercaptobenzyl-bis(2-pyridylmethyl)amine (**MBPA-H**). Their treatment with zinc halides yields the neutral complexes **L** · ZnHal (Hal = Cl, Br, I). With zinc perchlorate **MBPA** forms the ionic compound [**L** · Zn] ClO_4, presumed to be a thiolate bridged dimer. Structure determinations of **MBPA** · ZnHal (Hal = Cl, Br) have confirmed the tripodal nature of the ligand in the trigonal-bipyramidal complexes.

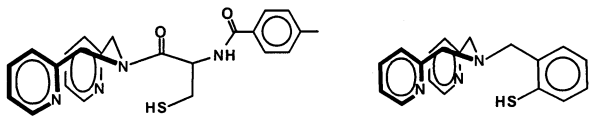
Metal ions in biological systems are coordinated by the aminoacids′ side chain donor functions (O of aspartate and glutamate, N of histidine, S of cysteine). In terms of modelling their structural and functional properties this asks for the design of ligands with an arrangement of the donor atoms similar to that in the protein. As a result modern model ligands are polydentate and chelating.

For complexes modelling zinc enzymes the requirements on the suitability of the polydentate ligands are especially pronounced, because the zinc ion profits neither from preferred coordination numbers or geometries nor from ligand field effects. Typically, all attempts to model the tetrahedral $ZnNS_2O$ coordination in the enzyme alcohol dehydrogenase[1] using amine-bisthiols as tridentate NS_2 ligands have resulted in thiolate-bridgted oligonuclear zinc complexes so far[2][3][4][5]. The high tendency for thiolate bridging has prevented the formation of the desired complexes, and similarly the highly preferred tetrahedral ZnN_2S_2 coordination has rendered futile many efforts invested in the synthesis of N_2S or N_3S ligands[6][7][8].

The ligands of choice for zinc complex model chemistry seem to be the tripodal ones, especially when they serve the further need of encapsulating the zinc ion by suitably attached substituents. The best results so far have been achieved here with the pyrazolylborates[9][10][11]. The pyrazolylborates, however, are confined for synthetic reasons to be N_3 ligands, and only recently have ways been found to modify them in the form of N_2S[12] or NS_2[13] ligands. It is this limitation of the pyrazolylborates that has directed the attention of other researchers and ourselves to the class of tetradentate tripodal ligands derived from ammonia, for which tripicolylamine (**A**) is the prototype. Ligands of this class can be synthesized step by step from ammonia or amines, and in the mono- and difunctionalized variants **B** and **C** all kinds of donor functions can be incorporated[14]. Thereby the disadvantage of these ligands in zinc model chemistry (their tetradentate nature) may be overcome by their versatility.



In the field of zinc model complexes N_4 ligands like **A** have been used mostly so far[15], followed by N_3O ligands like **B**[16]. We have contributed variations of **A**[17][18][19] and complexes of N_3O ligands with caboxylate and phenolate functions including a chiral variant[20][21][22]. In this paper we wish to present two thiolate-containing ligands of type **B**. **CBPA-H** is a derivative of cysteine, **MBPA-H** one of 2-mercaptobenzylamine. To our knowledge no such thiolate ligands with a N_3S donor set have been reported so far[23][24]. Some simple zinc complexes of the two ligands have been prepared to establish an entry to the modelling of zinc enzymes in which the metal is anchored, among others, by one thiolate function to the protein.

