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A New Tridentate N,N,S Ligand and Its Zinc Complexes

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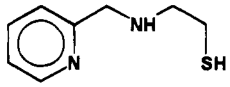
The tridentate thiol ligand *N*-(2-mercaptoethyl)picolylamine (MEPAH) which is obtained from picolylamine and ethylene sulfide shows a very variable zinc complex chemistry. With zinc salts of noncoordinating anions it forms the trinuclear complexes [(MEPA)$_4$Zn$_3$]X$_2$ (**1a**−**c**: X = BF$_4$, ClO$_4$, NO$_3$). With zinc halides it produces the polymeric 1:1 complexes (MEPA)ZnHal (**2a**,**b**: Hal = Cl, Br), and with zinc acetate the dimeric 1:1 complex (MEPA)ZnOAc (**3**) results. The 2:1 complex (MEPA)$_2$Zn (**4**) is obtained by the reaction with Zn[N(SiMe$_3$)$_2$]$_2$. The mixed-ligand complex (MEPA)Zn(2-(hydroxymethyl)benzenethiolate) (**5**) results from Zn[N(SiMe$_3$)$_2$]$_2$, MEPAH, and the thiol, and the mixed-ligand complex (MEPA)Zn(quinoline-2-carboxylate) (**6**) is formed from Zn(ClO$_4$)$_2$, MEPAH, and the acid. Crystal structure determinations have revealed one tetrahedral ZnS$_4$ and two octahedral ZnN$_4$S$_2$ units in **1a**, trigonal-bipyramidal ZnN$_2$S$_2$Cl coordination in **2a**, square-pyramidal ZnN$_2$S$_2$O coordination in **3**, tetrahedral ZnN$_2$S$_2$ coordination in **4**, and a trigonal-bipyramidal arrangement of the two chelate ligands in **6** yielding a ZnN$_3$SO coordination. The unusual bonding situation (only bidentate) of the MEPA ligand in the 2:1 complex **4** results in the facile conversion of **4** to the trinuclear complexes **1a**−**c** upon reaction with the zinc salts and to the polymeric complex **2a** upon reaction with CH$_2$Cl$_2$ or HCl.

Introduction

The Zn^{2+} ion is known to have a high affinity toward nitrogen and sulfur donor ligands, as demonstrated by a considerable body of knowledge on Zn(N,S ligand) complexes.[1] In biological systems the so-called structural zinc in enzymes or zinc fingers[2,3] is almost always attached to at least one sulfur atom of cysteine, as is the zinc in the active centers of the enzymes liver alcohol dehydrogenase,[4] spinach carbonic anhydrase,[5] or bovine aminolaevulinate dehydratase.[6] In these enzymes the functional zinc is surrounded by a N$_x$S$_y$ donor set provided by the amino acids histidine and cysteine.

In order to model such ZnN$_x$S$_y$ environments one needs multidentate N,S ligands which ideally should fulfill the following conditions: (i) they should contain the correct number of N and S donors, (ii) they should encapsulate the metal such that oligomerizations via bridging sulfur atoms are prevented, (iii) they should leave room for a labile ligand which may be replaced by a reacting substrate, and (iv) they should provide the right charge and electronic environment to the metal to tune it for its catalytic function. No such ligand has been found yet for zinc complexes, despite noticeable achievements in the modeling of alcohol dehydrogenase[7,8] or of zinc finger motifs.[9]

After putting some effort in constructing ligands that model a ZnN$_3$X[10] or ZnN$_3$OX[11] environment of zinc enzymes, we have now tackled the more difficult task of finding ligands for a ZnN$_2$SX, ZnN$_3$SX, or ZnNS$_2$X environment. This paper reports our findings for the new N$_2$S ligand *N*-(2-mercaptoethyl)picolylamine (MEPAH). They complement and extend the work on zinc complexes of chelating amine−thiol ligands by other research groups like those of Sellmann,[12] Darensbourg,[13] Gonzales-Duarte,[14] Audeev,[15] and Kellogg.[8]



MEPAH

Experimental Section

General Methods. All experimental techniques and the standard IR and NMR equipment were described previously.[16] Starting materials were obtained commercially. All sulfur-containing materials were handled and kept under an atmosphere of prepurified nitrogen. All organic solvents were dried and degassed; water was deionized and saturated with nitrogen. Zn[N(SiMe$_3$)$_2$]$_2$[17] and 2-(hydroxymethyl)benzenethiol[18] were prepared according to the published procedures.

