Zinc Complexes of the N,N,S Ligand (Mercaptophenyl)(Picolyl)Amine

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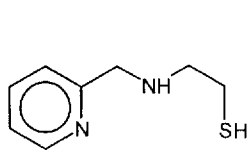
The zinc complex chemistry of the tridentate thiol ligand *N*-(2-mercaptophenyl)(2-picolyl)amine (**MPPAH**) differs considerably from that of the aliphatic analogue *N*-(2-mercaptoethyl)(2-picolyl)amine reported previously. This is due to the lower basicity and hence bridging tendency of its aromatic thiolate function. With zinc salts of oxo anions the 1:1 complexes (**MPPA**)ZnX (**1a–c**: X = ONO_2, OAc, OBz) are formed which according to spectroscopic data are monomeric while the halide (**MPPA**)ZnBr (**2**) seems to be polymeric. In the absence of coordinating anions the monomeric 2:1 complex $(\mathbf{MPPA})_2Zn$ (**3**) results which according to a crystal structure determination contains tetrahedral zinc coordinated by one **MPPA** ligand in a tridentate fashion while the other is only monodentate and sulfur-bound. A similar N_2S_2 coordination can be deduced for the 1:1:1 complex (**MPPA**)Zn(STrt) (**4**) resulting from $ZnEt_2$, **MPPAH** and triphenylmethanethiol.

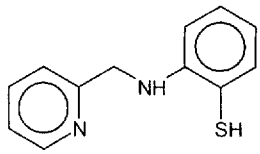
The purpose of our investigations into the zinc complex chemistry of chelating ligands with N and S donors is twofold. Firstly we want to gain an understanding of the factors controlling their coordinative behaviour (stoichiometries, coordination numbers, thiolate bridging, stabilities, etc.). Secondly, we want to learn how to construct structural and possibly functional models of enzymes containing zinc in a ZnN_xS_y environment like liver alcohol dehydrogenase[1], spinach carbonic anhydrase[2], or bovine aminolaevulinate dehydratase[3]. In order to do this we screen known or newly synthesized polydentate amine-thiol ligands for their ligation behavior toward various zinc salts.

In the previous paper of this series[4] we outlined our main objectives and the synthetic approach used to obtain zinc complexes in which the metal is placed into the right steric and electronic environment of N and S donors, the desirable ligand combinations being ZnN_2SX, ZnN_3SX, or $ZnNS_2X$. In these combinations the N and S donors are meant to be provided by one chelating ligand while the group X represents a labile coligand or the substrate of a possible enzyme model. While many chelating ligands exist with the appropriate number of N and S donor functions it must be said that their use for the modelling of the abovementioned enzymes is still an open challenge, despite some impressive results obtained with alcohol dehydrogenase models[5,6].

This paper reports on our investigations with another ligand suitable for the ZnN_2SX combination. This ligand, *N*-(2-mercaptophenyl)(2-picolyl)amine (**MPPAH**) is the aromatic analogue of the aliphatic thiol *N*-(2-mercaptoethyl)(2-picolyl)amine (**MEPAH**)[4]. We found[4] that **MEPAH** yields a puzzling variety of zinc complexes, a dominating feature of which is the tendency of thiolate bridging and hence oligomerization. We hoped that the more rigid nature of the aromatic NCCS unit in **MPPAH** and the lower basicity of its thiolate function would help to suppress this unfavorable property.



MEPAH



MPPAH

Ligand **MPPAH** was first described by Corbin and Work[7]. They reduced the zinc complex of the corresponding picolylimine, described by Livingstone and Lindoy[8], and actually obtained complex **3** (see below) as an intermediate without subjecting it to a detailed characterization. The coordination chemistry of **MPPAH** has not been developed yet to any extent. To our knowledge only some gold complexes have been reported[9].

Syntheses

The reported synthesis of ligand **MPPAH** is a multistep process involving zinc complexes as intermediates[7]. We found a direct process more convenient, using the procedure of Liso et al.[10] with a large excess of $NaBH_4$ for the reduction step. In this way the easily accessible 2-(2-pyridyl)-benzothiazoline[8] could be reduced directly to **MPPAH**. **MPPAH** which is a greenish-yellow viscous oil, insoluble in water and only moderately soluble in methanol, was obtained in almost quantitative yield.

MPPAH was first treated with zinc salts of oxo acids with the aim of obtaining complexes with a ZnN_2SO ligand environment which would be similar to that in enzymes with zinc bound to two histidine units and one cysteine unit like in bovine aminolaevulinate dehydratase[3]. The reaction worked with zinc nitrate, zinc acetate, and zinc benzoate. It did not require the presence of a base to deprotonate the

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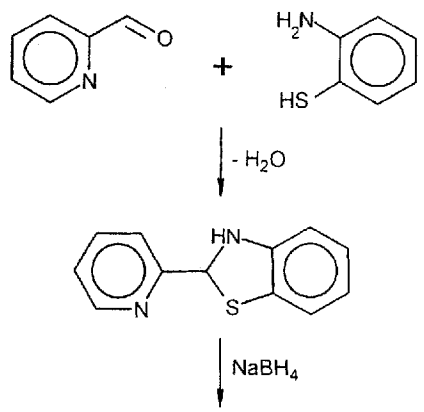
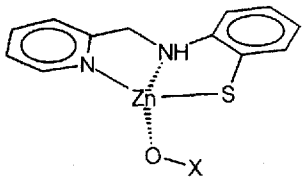