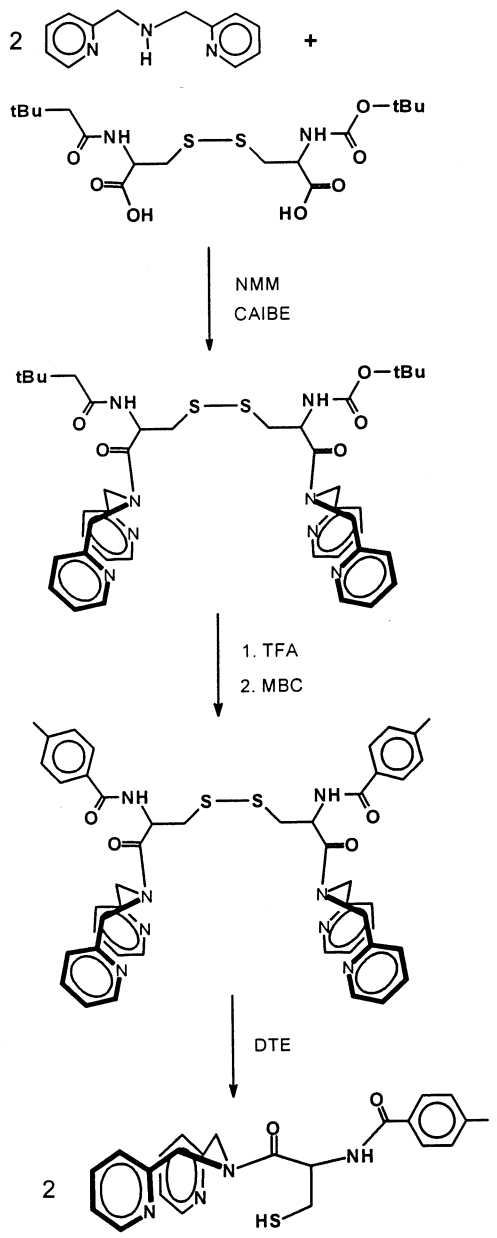


Ligand Synthesis

Both new ligands are derived from amine thiols, derivatized to contain two additional pyridyl donor functions. For the syntheses this meant that the thiol functions had to be protected until the last synthetic step. We found the use of the corresponding disulfides to be the only approach to do that. Schemes 1 and 2 show the reaction sequences.

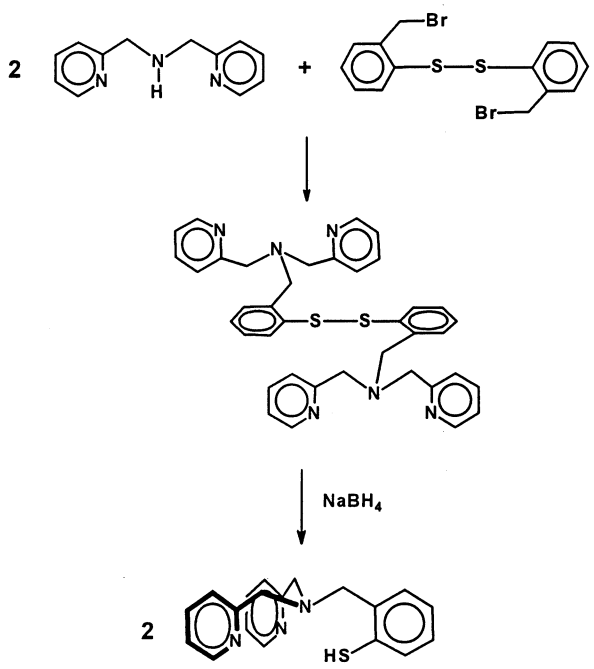
  1434−1948/98/1111−1759 $ 17.50+.50/0

Scheme 1. Synthesis of **CBPA-H**. Abbreviations: CAIBE = isobutylchloroformate, NMM = *N*-methylmorpholine, TFA = trifluoroacetic acid, MBC = 4-methylbenzoylchloride, DTE = dithioerythritol



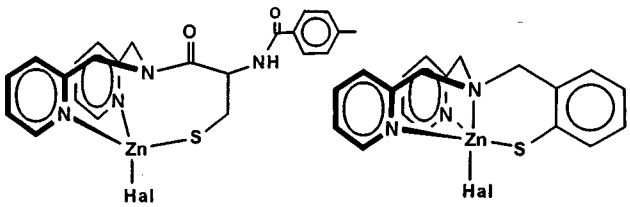
Ligand **CBPA-H** was obtained from cystine (in the *t*Boc protected form) by the standard procedures of activation, coupling, and deprotection. Ligand **MBPA-H** resulted from bis[(2-bromomethyl)phenyl] disulfide[25] in two reaction steps. The two pyridyl donor functions were introduced in the form of dipicolylamine in both cases. The sluggish reactions of the voluminous molecules allowed only mediocre overall yields. After the reductive cleavage of the disulfide precursors the thiol ligands had to be purified by HPLC. Thereby **CBPA-H** and **MBPA-H** were obtained pure, as evidenced by ^{1}H-NMR spectroscopy, but containing variable amounts of trifluoroacetic acid. Their identification rests on the spectra, their EI mass spectra showing the parent peak, and the full characterization of their zinc complexes.

Scheme 2. Synthesis of **MBPA-H**



Zinc Complexes

Reactions of **CBPA-H** with the zinc halides in acetonitrile in the presence of triethylamine produced complexes **1a**−**c** in good yields. **1a**−**c** precipitate from the reaction solutions and are soluble only in very polar solvents like water, DMSO or DMF. In addition to the spectra (see below) a EI mass spectrum of **1c** has verified the identity and monomeric nature of the complexes.