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1995.

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Preparations. Warning: Perchlorate salts of metal complexes are potentially explosive.[19] They must be handled with great caution and in small quantities. Laboratories not equipped with appropriate safety gear are advised to perform the preparations of **1b** and **6** with quantities of 1 g or less of zinc perchlorate.

N-(2-Mercaptoethyl)picolylamine (MEPAH). 2-Picolylamine was freshly distilled from CaH_2. A solution of 2-picolylamine (5.79 g, 53.5 mmol) in toluene (20 mL) was heated to reflux. A solution of ethylene sulfide (1.56 g, 26.0 mmol) in toluene (40 mL) was slowly added dropwise. After stirring of the boiling solution for 15 h, the solvent was removed in vacuo. Fractional distillation over a 15 cm Vigreux column yielded 3.02 g (69%) of MEPAH boiling at 96−105 °C (0.5 mm) as a colorless liquid. Anal. Calc for $C_8H_{12}N_2S$ (168.3): C, 57.10; H, 7.19; N, 16.65. Found: C, 57.29; H, 7.15; N, 16.85. IR (film, cm^{-1}): 3309 m, N−H; 3079 w, 3059 w, 3008 w, pyridine C−H; 2929 m, 2892 sh, w, 2824 m, alkyl C−H; 2540 w, S−H; 1589 vs, 1568 s, pyridine C=N; 1473 s, 1453 s, pyridine C=C; 1432 vs, 1358 w, 1332 w, 1293 w, 1225 w, 1146 m, 1125 s, 1047 m, 994 m, 839 w, 755 vs, 728 m, 669 sh, 654 sh, 627 w. ^{1}H-NMR ($CDCl_3$): 1.90 [s, br, 2H, SH and NH], 2.69 [t, $^3J = 6.1$ Hz, 2H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{S}$], 2.87 [t, $^3J = 6.1$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2S}$], 3.92 [s, 2H, pyridine-CH_2], 7.15 [dt, $^3J = 7.1$ Hz, $^4J = 1.6$ Hz, 1H, pyridine H_β], 7.32 [d, $^3J = 8.5$ Hz, 1H, pyridine H_δ], 7.64 [dt, $^3J = 8.5$ Hz, $^4J = 1.8$ Hz, 1H, pyridine H_γ], 8.54 [d, $^3J = 7.1$ Hz, 1H, pyridine H_α]. ^{13}C-NMR ($CDCl_3$): 24.8 [$\mathrm{NCH_2}\mathit{C}\mathrm{H_2S}$], 51.7 [$\mathrm{N}\mathit{C}\mathrm{H_2CH_2S}$], 54.4 [pyridine-$CH_2$], 121.7 [pyridine C_β or C_δ], 121.9 [pyridine C_β or C_δ], 136.2 [pyridine C_γ], 149.1 [pyridine C_α], 159.4 [pyridine C_{quat}].