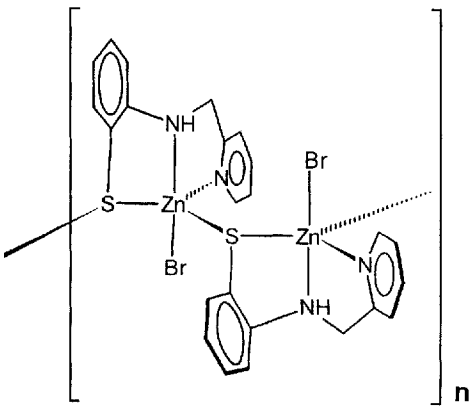
MPPAH

ligand. In all three cases the 1:1 complexes (**MPPA**)ZnX (**1a–c**) were formed. Their good solubility in organic solvents like ethanol or acetonitrile and their spectroscopic data (see below) make us assume (although not with high certainty) that they are mononuclear molecular entities with the shown constitutions.



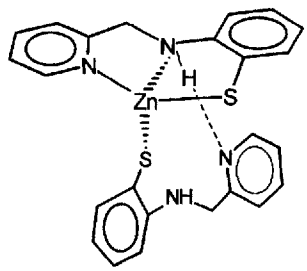
1a: OX = ONO_2
1b: OAc
1c: OBz

In contrast, zinc halides seem to form polymeric complexes with **MPPA**, as evidenced by reactions of deprotonated **MPPAH** with $ZnCl_2$ and $ZnBr_2$. While the use of $ZnCl_2$, as before with **MEPA**[4], leads to impure precipitates of the presumed compound (**MPPA**)ZnCl, an analytically pure complex of composition (**MPPA**)ZnBr (**2**) was obtained with $ZnBr_2$ in good yield. The solubility of **2** in water and organic solvents is only a fraction of that of the complexes **1**. We therefore assume that **2** is a thiolate-bridged oligomer. In analogy to the crystallographic results for the (**MEPA**)ZnHal complexes[4] we therefore suggest the shown constitution for **2**.



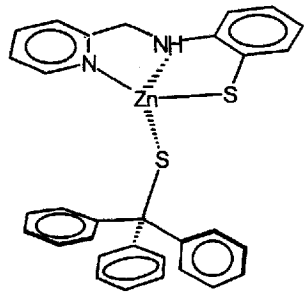
2

The binary compound (**MPPA**)$_2$Zn (**3**) is accessible in many ways. As mentioned above, it was first obtained from a precursor zinc complex as an intermediate in the synthesis of **MPPAH**[7]. We observed that it is accessible, although in low purity, like the binary compound (**MEPA**)$_2$Zn[4] by the solvolysis of molecular zinc compounds like Zn[N(SiMe$_3$)$_2$]$_2$ or $ZnEt_2$ with **MPPAH**. The most efficient method for the preparation of **3** is the reaction of $Zn(ClO_4)_2$ with deprotonated **MPPAH**, a reaction which in the case of **MEPAH** leads to the multiple thiolate-bridged trinuclear cation $[(MEPA)_4Zn_3]^{2+}$[4]. This is the clearest demonstration of the different donor capacities of **MEPA** and **MPPA**, and it is underlined by the fact that the following molecular constitution, obtained from the structure determination (see below), is principally different from that of (**MEPA**)$_2$Zn[4].



3

Complex **3** shows the tetrahedral ZnN_2S_2 coordination which is the most common one for zinc complexes with sulfur and nitrogen ligands[11]. In this way the donor capacity of two suitably placed nitrogen donors is lost. This indicates that a plain monodentate thiolate ligand might be incorporated in place of the monodentate **MPPA** unit of **3**. The realization of this idea was possible by using the sterically demanding triphenylmethanethiolate: treatment of diethylzinc in toluene with **MPPAH** and triphenylmethanethiol yielded (**MPPA**)Zn(STrt) (**4**). The high solubility of **4** in aprotic solvents supports its monomolecular constitution, as derived from that of **3**.



4

Spectra and Constitutions

As crystal suitable for a structure determination were only obtained of **3**, the constitutions of the other complexes had to be deduced by indirect means. An important one of

these is the solubility of the compounds, as mentioned above. In the cases of polymeric **2** and monomeric **4** where supporting spectroscopic information is missing the assignments rest on the solubilities alone. In the cases of **1a** and **1c** the EI-mass spectra support the monomeric formulation although they do not prove it since breaking up of possible dimers in the mass spectrometer cannot be ruled out. Both spectra show the parent ions (m/z = 343 for **1a** and 403 for **1c**) with very small intensity, both show the **MPPA** · Zn cation (m/z = 281) with good intensity, and the **MPPA** ligand ion (m/z = 212) with the highest intensity.