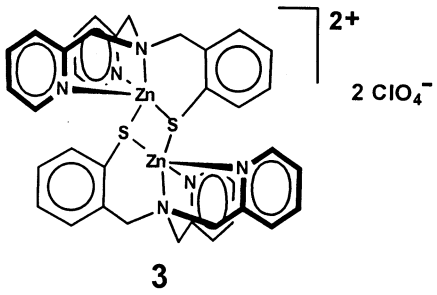
1a: Hal = Cl
1b: Hal = Br
1c: Hal = I

2a: Hal = Cl
2b: Hal = Br
2c: Hal = I

It was possible to prepare the zinc halide complexes of ligand **MBPA-H** the same way. **2a**−**c** could, however, be obtained in a more convenient way when after the last synthetic step in the formation of **MBPA-H**, i.e. the disulfide cleavage with $NaBH_4$, the corresponding hydrohalic acid was used for acidification and the corresponding zinc halide was added in excess. After neutralization **2a**−**c** were precipitated in a crystalline form. **2a**−**c** are of equally low solubility as **1a**−**c** in nonpolar solvents. This time in addition

to the spectra the structure determinations (see below) ascertained the constitution of the complexes.

When $HClO_4$ was used as before for acidifying and zinc perchlorate was added, complex **3** was precipitated. **3** could not be obtained in the form of X-ray quality crystals, nor were informative MS data obtained from it. Its ^{1}H-NMR spectrum is, however quite similar to that of the zinc perchlorate derivative of the analogous phenolate containing ligand which was characterized by a structure determination[22]. We therefore feel safe in assigning the given constitution to **3**. In contrast to the molecular complexes **1** and **2** the ionic complex **3** has a reasonable solubility not only in water, but also in methanol. It is therefore conceivable that a derivative chemistry of $[MBBA \cdot Zn]^+$ species may start with **3**.



3

Product Identification

The free ligands are characterized by their ^{1}H-NMR spectra (see Experimental). In their IR spectra they show the SH band and their typical double bond bands. The pertinent ^{1}H-NMR data of the zinc halide complexes are listed in Tables 1 and 2 in comparison to those of the free ligands. Typical coordination shifts are observed for the pyridyl H_A and for the NCH_2 signals. In the IR spectra of the zinc halide complexes (see Experimental Section) the SH band is missing as expected, and the intense pyridine band around 1600 cm^{-1} is shifted to lower wavenumbers. As a rule, the IR and ^{1}H-NMR spectra of complexes **2** are very similar to those of the zinc complexes of the ligand which is the phenolate analogue of **MBPA**[22]. This holds also for complex **3** whose IR and NMR data (see Table 2) are noticeably different from those of complexes **2**.

Table 1. Characteristic ^{1}H-NMR data (DMSO, 50°C, δ [ppm]/*J* [Hz]) of the free ligand **L** = **CBPA-H** and its zinc complexes

	L	**1a**	**1b**	**1c**
CH_3	2.31	2.35	2.35	2.36
SCH_2	2.70/m	2.77/m	2.78/m	2.81/m
NCH_2[a]	4.38−4.61	4.67−5.11	4.71−5.22	4.67−5.28
Py-H_A^1	8.25/5.7	8.66/5.7	8.69/5.7	8.71/5.7
Py-H_A^2	8.63/5.7	8.99/br	8.96/br	8.91/5.7

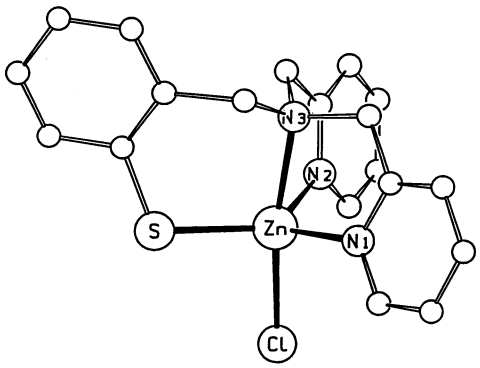
[a] Multiplets due to the inequivalence of the CH protons and due to superposition by the Cys-CH_α signal.