[(MEPA)$_4$Zn$_3$](BF$_4$)$_2$·2H$_2$O (1a). MEPAH (563 mg, 3.34 mmol) and NaOH (134 mg, 3.35 mmol) were dissolved in water (20 mL). A solution of $Zn(BF_4)_2.6H_2O$ (581 mg, 1.67 mmol) in water (10 mL) was added dropwise with stirring. After being stirred for 30 min, the solution was freeze-dried. The solid residue was picked up in 5 mL of water, 10 mL of ethanol was added, and the solution was placed in a desiccator over $CaCl_2$. Within 10 d a total of 321 mg (48% yield based on Zn) of **1a** had precipitated as colorless crystals of mp 240 °C (dec) which were washed with cold ethanol and dried. Anal. Calc for $C_{32}H_{44}B_2F_8N_8S_4Zn_3{\cdot}2H_2O$ (1038.8 + 36.0): C, 35.76; H, 4.50; N, 10.43; Zn, 18.3. Found: C, 36.00; H, 4.50; N, 10.47; Zn, 18.2. IR (KBr, cm^{-1}): 3545 s, 3438 s, O−H; 3272 s, 3221 s, N−H; 3084 w, 3059 w, pyridine C−H; 2950, 2921 m, 2873 m, 2835 w, alkyl C−H; 1639 m; 1606 vs, 1573 w, pyridine C=N; 1486 m, 1459 m, pyridine C=C; 1445 s, 1426 m, 1385 w, 1342 w, 1322 m, 1313 s, 1296 s, 1275 w, 1233 w, 1182 m, 1160 m; 1108 vs, 1085 vs, 1060 vs, 1037 vs, 1015 vs, tetrafluoroborate; 995 vs, 959 s, 937 s, 894 w, 844 m, 828 sh, 817 w, 763 vs, 734 w, 666 w, 642 w, 619 w. Raman (powder, cm^{-1}): 1608 w, 1573 w, pyridine C=N; 1461 m, 1428 w, 1233 m, 1058 vs, 1017 w, 819 w, 667 s, 643 m, 469 w, 332 m, 292 m, 257 m, 233 m, 120 m, 94 m, 77 m. ^{1}H-NMR (d_6-DMSO): 2.35−3.05 [m, br, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$], 3.80−4.09 [m, br, 4H, pyridine $\mathrm{C}\mathit{H}\mathrm{H}$], 4.31−4.47 [m, br, 4H, pyridine $\mathrm{CH}\mathit{H}$], 4.63−4.80 [s, br, 4H, NH], 7.37−7.54 [s, br, 4H, pyridine H_β], 7.61 [d, $^3J = 8.3$ Hz, 4H, pyridine H_δ], 8.01 [t, $^3J = 7.9$ Hz, 4H, pyridine H_γ], 8.28−8.59 [m, br, 4H, pyridine H_α]. ^{13}C-NMR (d_6-DMSO): 26.8 [br, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2S}$], 50.3 [br, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2S}$], 51.8 [br, pyridine CH_2], 123.4 [pyridine C_β or C_δ], 124.1 [pyridine C_β or C_δ], 139.5 [pyridine C_γ], 146.7 [pyridine C_α], 155.4 [pyridine C_{quat}].

[(MEPA)$_4$Zn$_3$](ClO$_4$)$_2$·2H$_2$O (1b). MEPAH (303 mg, 1.80 mmol) and NaOH (72 mg, 1.80 mmol) were dissolved in water (40 mL). A solution of $Zn(ClO_4)_2.6H_2O$ (504 mg, 1.35 mmol) in water (15 mL) was added dropwise with stirring. The resulting precipitate was stirred for 30 min and then filtered off, washed with a few milliliters of water, and dried in vacuo. Recrystallization from water/methanol (1:1) yielded 418 mg (84% based on Zn) of **1b** as colorless crystals, mp 220 °C (dec). Anal. Calc for $C_{32}H_{44}Cl_2N_8O_8S_4Zn_3{\cdot}2H_2O$ (1064.1 + 36.0): C, 34.94; H, 4.40; N, 10.19. Found: C, 35.01; H, 4.29; N, 10.12. IR (KBr, cm^{-1}): 3511 m, 3431 m, O−H; 3259 m, 3222 m, N−H; 3078 w, 3056 w, pyridine C−H; 1637 w, 1606 s, 1572 w, pyridine C=N; 1486 m, 1459 m, pyridine C=C; 1444 s, 1426 m, 1385 w, 1312 m, 1294 m, 1263 w, 1220 w, 1179 w, 1157 m; 1116 sh, 1090 vs, br, 1056 sh, perchlorate; 1031 m, 1016 s, 988 m, 958 w, 933 m, 843 w, 818 w, 764 s, 732 w, 666 w, 623 w. The NMR spectra of **1b** are identical with those of **1a**.