The IR, ^{1}H-, and ^{13}C-NMR data of the compounds are listed in the experimental part. While the ^{13}C-NMR shifts are mainly of diagnostic value the ^{1}H-NMR shifts provide relevant information. With respect to the bonding of the **MPPA** ligand the resonances due to the NCH_2 group and the *para*-H atom of the pyridine ring (H_γ) give the clearest indications. The NCH_2 signals move upfield, those of H_γ downfield upon coordination. The coordination shifts amount to ca. 0.4 ppm except for the binary complex **3** where they are 0.26 and 0.15 ppm, respectively. This latter observation corresponds to the fact that the two **MPPA** ligands in **3** which are nonequivalent in the solid state give rise to only one set of NMR resonances. The simplest explanation for this is a fluxional behavior of **3** in solution consisting in an intramolecular exchange of the tridentate and monodentate **MPPA** ligands. Thus the ^{1}H-NMR resonances of **3** would represent an average of the coordinated and the noncoordinated mode of the picolylamine part of **MPPA**.

Further support for the monomeric nature of the oxo anion complexes **1** can be derived from the NMR data of the carboxylates **1b** and **1c**. If these were dimeric or oligomeric, the substituents of the carboxylate ligands (methyl for **1b**, phenyl for **1c**) would be exposed to the upfield-shift ring-current effects of the aromatic N,N,S ligand on the other zinc ion (for an understanding of the spatial arrangement cf. the formula drawing of **2**), and in the case of **1c** the reverse effect should be visible for the **MPPA** NMR resonances. We have found that such effects can amount to δ = 0.5–0.7 for the acetate ^{1}H-NMR resonance[12]. They are absent in the case of **1b** and **1c** (see Experimental). Instead, the ^{1}H-NMR shift of the OAc group of **1b** corresponds to that of other Zn–OAc groups in an aliphatic environment[4,13]. This and the general similarity of all spectral data and physical properties made us assign the monomeric nature to all three complexes **1**.

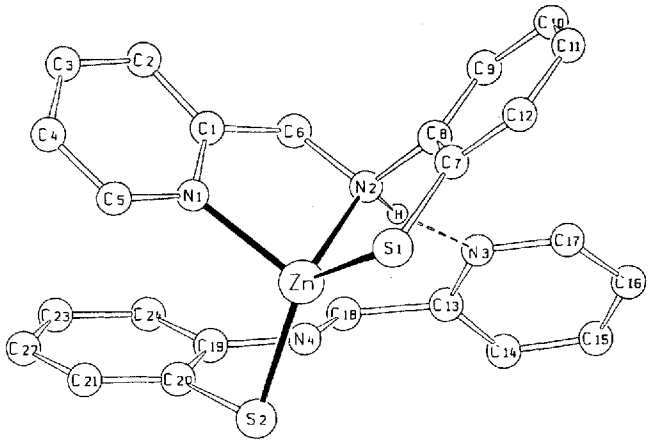
The simplest information obtained from the IR data is the absence of a ν(SH) band (2519 cm^{-1} for free **MPPAH**) for all complexes, proving the thiolate bonding of the **MPPA** ligand. Likewise, the pyridine bonding is evident from the characteristic highfrequency shift[14] of the intensive ring vibration band by 15–20 cm^{-1}, compared to that at 1588 cm^{-1} in free **MPPAH**. While the ν(NH) band is shifted erratically in the IR spectra of the complexes the ^{1}H-NMR resonance of the NCH_2 group (see above) proves the coordination of the amine donor function, thus certifying the tridentate nature of the **MPPA** ligand. An exception to this rule occurs for the ZnL_2 complex **3** showing two strong ring vibration bands at 1606 and 1582 cm^{-1} fitting the coordinated and the non-coordinated pyridine donors.

The only further significant IR information comes from the absorptions due to the oxo anions. The ν(CO) bands of the acetate (1595 and 1394 cm^{-1}) as well as of the benzoate complex (1624 and 1387 cm^{-1}) are indicative of monodentate coordination[15], supporting a truly tetrahedral ZnN_2SO environment. The nitrate bands of **1a** (1475 and 1292 cm^{-1}) indicate neither a clearly monodentate nor a clearly bidentate coordination[15], and it seems to us that they are generally of little value in this respect[16].

Structure Determination

The ZnL_2 complex **3** containing six donor functions offers a rich variety of possible structures including one which would be analogous to that of $(MEPA)_2Zn$[4] containing zinc in a tetrahedral ZnN_2S_2 environment with both pyridine donors being unused. The actual structure, depicted in Figure 1, must be considered a surprise due to the complete disparity of both **MPPA** ligands in terms of their geometry and mode of attachment.

Figure 1. Molecular structure of $(MPPA)_2Zn$ (**3**) in the solid state[a]



[a] Selected bond lengths [Å]: Zn–N1 2.068(2), Zn–N2 2.099(2), Zn–S1 2.261(1), Zn–S2 2.246(1); selected bond angles [°]: N1–Zn–N2 82.58(7), N1–Zn–S1 111.50(5), N1–Zn–S2 109.52(5), N2–Zn–S1 91.87(5), N2–Zn–S2 124.48(5), S1–Zn–S2 127.74(3).