Table 2. Characteristic ^{1}H-NMR data (DMSO, 50°C, δ [ppm]/*J* [Hz]) of the free ligand **L** = **MBPA-H** and its zinc complexes

	L	**2a**	**2b**	**2c**	**3**
N-CH_2-Ph	3.68	3.78	3.81	3.93	3.82
N-CH_2-Py^1	3.82/s	3.94/15.9	3.97/16.1	3.98/16.1	4.21/br
N-CH_2-Py^2	−	4.05/15.9	4.08/16.1	4.09/16.1	−
Py-H_A	8.69/6.2	9.15/4.4	9.13/5.2	8.79/4.7	7.48

Confirmation of the tetradentate nature of the tripodal ligands and the molecular nature of the halide complexes was obtained by the structure determinations of **2a** and **b**. The two compounds are isostructural and share the property that the asymmetric unit contains two independent molecules. Hence only **2a** is discussed here. Figure 1 shows one of the two molecules. The geometrical differences between the two molecules are significant, becoming most visible for the axial and equatorial intraligand angles.

Figure 1. Molecular structure of complex **2a**. Pertinent bond lengths and angles: molecule 1: Zn−Cl 2.371(1), Zn−S 2.289(1), Zn−N1 2.091(2), Zn−N2 2.096(2), Zn−N3 2.304(2) Å; N3−Zn−Cl 170.52(4), N1−Zn−N2 107.00(7), N1−Zn−S 121.58(6), N2−Zn−S 126.75(6)°. Molecule 2: Zn−Cl 2.335(1), Zn−S 2.302(1), Zn−N1 2.092(2), Zn−N2 2.100(2), Zn−N3 2.325(2); N3−Zn−Cl 163.79(5), N1−Zn−N2 124.23(7), N1−Zn−S 108.49(5), N2−Zn−S 120.27(6)°



The coordination geometry of the complexes is severely distorted trigonal bipyramidal. The distortion cannot be related to the binding preferences of the tripodal ligand, as the two independent molecules are distorted in quite different ways. Furthermore the complex whose molecular shape is most similar to that of **2a**, i.e. the one with oxygen in place of sulfur[22], shows yet another kind of distortion and does not crystallize with two independent molecules. This is a good demonstration of the fact that the transitions between trigonal bipyramidal and square pyramidal geometries are "soft" in the coordination chemistry of zinc. The bond lengths at zinc are in the normal range. For the axial ligands the Zn−Cl bond length is at the upper end of the range observed for axial Zn−Cl bonds[22][26][27][28][29], and correspondingly the Zn−N3 bond length is at the lower end of its range[15][16][17][18][20][21][22][26][27][28][29]. To our knowledge no other zinc complexes with a ZnN_3SHal ligand set have been described yet.

Conclusions

This paper has shown that tripodal ligands offering a N_3S donor set for trigonal bipyramidal metal complexes with equatorial N_2S coordination are accessible, though with some synthetic effort. As a first step in exploiting their zinc complex chemistry the compounds L·ZnHal have been prepared which may serve as a starting point for obtaining functional species L·Zn−X. In the complexes L·Zn−Hal the tendency of the thiolate sulfur to bridge two zinc ions is suppressed. It seems to be operative, however, in the cationic species $[(MBPA)Zn]^+$ resulting in its existence as a sulfur-bridged dimer.

This work was supported by the *Deutsche Forschungsgemeinschaft*. We thank *A. Trösch* and *M. Tesmer* for help with the spectra and the structure determinations.

Experimental Section

General experimental methods and measuring techniques: see ref.[30]. All reactions were carried out in a nitrogen atmosphere. Starting materials were obtained commercially or prepared according to the given references. The complete ^{1}H-NMR data are given here for the two ligands only. Those of the complexes are very similar except for the resonances given in Tables 1 and 2.

Ligand Syntheses

CBPA-H: Step 1: 5.00 g (11.35 mmol) of bis(*tert*-butyloxycarbonyl)-L,L-cystine in 100 ml of THF at −15°C were stirred and treated with 2.49 ml (2.29 g, 22.70 mmol) of NMM and 2.94 ml (3.09 g, 22.70 mmol) of CAIBE. After 15 min 4.51 g (22.70 mmol) of bis(2-pyridylmethyl)amine were added. Within 24 h of stirring the temperature was raised to ambient. After filtration and evaporation to dryness the residue was picked up in 200 ml of ethylacetate. The solution was extracted three times with 70 ml of water, three times with 70 ml of a 4% $NaHCO_3$ solution, and five times with 100 ml of water. After drying with Na_2SO_4, filtration, and evaporation to dryness 8.25 g (91%) of bis(*tert*-butoxycarbonyl)-L,L-cystinebis[bis(2-pyridylmethyl)amide] remained as a colourless solid.

Step 2: The material obtained in the preceding step (8.25 g, 10.28 mmol) was treated with 50 ml of TFA and stirred for 2 h. Then the mixture was evaporated to dryness and the remaining brownish oil washed three times with 20 ml of ether. 13.22 g of a colourless powder remained which corresponds to a quantitative formation of L,L-cystinebis[bis(2-pyridylmethyl)amide] as the TFA adduct.