[(MEPA)$_4$Zn$_3$](NO$_3$)$_2$·2H$_2$O (1c). **1c** was synthesized in the same manner as **1b** from MEPAH (355 mg, 2.11 mmol) and NaOH (84 mg, 2.10 mmol) in methanol (20 mL) as well as $Zn(NO_3)_2{\cdot}4H_2O$ (552 mg, 2.11 mmol) in methanol (10 mL). The precipitate, containing analytically pure **1c** (479 mg, 89% based on MEPAH), was filtered off, washed with methanol, and dried in vacuo, mp 240 °C (dec). Anal. Calc for $C_{32}H_{44}N_{10}O_6S_4Zn_3{\cdot}2H_2O$ (989.1 + 36.0): C, 37.49; H, 4.72; N, 13.66. Found: C, 37.63; H, 4.52; N, 13.71. IR (KBr, cm^{-1}): 3472 m, 3385 sh, m, O−H; 3199 m, N−H; 3067 w, 3058 sh, w, pyridine C−H; 2927 m, 2865 w, alkyl C−H; 1638 s; 1604 s, 1571 w, pyridine C=N; 1485 m, 1459 m, pyridine C=C; 1444 m, 1426 m, 1400 sh, s; 1383 vs, nitrate; 1356 sh, s, 1330 s, 1311 s, 1294 s, 1271 m, 1223 w, 1177 w, 1157 w, 1102 m, 1085 s; 767 s, C-S; 737 w, 666 w, 646 w, 619 w. The NMR spectra of **1c** are identical to those of **1a**.

(MEPA)ZnCl (2a). Attempts to prepare **2a** from $ZnCl_2$ according to the procedure given below for **2b** resulted in a product of only 90% or less purity, probably due to the high tendeny of $ZnCl_2$ for hydrolysis. Analytically pure **2a** was, however, obtained from the reactions of **4** with CH_2Cl_2 or HCl (see below). **2a** forms colorless crystals of mp 200 °C (dec) after crystallization from dichloromethane. Anal. Calc for $C_8H_{11}N_2SZnCl{\cdot}{}^1/_2CH_2Cl_2$ (268.1 + 42.5): C, 32.87; H, 3.89; N, 9.02; Zn, 21.1. Found: C, 32.76; H, 3.85; N, 8.90; Zn, 21.2. IR (KBr, cm^{-1}): 3219 vs, N−H; 3023 m, pyridine C−H; 2934 m, 2900 w, 2844 m, akyl C−H; 1607 m, 1572 w, pyridine C=N; 1487 w, 1477 w, 1436 m, pyridine C=C; 1417 w, 1368 w, 1297 m, 1281 m, 1266 w, 1218 w, 1183 w, 1153 w, 1147 m, 1101 w, 1056 m, 1034 m, 1019 m, 995 w, 946 m, 928 m, 813 w, 763 s, 729 s, 699 w, 671 w, 644 w. ^{1}H-NMR (d_6-DMSO): 2.36−2.57 [m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$], 4.02 [d, br, $^3J = 5.0$ Hz, 2H, CH_2N], 4.26 [s, br, 1H, NH], 5.74 [s, 1H, CH_2Cl_2], 7.50−7.56 [m, 2H, pyridine H_β and H_δ], 8.03 [dt, $^3J = 7.7$ Hz, $^4J = 1.6$ Hz, 1H, pyridine H_γ], 8.71 [m, br, 1H, pyridine H_α]. The compound was not soluble enough for ^{13}C-NMR measurements.