One of the two **MPPA** ligands is attached to zinc in the "normal", i.e. tridentate, fashion while the other is monodentate and bound like a simple thiolate. The resulting ZnN_2S_2 coordination is very far from being ideally tetrahedral. The intra-ligand bond angles at zinc are near or below 90° as usual for five-membered chelate rings. As a compensation for this two of the angles involving the non-chelating thiolate are near or above 125°. The distortion is so severe that the complex approaches a pseudotrigonal-bipyramidal geometry with N2 at one apex and the other apex being vacant. This is puzzling as the donors to fill the vacancy are available and ZnN_3S_2 complexes are not unknown[17,18]. But rather than occupying a coordination position, the free donor atoms prefer to be not involved

(N4) or get engaged in a hydrogen bond (between N3 and the NH function on N2).

The Zn−N and Zn−S bond lengths in **3** are very close to the average values obtainable from a large number of ZnN_2S_2 complexes[4,19]. This holds for other bond lengths or angles within the **MPPA** ligands as well. Thus, there are no unusual features of the ligands which might explain the observed zinc-**MPPA** combination, and except for the peculiar and unsymmetrical choice of the donor atoms complex **3** represents another example of the strict preference of zinc to adopt a N_2S_2 environment when surrounded by N and S donors, in classical complexes[11,19] as well as in many zinc fingers[20,21]. The fact, however, that **MEPA** and **MPPA** use different donor atoms to generate the ZnN_2S_2 combination and that several other arrangements (monomeric or oligomeric) of **MEPA** or **MPPA** ligands around a zinc ion producing the ZnN_2S_2 combination can be envisaged points once more to the subtleties (like the hydrogen bond in **3**) which govern the coordinative behavior of zinc and which we have yet to understand.

Discussion and Conclusions

Almost all differences in the zinc complex chemistry of **MEPA**[4] and **MPPA** can be related to the difference in basicity of their anionic thiolate functions. The main result of this is that Zn-**MEPA** complexes are in general oligomeric containing bridging thiolate while those of **MPPA** seem to prefer the monomeric state containing only terminally bound thiolate. This of course has to be reflected in different coordination modes (N_2S_2X vs. N_2SX) or coordination numbers (5 vs. 4). The most noticeable difference in the chemical behavior shows up in the reactivity towards zinc salts containing weakly coordinating anions: $Zn(ClO_4)_2$ or $Zn(NO_3)_2$ and **MEPAH**, irrespective of the stoichiometric ratio, produce the cations $[Zn_3(\mathbf{MEPA})_4]^{2+}$ in which two octahedral $Zn(\mathbf{MEPA})_2$ molecules offer four thiolate functions to coordinate the central zinc ion while NO_3^- or ClO_4^- remain uncoordinated. With **MPPAH**, in turn, $Zn(ClO_4)_2$ provides only the zinc ion for the formation of the $(\mathbf{MPPA})_2Zn$ complex **3** which is not further converted into a species like $[Zn_3(\mathbf{MPPA})_4]^{2+}$, even in the presence of excess $Zn(ClO_4)_2$, and $Zn(NO_3)_2$ provides the zinc ion and one nitrate ion for the generation of the 1:1 complex $(\mathbf{MPPA})ZnONO_2$ (**1a**). In both cases the possible intermediate $(\mathbf{MPPA})_2Zn$ is unable to function as a donor: it exists as such [**3** from $Zn(ClO_4)_2$] or it surrenders to the donor abilities of the nitrate ion [**1a** from $Zn(NO_3)_2$].

The similarity between **MEPA** and **MPPA** shows up in their halide complexes L · ZnHal which seem to be of the same polymeric nature. The seemingly similar nature of the binary compounds $(\mathbf{MEPA})_2Zn$ and $(\mathbf{MPPA})_2Zn$ has been shown by the structure determinations to exist only in their compositions. It seems, however, that an unexploited similarity between **MEPA** and **MPPA** can be utilized by studying the reactivity of the two binary compounds. As they contain unused donor functions they should be able to act as ligands for other transition metals thereby producing new types of polynuclear ligand-bridged complexes. So far this has been proven for $Zn(ClO_4)_2$ to be successful with $Zn(\mathbf{MEPA})_2$[4] and to fail with $Zn(\mathbf{MPPA})_2$ (see above). It can be predicted that hard Lewis acids will pick up the free nitrogen donors of $Zn(\mathbf{MPPA})_2$ while soft Lewis acids will make use of the bridging capacity of the thiolate functions in $Zn(\mathbf{MEPA})_2$.

The prospects of ligand **MPPAH** for the coordination chemistry of zinc are twofold: (i) it promises to be a reliable N,N,S coligand L for functional tetrahedral complexes L · ZnX, and (ii) the binary compound $(\mathbf{MPPA})_2Zn$ promises to be the starting point for a derivative chemistry based on the donor capacity of the two uncoordinated nitrogen functions.

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Experimental

All experimental techniques and the standard IR and NMR equipment were as described previously[22]. EI-mass spectra were recorded with a Finnigan-MAT 8230 spectrometer. Starting materials were obtained commercially. All sulfur-containing materials were handled and kept under prepurified nitrogen. All organic solvents were dried and degassed, water was deionized and saturated with nitrogen. 2-(2-Pyridyl)benzothiazoline was prepared according to the published procedure[8].