Step 3: The product obtained (13.22 g, 10.27 mmol) was dissolved in 100 ml of THF and treated at 0°C with 12.43 ml (11.43 g, 112.8 mmol) of NMM and then 3.42 ml (3.96 g, 25.67 mmol) 4-methylbenzoylchloride. After stirring for 24 h at room temp. the mixture was filtered and evaporated to dryness. After dissolving the residue in 300 ml of ethylacetate the yellow solution was washed three times with 60 ml of a 4% $NaHCO_3$ solution and then five times with 100 ml of water. After drying with Na_2SO_4 the solution was evaporated to dryness leaving behind 6.73 g (78%) of bis(4-methylbenzoyl)-L,L-cystinebis[bis(2-pyridylmethyl)amide] as a brownish oil.

Step 4: The brownish oil (6.73 g, 8.02 mmol) was dissolved in 70 ml of methanol and treated with 1.61 g (10.43 mmol) of DTE in 10 ml of methanol and then 12 ml of 0.2 M NaOH. After stirring for 4 h, 5 ml of TFA were added and then the mixture evaporated to dryness. The remaining brownish oil was dissolved in 80 ml of water and the solution washed four times with 30 ml of ether. After freeze-drying 6.83 g of the raw product remained as a yellowish oil. This was purified by HPLC using a reversed phase column (Merck LiChrosorb RP 18, 7 μm) eluting first for 45 min with acetonitrile/water/TFA (20:80:0.1) and then 20 min with acetonitrile/water/TFA (60:40:0.1). After freeze-drying 2.23 g (20%) of N^{α}-4-methylbenzoyl-L-cysteinebis(2-pyridylmethyl)amide (**CBPA-H**) were obtained as a pale yellow, very hygroscopic powder. The product contains approx. 2.5 mole equivalents of TFA as determined by potentiometric titration.

$C_{23}H_{24}N_4O_2S \cdot 2.5\ CF_3COOH$ (420.5 + 285.1), calcd.: C 47.66, H 3.79, N 7.94; found: C 47.47, H 3.91, N 8.07. − IR (KBr): $\tilde{\nu}$ = 3306 s (NH), 2516 w (SH), 1675 s (carboxylate), 1537 m (amide). −^{1}H NMR (D_2O): 2.18 [s, 3 H, CH_3], 2.84 [dd, J = 6.7, 14.1 Hz, 2 H, Cys-C_bH], 4.98 − 5.51 [m, 5 H, NCH_2 and Cys-C_aH], 7.09 [d, J = 8.0 Hz, 2 H, Ph (3,5)], 7.27 [d, J = 8.0 Hz, 2 H, Ph (2,6)], 7.55 [t, J = 6.7 Hz, 1 H, Py-H_B], 7.78 [d, J = 7.3 Hz, 1 H, Py-H_D], 7.87 [t, J = 6.7 Hz, 1 H, Py-$H_{B'}$], 8.19 [d, J = 7.3 Hz, 1 H, Py-$H_{D'}$], 8.28 [dt, J = 7.3, 1.3 Hz, 1 H, Py-H_C], 8.39 [dt, J = 7.3, 1.3 Hz, 1 H, Py-$H_{C'}$], 8.45 [d, J = 6.7 Hz, 1 H, Py-H_A], 8.59 [d, J = 6.7 Hz, 1 H, Py-$H_{A'}$].

MBPA-H: Step 1: 3.20 g (7.92 mmol) of bis[(2-bromomethyl)phenyl]disulfide were dissolved in 50 ml of dioxane. A mixture of 3.15 g (15.84 mmol) of bis(2-pyridylmethyl)amine and 2.21 ml (1.60 g, 15.84 mmol) of triethylamine in 50 ml of dioxane was added dropwise with stirring. The resulting red mixture was stirred overnight, filtered, and the filtrate evaporated to dryness. The remaining red oil was picked up in 200 ml of dichloromethane, washed three times with 20 ml of a 4% $NaHCO_3$ solution and then five times with 50 ml of water. After drying with Na_2SO_4 the solution was evaporated to dryness, the remaining red oil was dissolved in cyclohexane/ethylacetate (1/1) and chromatographed with neutral Al_2O_3, activity V, to yield 2.98 g (63%) of bis[{2-bis(2-pyridylmethyl)aminomethyl}phenyl] disulfide as an orange oil.