(MEPA)ZnBr (2b). MEPAH (439 mg, 2.61 mmol) and NaOH (104 mg, 2.61 mmol) were dissolved in methanol (20 mL). A solution of $ZnBr_2$ (588 mg, 2.61 mmol) in methanol (10 mL) was added dropwise with stirring. The precipitate was stirred for 1 h, filtered off, washed with methanol, and dried in vacuo to yield 664 mg (81%) of **2b** as colorless crystals, mp 225 °C (dec). Anal. Calc for $C_8H_{11}BrN_2SZn$ (312.5): C, 30.74; H, 3.55; N, 8.56. Found: C, 29.84; H, 3.41; N, 8.66. IR (KBr, cm^{-1}): 3199 vs, N−H; 3099 w, 3054 w, 3022 w, pyridine C−H; 2972 w, 2918 s, 2848 m, alkyl C−H; 1605 s, 1569 m, pyridine C=N; 1484 m, 1470 m, pyridine C=C; 1456 m, 1433 vs. 1421 m, 1367 m, 1344 w, 1294 s, 1279 m, 1270 m, 1218 m, 1182 w, 1154 m, 1117 s, 1103 m, 1052 m, 1034 m, 1021 m, 990 w, 980 w, 946 s, 930 m, 901 w, 810 m, 769 s, 724 w, 676 w, 646 w. Raman (powder, cm^{-1}): 1606 w, 1571 w, pyridine C=N; 1424 w, 1294 w, 1279 w, 1219 w, 1154 w, 1104 w, 1053 m, 1022 s, 813 m, 676 m, 646 w, 541 w, 333 w, 161 m, 129 s, 98 m, 83 m. ^{1}H-NMR (d_6-DMSO): 2.47−2.69 [m, br, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$], 3.94−4.14 [s, br, 2H, pyridine-CH_2], 4.14−4.32 [s, br, 1H, NH], 7.49−7.63 [m, 2H, pyridine H_β and H_δ], 8.05 [dt, $^3J = 6.2$ Hz, $^4J = 1.7$ Hz, 1H, pyridine H_γ], 8.67−8.71 [s, br, 1H, pyridine H_α]. ^{13}C-NMR (d_6-DMSO): 26.2 [$\mathrm{NCH_2}\mathit{C}\mathrm{H_2S}$], 50.2 [br, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2S}$], 51.1 [br, pyridine CH_2], 123.6 [pyridine C_β or C_δ], 124.0 [pyridine C_β or C_δ], 139.8 [pyridine C_γ], 147.6 [pyridine C_α], 156.0 [pyridine C_{quat}].

(MEPA)Zn(OAc) (3). MEPAH (380 mg, 2.26 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (496 mg, 2.26 mmol) were dissolved with stirring in ethanol (20 mL). After 1 h the clear solution was reduced in vacuo to 10 mL. Hexane (100 mL) was added and the mixture kept at −30 °C for 24 h. The cold mother liquor was decanted off and the precipitate dried in vacuo at room temperature. It was dissolved in a minimum amount of ethanol, treated with a 10-fold amount of diethyl ether, and kept at −30 °C for 24 h again. The precipitate which was filtered off, washed with a little ether, and dried in vacuo, consisted of **3** (231 mg, 35%), mp 95 °C, which is very hygroscopic. Anal. Calc for $C_{20}H_{28}N_4O_4S_2Zn_2$ (583.3): C, 41.18; H, 4.84; N, 9.61. Found: C, 41.94; H, 5.30; N, 10.27. IR (KBr, cm^{-1}): 3235 s, NH; 3027 sh, pyridine CH; 2919 s, 2854 m, alkyl CH; 1605 vs, pyridine C=N; 1562 vs, br, 1486 s, 1440 sh, 1408 vs, pyridine C=N and acetate C=O; 1339 m, 1316 m, 1296 m, 1271 sh, 1216 w, 1179 w, 1155 w, 1104 m, 1094 sh, 1053 m, 1031 sh, 1017 m, 990 m, 943 sh, 928 w, 842 w, 815 w, 766 m, 729 w, 661 m, 644 m, 617 w. ^{1}H-NMR (CD_3OD): 1.94 [s, 6H, acetate CH_3], 2.30−3.20 [m, br, 8H, $\mathrm{NC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{S}$], 4.17 [m, br,

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Table 1. Crystallographic details