N-(2-mercaptophenyl)(2-picolyl)amine (**MPPAH**): To a solution of 5.00 g (23.3 mmol) of 2-(2-pyridyl)benzothiazoline[8] in 200 ml of methanol 8.83 g (233 mmol) of $NaBH_4$ was added in small portions with stirring. After completion of the strongly exothermic reaction and cooling of the mixture to room temp. the solvent was removed in a rotary evaporator. The solid residue was suspended in 250 ml of ice water and the suspension neutralized carefully with glacial acetic acid. The greenish-yellow emulsion was extracted four times with 50 ml of dichloromethane each. The combined extracts were washed with 50 ml of water and dried with Na_2SO_4. Then the solvent was reduced in vacuo and the residue kept in vacuo with slight warming for 5 h. 4.76 g (94%) of chemically pure **MPPAH** remained as a greenish-yellow viscous oil. A solid sample for elemental analyses was obtained with big losses by crystallization from ethanol. – IR (film, cm^{-1}): $\tilde{\nu}$ = 3360 m, N−H; 3063 w, 3009 w, aryl C−H; 2923 w, 2852 w, alkyl C−H, 2519 w, S−H; 1588 vs, 1568 s, pyridine C=N; 1501 vs, 1472 vs, 1445 s, 1427 s, pyridine and phenyl C=C; 1353 w, 1319 s, 1286 m, 1246 w, 1231 w, 1212 w, 1183 w, 1162 w, 1147 w, 1138 w, 1109 w, 1088 w, 1040 w, 994 w, 958 w, 907 w, 823 w, 786 w, 746 vs, 713 w, 667 sh, m, 641 sh. – ^{1}H NMR ($CDCl_3$): δ = 4.53 [s, 2H, CH_2], 6.58 [dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, phenyl H6], 6.66 [dt, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, phenyl H4], 7.15 [dt, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, phenyl H5], 7.19 [t, br, ^3J = 7.2 Hz, 1H, pyridine H_β], 7.32 [d, br, ^3J = 7.2 Hz, 1H, pyridine H_δ], 7.43 [dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1H, phenyl H3], 7.65 [dt, ^3J = 7.2 Hz, ^4J = 1.7 Hz, 1H, pyridine H_γ], 8.61 [d, br, ^3J = 7.2 Hz, 1H, pyridine H_α]. – ^{13}C NMR ($CDCl_3$): δ = 48.9 [CH_2], 110.5 [phenyl C6], 111.4 [phenyl C2], 117.0 [phenyl C4], 121.0 [pyridine C_β or C_δ], 121.8 [pyridine C_β or C_δ], 129.1 [phenyl C5], 134.9 [phenyl C3], 136.3 [pyridine C_γ], 147.8 [phenyl C1], 148.9 [pyridine C_α], 157.8 [pyridine $C_{quat.}$]. – $C_{12}H_{12}N_2S$ (216.3): calcd. C 66.63, H 5.59, N 12.95; found C 66.79, H 5.32, N 12.87.

(MPPA)ZnONO$_2$ (**1a**): A solution of 339 mg (1.57 mmol) of **MPPAH** in 35 ml of ethanol was treated dropwise with stirring

with 411 mg (1.57 mmol) of $Zn(NO_3)_2 \cdot 4\ H_2O$ in 30 ml of ethanol. The solution was reduced in vacuo to 10 ml and allowed to stand for 2 d. Filtration yielded 87 mg (16%) of **1a** as colorless crystals, m.p. 192 °C (dec.). – Selected IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3183 m, N–H; 1609 m, 1585 w, pyridine; 1475 vs, 1292 vs, nitrate. – ^1H NMR ([D$_6$]DMSO): δ = 4.13 [d, br, ^3J = 6.7 Hz, CH_2], 6.16 [t, ^3J = 6.7 Hz, 1H, NH], 6.87–7.03 [m, 2H, phenyl H4 and H5], 7.23 [d, br, ^3J = 7.2 Hz, 1H, phenyl H6], 7.40 [dd, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, phenyl H3], 7.61–7.73 [m, br, 2H, pyridine H_δ and H_β], 8.14 [t, br, ^3J = 7.9 Hz, 1H, pyridine H_γ], 8.71 [d, br, ^3J = 5.3 Hz, 1H, pyridine H_α]. – ^{13}C NMR ([D$_6$]DMSO): δ = 52.8 [CH_2], 122.3 [pyridine C_β or C_δ], 123.8 [pyridine C_β or C_δ], 124.2, 124.7, 126.0, 132.0, 141.0 [aromatic], 141.9 [pyridine C_γ], 142.6 [phenyl C1], 148.0 [pyridine C_α], 156.5 [pyridine $C_{quat.}$]. – $C_{12}H_{11}N_3O_3SZn$ (342.7): calcd. C 42.06, H 3.24, N 12.26; found C 42.00, H 3.32, N 12.09.