Step 2: 212 mg (0.331 mmol) of the product obtained before were dissolved in 30 ml of methanol. 50 mg (1.32 mmol) of $NaBH_4$ were added with stirring, resulting in a colour change of the solution from orange to yellow. After stirring overnight the mixture was evaporated to dryness. The residue was picked up in 10 ml of doubly distilled water and acidified to pH 6 with TFA. The solution was extracted three times with 20 ml of dichloromethane. The combined extracts were evaporated to dryness. Purification by HPLC as above using water/acetonitrile/TFA (80:20:0.1) as eluent yielded 191 mg (47%) of [*N*,*N*-bis(2-pyridylmethyl)-*N*-(2-mercaptobenzyl)]-amine (**MBPA-H**) as a yellow oil. The product contains approx. 2.5 mole equivalents of TFA as determined by potentiometric titration.

$C_{19}H_{19}N_3S \cdot 2.5\ CF_3COOH$ (321.4 + 285.1), calcd.: C 47.53, H 3.57, N 6.93; found: C 47.88, H 3.55, N 7.17. − IR (KBr): = $\tilde{\nu}$ = 2498w (SH), 1684s (carboxylate), 1620s, 1588m (pyridine). ^{1}H NMR ($CDCl_3$): 3.79 [s, 2 H, NCH_2Ph], 4.25 [s, 1 H, SH], 4.32 [s, 4 H, NCH_2Py], 6.95−7.35 [m, 4 H, Ph], 7.62−7.73 [m, 2 H, Py-H_B], 7.90 [d, J = 7.8 Hz, 2 H, Py-H_D], 8.13−8.24 [m, 2 H, Py-H_C], 8.83 [d, J = 5.6 Hz, 2 H, Py-H_A], 13.27 [s, 3 H, Py-NH^+].

Complex **1a**: To 134 mg (0.19 mmol) of **CBPA-H**·2.5 TFA in 30 ml of acetonitrile were added with stirring 0.09 ml (67 mg, 0.67 mmol) of triethylamine and 26 mg (0.19 mmol) of $ZnCl_2$ in 5 ml of acetonitrile. After reducing the volume to 10 ml in vacuo the solution was allowed to stand, slowly precipitating the product. Filtration, washing with a few ml of cold acetonitrile and drying in vacuo yielded 55 mg (56%) of colourless **1a** of m.p. 252°C. − $C_{23}H_{23}ClN_4O_2SZn$ (520.4), calcd.: C 53.09, H 4.45, N 10.77, Zn

Table 3. Crystallographic details

	2a	**2b**
formula	$C_{19}H_{18}ClN_3SZn$	$C_{19}H_{18}BrN_3SZn$
mol. mass	421.3	465.7
cryst. from	methanol	methanol/water
crystal size [mm]	1.0 × 0.9 × 0.9	0.4 × 0.5 × 0.4
space group	*P*-1	*P*-1
Z	4	4
a [Å]	10.378(2)	10.361(1)
b [Å]	13.191(3)	13.244(1)
c [Å]	14.361(3)	14.423(1)
α [°]	107.84(3)	107.92(1)
β [°]	105.92(3)	105.75(1)
γ [°]	94.52(3)	93.95(1)
V [Å^3]	1771.0(6)	1787.1(2)
d (calc.) [g·cm^{-3}]	1.58	1.73
temp. [K]	200	183
μ (Mo-*Kα*) [mm^{-1}]	1.66	3.73
Θ range [°]	2.9−26.0	2.6−26.0
hkl range	*h*: −12 to 0	h: −12 to 0
	k: −16 to 16	k: −16 to 16
	l: −17 to 17	l: −17 to 17
refl. measd.	7342	7424
indep. refl.	6936	7011
obs. refl. [$I>2\sigma(I)$]	6520	6017
parameters	451	451
refl. refined	6936	7008
R_1 (obs. refl.)	0.029	0.041
wR_2 (all refl.)	0.087	0.130
residual el. density e/Å^3	+0.8 −0.6	+1.0 −2.1

12.57; found: C 51.95, H 4.41, N 10.70, Zn 12.97. − IR (KBr): $\tilde{\nu}$ = 3373s (NH), 1669vs, 1651s (amide bands).

1b: Like **1a** from 219 mg (0.31 mmol) of **CBPA-H**·2.5 TFA, 0.15 ml (110 mg, 1.09 mmol) of triethylamine and 70 mg (0.31 mmol) of $ZnBr_2$. Yield 95 mg (54%) of colourless **1b**, m.p. 255°C. − $C_{23}H_{23}BrN_4O_2SZn$ (564.8), calcd.: C 48.91, H 4.10, N 9.92, Zn 11.58; found: C 49.31, H 4.21, N 10.25, Zn 11.94. − IR (KBr): $\tilde{\nu}$ = 3366m (NH), 1670s, 1652s (amide bands).