	1a	**2a**	**3**	**4**	**6**
formula	$C_{32}H_{44}B_2F_8N_8S_4Zn_3\cdot 2H_2O$	$C_8H_{11}ClN_2SZn\cdot{}^1/_2CH_2Cl_2$	$C_{20}H_{28}N_4O_4S_2Zn_2$	$C_{16}H_{22}N_4S_2Zn$	$C_{18}H_{17}N_3O_2SZn$
mol wt	1038.8 + 36.0	268.1 + 42.5	583.3	399.9	404.8
cryst size (mm)	0.5 × 0.5 × 0.4	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.4	0.4 × 0.3 × 0.3
space group	$I\bar{4}$	$C2/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
Z	4	8	1	4	4
a (Å)	17.188(2)	22.789(5)	7.709(2)	19.998(1)	13.632(1)
b (Å)	17.188(2)	7.278(1)	8.708(2)	8.795(1)	9.451(1)
c (Å)	15.239(3)	17.729(4)	10.241(2)	11.790(1)	14.574(1)
α (deg)	90	90	67.16(3)	90	90
β (deg)	90	122.31(3)	67.22(3)	117.84(1)	110.14(1)
γ (deg)	90	90	84.06(3)	90	90
V (Å^3)	4502.0(12)	2485.2(9)	583.3(2)	1833.6(3)	1762.8(3)
d_{calc}(g/cm^3)	1.59	1.66	1.66	1.45	1.52
d_{obs} (g/cm^3)	1.61	1.60		1.39	1.47
μ (mm^{-1})	1.84	2.54	2.27	1.57	1.53
hkl range	h: −20 to 0	h: −28 to 0	h: −10 to 0	h: −25 to +22	h: −16 to +15
	k: 0 to +20	k: −9 to 0	k: −11 to +11	k: −11 to 0	k: 0 to +11
	l: 0 to +18	l: −18 to +22	l: −13 to +12	l: 0 to +15	l: 0 to +17
refls measd	2207	2582	3026	2114	3607
independent refls	2197	2517	2818	2011	3461
R(int)	0.027	0.019	0.015	0.021	0.020
refls used ($I > 2\sigma(I)$)	2023	2173	2629	1703	2580
params	241	132	145	105	226
R(unweighted)	0.058	0.027	0.026	0.028	0.035
res el density(e/Å^3)	+0.9, −0.7	+0.6, −0.3	+0.7, −0.7	+0.4, −0.2	+0.5, -0.3

4H, pyridine CH_2], 7.50−7.59 [m, 4H, pyridine H_β and H_δ], 8.03 [dt, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2H, pyridine H_γ], 8.77 [s, br, 2H, pyridine H_α]. ^{13}C-NMR (CD_3OD): 23.6 [acetate CH_3], 26.8 [$NCH_2\mathit{C}H_2S$], 51.1 [$N\mathit{C}H_2CH_2S$], 51.8 [pyridine CH_2], 125.2 [pyridine C_β or C_δ], 125.4 [pyridine C_β or C_δ], 141.5 [pyridine C_γ], 149.5 [pyridine C_α], 157.8 [pyridine C_{quat}], 180.8 [acetate COO].

(MEPA)$_2$Zn (4). A stirred solution of MEPAH (1.75 g, 10.4 mmol) in toluene (40 mL) was treated dropwise with a solution of Zn[$N(SiMe_3)_2$]$_2$ (2.00 g, 5.20 mmol) in toluene (20 mL). The precipitate was filtered off, washed three times with toluene (5 mL), and dried in vacuo, yielding 1.76 g (82%) of **4** as a colorless powder, mp 125 °C (dec). Anal. Calc for $C_{16}H_{22}N_4S_2Zn$ (399.9): C, 48.05; H, 5.55; N, 14.01; Zn, 16.4. Found: C, 48.00; H, 5.53; N, 13.94; Zn, 16.6. IR (KBr, cm^{-1}): 3227 s, N−H; 3064 w, 3029 w, pyridine C−H; 2998 w, 2944 m, 2893 m, 2840 m, alkyl C−H; 1606 w, 1591 s, 1563 m, pyridine C=N; 1482 m, 1454 m, pyridine C=C; 1447 m, 1421 s, 1294 m, 1206 w, 1173 w, 1151 m, 1107 w, 1084 m, 1057 m, 1048 m, 1028 m, 993 m, 946 s, 936 m, 837 w, 822 w, 775 vs, 731 w, 665 w, 633 w. ^{1}H-NMR (d_6-DMSO): 2.23−2.39 [m, 4H, $NCH_2C\mathit{H}_2S$], 2.47−2.56 [m, 4H, $NC\mathit{H}_2CH_2S$], 3.96 [d, J = 6.2 Hz, 4H, pyridine CH_2], 4.31 [t, ^3J = 6.2 Hz, 2H, NH], 7.35 [dd, ^3J = 6.1 Hz, ^4J = 1.7 Hz, 2H, pyridine H_δ], 7.44 [d, ^3J = 7.7 Hz, 2H, pyridine H_β], 7.83 [dt, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2H, pyridine H_γ], 8.60 [d, ^3J = 6.1 Hz, 2H, pyridine H_α]. ^{13}C-NMR (d_6-DMSO): 25.3 [$NCH_2\mathit{C}H_2S$], 51.7 [$N\mathit{C}H_2CH_2S$], 52.2 [pyridine CH_2], 123.0 [pyridine C_β or C_δ], 123.2 [pyridine C_β or C_δ], 137.9 [pyridine C_γ], 148.2 [pyridine C_α], 157.9 [pyridine C_{quat}].