(MPPA)ZnOAc (**1b**). A solution of 1.13 g (5.21 mmol) of **MPPA** in 20 ml of ethnol was treated with 1.14 g (5.21 mmol) of $Zn(OAc)_2 \cdot 2\ H_2O$ with stirring. The resulting brownish solution was stirred for 1 h. Dropwise addition of 20 ml of diethyl ether produced a precipitate which was filtered off, washed with diethyl ether, and dried in vacuo to furnish 683 mg (39%) of **1b** as an off-white powder, m.p. 140 °C (dec.). – Selected IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3259 w, N–H; 1607 s, 1583 sh, pyridine; 1595 s, 1394 m, acetate. – ^1H NMR (CD_3OD): δ = 1.92 [s, 3H, CH_3], 4.23 [s, 2H, CH_2], 6.90 [dt, ^3J = 7.3 Hz, ^4J = 2.1 Hz, 1H, phenyl H4], 6.95 [dt, ^3J = 7.4 Hz, ^4J = 1.7 Hz, 1H, phenyl H5], 7.16 [dd, ^3J = 7.3 Hz, ^4J = 1.9 Hz, 1H, phenyl H6], 7.43 [dd, ^3J = 7.4 Hz, ^4J = 2.3 Hz, 1H, phenyl H3], 7.54–7.63 [m, br, 2H, pyridine H_β and H_δ], 8.07 [dt, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, pyridine H_γ], 8.74 [d, br, ^3J = 4.8 Hz, 1H, pyridine H_α]. – ^{13}C NMR (CD_3OD): δ = 23.1 [CH_3], 54.7 [CH_2], 124.6 [pyridine C_β or C_δ], 125.1 [pyridine C_β or C_δ], 125.7, 127.4, 134.1 [aromatic], 141.9 [pyridine C_γ], 144.5 [phenyl C1], 149.4 [pyridine C_α], 158.1 [pyridine $C_{quat.}$]. – $C_{14}H_{14}N_2O_2SZn$ (339.7): calcd. C 49.49, H 4.15, N 8.25; found C 48.82, H 4.08, N 7.92.

(MPPA)Zn(OBz) (**1c**): To a solution of 224 mg (1.04 mmol) of **MPPAH** in 15 ml of acetonitrile 319 mg (1.04 mmol) of $Zn(OBz)_2$ was added and the mixture was stirred for 8 h. The resulting precipitate was filtered off, washed with a small amount of acetonitrile and dried in vacuo to afford 293 mg (70%) of **1c** as a greenish-white powder, m.p. 225 °C (dec.). – Selected IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3139 w, N–H; 1608 s, 1566 m, pyridine; 1624 sh, 1387 s, benzoate. – ^1H NMR ([D$_6$]DMSO): δ = 4.26 [d, ^3J = 7.4 Hz, CH_2], 6.20 [t, ^3J = 7.4 Hz, 1H, NH], 6.83 [dt, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1H, phenyl H4], 6.90 [dt., ^3J = 7.0 Hz, ^4J = 1.7 Hz, 1H, phenyl H5], 7.24 [dd, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1H, phenyl H6], 7.31–7.40 [m, 4H, phenyl H3, benzoate H_{para} and H_{meta}), 7.58–7.66 [m, 2H, pyridine H_β and H_δ], 7.91 [dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 2H, benzoate H_{ortho}], 8.08 [dt, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, pyridine H_γ], 8.80 [dd, ^3J = 5.6 Hz, ^4J = 1.3 Hz, 1H, pyridine H_α]. – ^{13}C NMR ([D$_6$]DMSO): δ = 52.9 [CH_2], 121.6, 123.2 [aromatic], 124.0 [pyridine C_β or C_δ], 124.1 [pyridine C_β or C_δ], 125.4, 127.7, 129.3, 130.6, 131.9, 135.6, 137.8 [aromatic], 140.2 [pyridine C_γ], 143.5 [phenyl C1], 148.3 [pyridine C_α], 156.6 [pyridine $C_{quat.}$], 170.9 [benzoate COO]. – $C_{19}H_{16}N_2O_2SZn$ (401.8): calcd. C 56.79, H 4.01, N 6.97; found C 57.06, H 3.83, N 6.55.