1c: Like **1a** from 183 mg (0.26 mmol) of **CBPA-H**·2.5 TFA, 0.12 ml (92 mg, 0.91 mmol) of triethylamine and 85 mg (0.26 mmol) of ZnI_2. Yield 98 mg (62%) of colourless **1c**, m.p. 257°C. − $C_{23}H_{23}IN_4O_2SZn$ (611.8), calcd.: C 45.15, H 3.79, N 9.16; found: C 45.28, H 3.70, N 9.13. − IR (KBr): $\tilde{\nu}$ = 3363m (NH), 1672s, 1650s (amide bands).

2a: 150 mg (0.23 mmol) of bis[{2-bis(2-pyridylmethyl)aminomethyl}phenyl] disulfide (**BAPD**) in 15 ml of methanol were treated with 35 mg (0.92 mmol) of $NaBH_4$ in 15 ml of methanol. After stirring for 4 h 15 ml of water, 1 ml of conc. HCl and 125 mg (0.92 mmol) of $ZnCl_2$ in 5 ml of methanol were added. A saturated aqueous solution of $NaHCO_3$ was slowly added until $Zn(OH)_2$ began to precipitate. Then the mixture was filtered twice and the resulting clear solution slowly reduced to two thirds its volume under reduced pressure. The resulting precipitate was filtered off, washed with a few ml of cold methanol and dried in vacuo, yielding 52 mg (27%) of colourless **2a**, m.p. 248°C (dec.). − $C_{19}H_{18}ClN_3SZn$ (421.3), calcd.: C 54.17, H 4.31, N 9.97, Zn 15.52; found: C 54.05, H 4.38, N 9.95, Zn 15.83. − IR (KBr): $\tilde{\nu}$ = 1604s, 1569m (pyridine bands).

2b: Like **2a** from 150 mg (0.23 mmol) of **BAPD**; 35 mg(0.92 mmol) of $NaBH_4$, 207 mg (0.92 mmol) of $ZnBr_2$ and 1 ml of conc. HBr. Yield 79 mg (37%) of colourless **2b**, m.p. 262°C (dec.). − $C_{19}H_{18}BrN_3SZn$ (465.7), calcd.: C 49.00, H 3.90, N 9.02; found: C 48.25, H 3.81, N 8.77. − IR (KBr): $\tilde{\nu}$ = 1606 s, 1572 m (pyridine bands).

2c: Like **2a** from 150 mg (0.23 mmol) of **BAPD**, 35 mg (0.92 mmol) of $NaBH_4$, 294 mg (0.92 mmol) of ZnI_2, and 1 ml of conc. HI. Yield 92 mg (39%) of pale-yellow **2c**, m.p. 274°C (dec.). − $C_{19}H_{18}IN_3SZn$ (512.7), calcd.: C 44.51, H 3.54, N 8.20; found: C 43.90, H 3.40, N 7.89. − IR (KBr): $\tilde{\nu}$ = 16.05 s, 1570 m (pyridine bands).

3: Like **2a** from 150 mg (0.23 mmol) of **BAPD**, 35 mg (0.92 mmol) of $NaBH_4$, 343 mg (0.92 mmol) of $Zn(ClO_4)_2 \cdot 6\ H_2O$, and 1 ml of conc. $HClO_4$. Yield 156 mg (35%) of colourless **3**, m.p. 181°C. − $C_{19}H_{18}ClN_3O_4SZn$ (485.3), calcd.: C 47.03, H 3.74, N 8.66, Zn 13.47; found: C 48.11, H 3.75, N 8.59, Zn 13.10. − IR (KBr): $\tilde{\nu}$ = 1606s, 1574 m (pyridine bands), 1092 vs (ClO_4).

Structure Determinations[31]: Crystals were obtained from the reaction solutions. Diffraction data were recorded with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 0.7107 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite[32]. Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 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[33]. Table 3 lists the crystallographic data.

☆ Dedicated to Prof. *Bernt Krebs* on the occasion of his 60th birthday.