(MEPA)Zn(2-(hydroxymethyl)benzenethiolate) (5). Zn[$N(SiMe_3)_2$]$_2$ (1.13 g, 2.94 mmol) was dissolved in toluene (30 mL). A solution of MEPAH (494 mg, 2.94 mmol) and 2-(hydroxymethyl)benzenethiol (412 mg, 2.94 mmol) in toluene (20 mL) was added dropwise within 1 h with stirring. The precipitate was stirred for another 2 h, filtered off, washed with toluene, and dried in vacuo. The compound was purified three times by dissolving in CH_2Cl_2 and precipitation by slow addition of hexane. A 612 mg (56%) amount of **5** resulted as a yellowish powder, mp 112 °C. Anal. Calc for $C_{15}H_{18}N_2OS_2Zn$ (371.9): C, 48.45; H, 4.88; N, 7.54. Found: C, 47.97; H, 4.64; N, 7.24. IR (KBr, cm^{-1}): 3380 m, br, OH; 3295 m, NH; 3080 m, 3050 m, 3000 w, pyridine and phenyl C−H; 2954 sh, 2913 m, 2851 m, alkyl C−H; 1604 vs, 1583 s, 1571 s, pyridine C=N; 1558 w, 1484 s, 1459 vs, 1435 vs, pyridine and phenyl C=C; 1382 m, 1366 m, 1295 s, 1262 s, 1212 m, 1189 m, 1154 m, 1121 m, 1101 m, 1063 vs, 1023 vs, 1000 sh, 953 sh, 936 m, 869 sh, 841 w, 823 w, 801 w, 752 vs, 734 s, 695 m, 675 m, 640 w, 608 w. ^{1}H-NMR ($CDCl_3$): 2.53−2.78 [m, 4H, $NC\mathit{H}_2C\mathit{H}_2S$], 3.86 [s, br, 2H, pyridine−CH_2], 4.76 [s, br, 2H, phenyl-CH_2], 6.82−6.93 [m, br, 2H, phenyl H4 and H5], 7.02−7.11 [m, br, 1H, phenyl H6], 7.21 [d, ^3J = 8.5 Hz, 1H, phenyl H3], 7.33 [m, br, 2H, pyridine H_β and H_δ], 7.78 [dt, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, pyridine H_γ], 8.58−8.64 [s, br, 1H, pyridine H_α]. ^{13}C-NMR ($CDCl_3$): 26.6 [$NCH_2\mathit{C}H_2S$], 51.5 [$N\mathit{C}H_2CH_2S$], 52.3 [pyridine−CH_2], 66.0 [CH_2OH], 123.3 [pyridine C_β or C_δ], 123.9 [pyridine C_β or C_δ], 127.5, 128.7, 135.3 aromatic carbon, 138.9 [pyridine C_γ]; 141.2 [phenyl C1 or C2], 141.7 [phenyl C1 or C2], 148.5 [pyridine C_α], 155.7 [pyridine C_{quat}].