(MPPA)ZnBr (**2**): 278 mg (1.29 mmol) of **MPPAH** was dissolved in a solution of 52 mg (1.3 mmol) of NaOH in 10 ml of methanol. To this solution, a solution of 289 mg (1.29 mmol) of $ZnBr_2$ in 4 ml of methanol was added dropwise with stirring. Within a few minutes precipitation of the product began which was complete after 2 h of stirring. The precipitate was filtered off, washed with methanol and dried in vacuo to afford 307 mg (66%) of **2** as an ocherous powder, m.p. 275 °C (dec.). – Selected IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3163 s, N–H, 1608 s, 1583 m, pyridine. – ^1H NMR ([D$_6$]DMSO): δ = 4.09 [d, ^3J = 6.9 Hz, 2H, CH_2], 5.88 [t, br, ^3J = 6.9 Hz, 1H, NH], 6.83 [dt, ^3J = 7.4 Hz, ^4J = 1.7 Hz, 1H, phenyl H4], 6.89 [dt, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1H, phenyl H5], 7.15 [dd, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1H, phenyl H6], 7.33 [dd, ^3J = 7.3 Hz, ^4J = 1.8 Hz, 1H, phenyl H3], 7.56–7.67 [m, 2H, pyridine H_β and H_δ], 8.08 [dt, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1H, pyridine H_γ], 8.75 [d, br, ^3J = 4.9 Hz, 1H, pyridine H_α]. – ^{13}C NMR ([D$_6$]DMSO): δ = 52.8 [pyridine CH_2], 121.7, 123.3 [pyridine C_β or C_δ], 123.7 [pyridine C_β or C_δ], 124.2, 125.2, 131.8, 140.3 [aromatic], 142.4 [pyridine C_γ], 143.4 [phenyl C1], 148.1 [pyridine C_α], 156.5 [pyridine $C_{quat.}$]. – $C_{12}H_{11}BrN_2SZn$ (360.6): calcd. C 39.97, H 3.07, N 7.77; found C 39.72, H 2.95, N 7.69.

(MPPA)$_2$Zn (**3**): Solutions of 457 mg (2.11 mmol) of **MPPAH** in 20 ml of dichloromethane and 279 mg (4.22 mmol) of KOH in 7 ml of methanol were combined. A solution of 789 mg (2.12 mmol) of $Zn(ClO_4)_2 \cdot 6\ H_2O$ in 10 ml of methanol and 10 ml of dichloromethane was added dropwise with stirring. After 1 h of stirring the solution was filtered and the filtrate reduced to 15 ml in vacuo. Within 2 days a precipitate of **3** was formed which was filtered off and dried in vacuo to yield 137 mg (26%) of **3** as colorless crystals of X-ray quality, m.p. 148 °C (dec.). – Selected IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3329 w, N–H, 1606 s, 1582 s, 1569 sh, pyridine. – ^1H NMR ([D$_6$]DMSO): δ = 4.27 [s, 4H, CH_2], 6.04 [s, br, 2H, NH], 6.57 [dt, ^3J = 7.7 Hz, ^4J = 2.3 Hz, 2H, phenyl H4], 6.68–6.82 [m, 4H, phenyl H5 and H6], 7.24–7.38 [m, 6H, phenyl H3, pyridine H_β and H_δ], 7.80 [dt, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 2H, pyridine H_γ], 8.35 [dd, ^3J = 4.9 Hz, ^4J = 1.8 Hz, 2H, pyridine H_α]. – ^{13}C NMR ([D$_6$]DMSO): δ = 51.2 [CH_2], 116.5, 120.8, 122.1 [aromatic], 122.7 [pyridine C_β or C_δ], 122.9 [pyridine C_β or C_δ], 133.0, 134.9 [aromatic], 138.2 [pyridine C_γ], 145.4 [phenyl C1], 148.3 [pyridine C_α], 157.5 [$C_{quat.}$]. – $C_{24}H_{22}N_4S_2Zn$ (496.0): calcd. C 58.12, H 4.47, N 11.30; found C 58.21, H 4.50, N 11.33.

(MPPA)Zn(STrt) (**4**): To a solution of 619 mg (2.87 mmol) of **MPPAH** and 791 mg (2.86 mmol) of triphenylmethanethiol in 50 ml of oxygen- and water-free toluene, stirring with 3.80 ml (3.80 mmol) of a 1 M solution of diethylzinc in toluene was slowly added dropwise. Then 4 ml of ethanol was added to destroy excess $ZnEt_2$ and the mixture was stirred for 30 min. The solution was reduced to 10 ml in vacuo and the precipitate of **4** filtered off. Recrystallization from hot acetonitrile yielded 853 mg (54%) of **4** as an ocherous powder, m.p. 158 °C. – Selected IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3281 w, N–H; 1602 m, 1585 w, pyridine. – ^1H NMR ($CDCl_3$): δ = 3.08–3.21 [s, br, 1H, NH], 4.17 [d, ^3J = 7.4 Hz, CH_2], 6.78–6.90 [m, 2H, phenyl H4 and H6], 6.97 [dt, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, phenyl H5], 7.03–7.12 [m, 9H, trityl H_{para} and H_{meta}], 7.17 [d, ^3J = 7.7 Hz, 1H, phenyl H3], 7.33–7.52 [m, 8H, trityl H_{ortho}, pyridine H_β and H_δ], 7.81 [dt, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, pyridine H_γ], 8.56 [d, br, ^3J = 5.4 Hz, 1H, pyridine H_α]. – The ^{13}C NMR spectrum ($CDCl_3$) was so dominated by the aromatic carbon signals that the aliphatic signals could not be assigned with certainty. – $C_{31}H_{26}N_2S_2Zn$ (556.1): calcd. C 66.96, H 4.71, N 5.04; found C 66.77, H 4.74, N 5.22.