[1] C. I. Bränden, H. Eklund, B. Nordström, T. Boiwe, G. Söderlund, E. Zeppezauer, I. Ohlsson, A. Akeson, *Proc. Natl. Acad. Sci. U. S.* **1973**, *70*, 2439−2442. H. Cho, S. Ramaswamy, B. V. Plapp, *Biochemistry* **1997**, *36*, 382−389.
[2] N. J. Curtis, R. S. Brown, *Can. J. Chem.* **1981**, *59*, 65−75.
[3] B. Kaptein, L. Wang-Griffin, G. Barf, R. M. Kellogg, *J. Chem. Soc. Chem. Commun.* **1987**, 1457−1459; B. Kaptein, G. Barf, R. M. Kellogg, F. van Bolhuis, *J. Org. Chem.* **1990**, *55*, 1890−1901.
[4] M. Bochman, K. J. Webb, M. B. Hursthouse, M. Mazid, *J. Chem. Soc. Chem. Commun.* **1991**, 1735−1737.
[5] U. Brand, H. Vahrenkamp, *Z. Anorg. Allg. Chem.* **1996**, *622*, 213−218.
[6] Quite often ZnN_2S_2 coordination occurs even at the expense of other donor functions being unused when a ligand contains one SH and one heterocyclic nitrogen donor. For examples see refs.[7] and[8].
[7] U. Brand, H. Vahrenkamp, *Inorg. Chem.* **1995**, *34*, 3285−3293.
[8] U. Brand, H. Vahrenkamp, *Chem. Ber.* **1996**, *129*, 435−440.
[9] N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, *43*, 419−531.
[10] G. Parkin, *Adv. Inorg. Chem.* **1995**, *42*, 291−393.
[11] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943−980.
[12] P. Ghosh, G. Parkin, *J. Chem. Soc. Chem. Commun.* **1998**, 413−414.
[13] C. Kimblin, T. Hascall, G. Parkin, *Inorg. Chem.* **1997**, *36*, 5680−5681.
[14] cf. *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty) Pergamon Press, Oxford, **1982**, vol. 2.
[15] For a recent example, cf. H. Adams, N. A. Bailey, D. E. Fenton, Q.-Y. He, *J. Chem. Soc. Dalton Trans.* **1997**, 1533−1539.
[16] For a recent example, cf. H. Adams, N. A. Bailey, D. E. Fenton, Q.-Y. He, *J. Chem. Soc. Dalton Trans.* **1996**, 2857−2865.
[17] R. Gregorzik, U. Hartmann, H. Vahrenkamp, *Chem. Ber.* **1994**, *127*, 2117−2122.
[18] U. Hartmann, R. Gregorzik, H. Vahrenkamp, *Chem. Ber.* **1994**, *127*, 2123−2127.
[19] R. Burth, H. Vahrenkamp, *Z. anorg. allg. Chem.* **1998**, *624*, 381−385.
[20] A. Abufarag, H. Vahrenkamp, *Inorg. Chem.* **1995**, *34*, 2207−2216.

[21] A. Abufarag, H. Vahrenkamp, *Inorg. Chem.* **1995**, *34*, 3279−3284.
[22] A. Trösch, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **1998**, 827−832.
[23] For a triazacyclononane-derived N_3S ligand cf. R. P. Houser, J. A. Halfen, V. G. Young, N. J. Blackburn, W. B. Tolman, *J. Am. Chem. Soc.* **1995**, *117*, 10745−10746.
[24] For related thioether ligands cf. K. Takahashi, E. Ogawa, N. Oishi, Y. Nishida, S. Kida, *Inorg. Chim. Acta* **1982**, *66*, 97-103.
[25] D. Pearson, *J. Polymer. Sci.* **1955**, *17*, 221−233.
[26] J. W. Canary, C. S. Allen, J. M. Castagnetto, Y. Wang, *J. Am. Chem. Soc.* **1995**, *117*, 8484−8485.
[27] A. Marzotto, D. A. Clemente, G. Valle, *Acta Crystallogr., Sect. C.* **1994**, *C 50*, 1451−1456.
[28] N. Matsumoto, T. Akui, A. Okyoshi, H. Okawa, *Bull. Soc. Chim. Jpn.* **1988**, *61*, 2250−2252.
[29] R. J. Sime, R. F. Dodge, A. Zalkin, D. H. Templeton, *Inorg. Chem.* **1971**, *10*, 537−541.
[30] M. Förster, R. Burth, A. K. Powell, T. Eiche, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 2643−2648.
[31] The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre as "supplementary publication no. CCDC-101628 (for **2a**) and -101629 (for **2b**)". Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Telefax: Int. +44-1223/ 336 033; E-mail: deposit@chemcrys.cam.ac.uk).
[32] G. M. Sheldrick, *SHELX-86* and *SHELXL-93*, Programs for Crystal Structure Determination, Universität Göttingen, **1986** and **1993**.
[33] E. Keller, Program *SCHAKAL*, Universität Freiburg, **1993**.
[I98159]