Structure Determination[23]. Crystals of **3** were obtained from the reaction solution: $C_{24}H_{22}N_4S_2Zn$, mol. wt. 496.0, colorless, crystal size 0.5 · 0.4 · 0.3 mm, space group *P*-1, Z = 2, a = 8.650(2), b = 11.543(2), c = 11.839(2) Å, α = 79.89(3), β = 83.26(3), γ = 78.90(3)°, V = 1137.7(4) Å^3, $d_{calcd.}$ = 1.45, $d_{exp.}$ = 1.48 g/cm^3, μ(Mo-K_α) = 12.8 cm^{-1}. Diffraction data were recorded with the ω/2Θ technique in the 2Θ range 5–53° with a Nonius CAD4 dif-

fractometer with molybdenum radiation (λ = 0.71073 Å) and a graphite monochromator, for the index ranges $-10 \leq h \leq 0$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$. 4937 reflections were recorded of which 4618 were independent ($R_{int.}$ = 0.011), and 4075 with $I \geq 2\sigma(I)$ were used. After an empirical absorption correction[24] the structure was solved with direct methods and refined anisotropically. Hydrogen atoms were included at fixed positions (C–H = N–H = 0.96 Å), their isotropic temperature factors were fixed at 1.2 times the value of the C or N atoms attached to them. The final unweighted R value was 0.033 for 280 parameters. The residual electron density extrema were +0.6 and −0.7 e/Å^3. All crystallographic computations were performed with the SHELX program system[25], the drawing was produced by using SCHAKAL[26].

[1] H. Eklund, B. Nordström, E. Zeppezauer, G. Soderlund, I. Ohlsson, T. Bowie, B. O. Soderberg, O. Tapia, C. I. Brändén, *J. Mol. Biol.* **1976**, *102*, 27–59.

[2] M. H. Bracey, J. Christiansen, P. Tovar, S. P. Cramer, S. G. Bartlett, *Biochemistry* **1994**, *33*, 13126–13131.

[3] A. J. Dent, D. Beyersmann, C. Block, S. S. Hasnain, *Biochemistry* **1990**, *29*, 7822–7828.

[4] U. Brand, H. Vahrenkamp, *Inorg. Chem.* **1995**, *31*, 3285–3293.

[5] B. Kaptein, L. Wang-Griffin, G. Barf, R. M. Kellogg, *J. Chem. Soc., Chem. Commun.* **1987**, 1457–1459.

[6] N. J. Curtis, R. S. Brown, *Can. J. Chem.* **1981**, *59*, 65. M. Bochmann, K. J. Webb, M. B. Hursthouse, M. Mazid, *J. Chem. Soc., Chem. Commun.* **1991**, 1735–1737.

[7] J. L. Corbin, D. E. Work, *Can. J. Chem.* **1974**, *52*, 1054–1058.

[8] L. F. Lindoy, S. E. Livingstone, *Inorg. Chim. Acta* **1967**, *1*, 365–369.

[9] A. P. Koley, R. Nirmala, L. S. Prasad, S. Ghosh, P. T. Manoharan, *Inorg. Chem.* **1992**, *31*, 1764–1769.

[10] G. Liso, G. Trapani, A. Reho, A. Latrofa, *Synthesis* **1985**, *3*, 288–290.

[11] R. H. Prince in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, Oxford, **1987**, Vol. 5, pp. 925–1045.

[12] R. Alsfasser, A. K. Powell, S. Trofimenko, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 685–694. Cf. I. B. Gorell, A. Looney, G. Parkin, *J. Chem. Soc., Chem. Commun.* **1990**, 220–222.

[13] U. Brand, H. Vahrenkamp, *Inorg. Chim. Acta* **1992**, *198*, 663–669.

[14] M. M. da Mota, J. Rodgers, S. M. Nelson, *J. Chem. Soc. (A)* **1969**, 2036–2046.

[15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Ed., Wiley, New York, **1978**.

[16] R. Gregorzik, U. Hartmann, H. Vahrenkamp, *Chem. Ber.* **1994**, *127*, 2117–2122. R. Gregorzik, J. Wirbser, H. Vahrenkamp, *Chem. Ber.* **1992**, *125*, 1575–1581.

[17] P. G. Harrison, M. J. Begley, T. Kikabhai, F. Killer, *J. Chem. Soc. Dalton Trans.* **1986**, 929–938.

[18] V. L. Goedken, G. G. Christoph, *Inorg. Chem.* **1973**, *12*, 2316–2320.

[19] D. T. Corwin, S. A. Koch, *Inorg. Chem.* **1988**, *27*, 493–496, and references cited therein.

[20] G. P. Diahun, L. Fairall, A. Klug, *Nature* **1986**, *324*, 698–699. J. G. Omichinski, G. M. Clore, E. Appella, K. Sakaguchi, A. M. Gronenborn, *Biochemistry* **1990**, *29*, 9324–9334. J. E. Coleman, *Ann. Rev. Biochem.* **1992**, *61*, 897–945.

[21] J. M. Berg, *Acc. Chem. Res.* **1995**, *28*, 14–19.

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

[23] Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, giving reference to the depository number CSD-404379 and citing the authors and this paper.

[24] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158–166.

[25] G. M. Sheldrick, SHELXS and SHELXL, Universität Göttingen, **1986** and **1993**.

[26] E. Keller, SCHAKAL, Universität Freiburg, **1993**.

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