(MEPA)Zn(quinoline-2-carboxylate) (6). MEPAH (401 mg, 2.38 mmol), quinoline-2-carboxylic acid (413 mg, 2.38 mmol), and NaOH (191 mg, 4.78 mmol) were dissolved in water/methanol (20 mL/40 mL). A solution of $Zn(ClO_4)_2.6H_2O$ (890 mg, 2.39 mmol) in water/methanol (10 mL/20 mL) was added dropwise with stirring. After the solution was stirred for 12 h the volume was reduced to 10 mL in vacuo, during which a precipitate was formed. It was filtered off, washed several times with water, and dried in vacuo to yield 580 mg (60%) of **6** as a brownish-white powder, mp 260 °C (dec). Anal. Calc for $C_{18}H_{17}N_3O_2SZn$ (404.8): C, 53.41; H, 4.23; N, 10.38; Zn, 16.2. Found: C, 53.27; H, 4.16; N, 10.35; Zn, 15.4. IR (KBr, cm^{-1}): 3235 m, N−H; 3098 w, 3051 w, 3004 w, pyridine and quinoline C−H; 2942 m, 2914 m, 2847 m, 2820 w, alkyl C−H; 1635 vs, C=O; 1611 sh, 1604 s, 1567 m, pyridine and quinoline C=N; 1508 m, 1476 m, 1462 m, 1438 m, pyridine and quinoline C=C; 1372 s, 1357 s, 1344 s, 1287 m, 1277 m, 1250 m, 1221 m, 1213 m, 1176 w, 1156 m, 1146 m, 1111 m, 1099 m, 1074 m, 1053 m, 1020 m, 989 w, 963 w, 929 w, 894 m, 880 m, 856 w, 799 s, 778 m; 766 s, 742 m, 670 w, 646 w, 631 w. ^{1}H-NMR (d_6-DMSO): 2.20−3.00 [m, br, $C\mathit{H}_2C\mathit{H}_2$], 4.12 [s, br, 2H, pyridine−CH_2], 4.48 [br, 1H, NH], 7.28 [t, ^3J = 6.6 Hz, 1H, quinoline H6], 7.58−7.67 [m, 2H, quinoline H5 and pyridine H_δ], 7.82 [t, ^3J = 7.9 Hz, 1H, pyridine H_β], 7.90−8.05 [m, 2H, pyridine H_γ and quinoline H7], 8.23 [d, ^3J = 7.9 Hz, 1H, quinoline H8], 8.35 [d, ^3J = 8.3 Hz, 1H, quinoline H4], 8.63 [d, ^3J = 8.7 Hz, 1H, pyridine H_α], 8.79 [d, ^3J = 8.3 Hz, 1H, quinoline H3]. ^{13}C-NMR (d_6-DMSO): 25.1 [$NCH_2\mathit{C}H_2S$], 49.2 [$N\mathit{C}H_2CH_2S$], 51.3 [pyridine−CH_2], 120.5 [pyridine C_β or C_δ], 124.5 [pyridine C_β or C_δ], 127.1, 128.5, 129.2, 131.7 (aromatic carbon), 140.3 [pyridine C_γ], 140.9, 144.1, 146.6 [pyridine C_α], 151.8, 157.3 [pyridine C_{quat}], 165.5 [COO].

Interconversions of (MEPA)$_2$Zn (4). Reaction with Zn(BF$_4$)$_2$. Complex **4** (117 mg, 0.29 mmol) was dissolved in methanol (15 mL). A solution of $Zn(BF_4)_2.6H_2O$ (51 mg, 0.15 mmol) in water (5 mL) was added with stirring. Within 2 days 83 mg (52%) of **1a** had precipitated, which was filtered off and washed with methanol.

Reaction with Zn(ClO$_4$)$_2$. A 120 mg (0.30 mmol) amount of **4** and 56 mg (0.15 mmol) of $Zn(ClO_4)_2.6H_2O$ were reacted as before. Yield: 98 mg (60%) of **1b**.

Reaction with Zn(NO$_3$)$_2$. A 158 mg (0.40 mmol) amount of **4** and 52 mg (0.20 mmol) of $Zn(NO_3)_2\cdot 4H_2O$ were reacted as before. Yield: 122 mg (60%) of **1c**.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **1a**

	x	y	z	U(eq)
Zn1	0	0	0	48(1)
Zn2	0	0	2244(1)	45(1)
S1	195(2)	1020(2)	1001(2)	49(1)
C11	−792(6)	1407(6)	1093(8)	58(3)
C12	−1394(5)	812(6)	1392(7)	54(2)
N11	−1155(4)	452(5)	2246(5)	47(2)
C13	−1672(5)	−209(6)	2479(7)	49(2)
C14	−1345(5)	−656(5)	3227(6)	46(2)
C15	−1797(7)	−1031(7)	3841(8)	60(3)
C16	−1476(7)	−1447(7)	4504(8)	67(3)
C17	−675(8)	−1468(7)	4546(7)	69(3)
C18	−246(7)	−1108(7)	3915(8)	58(3)
N12	−560(4)	−702(5)	3255(5)	50(2)
Zn3	5000	0	2500	42(1)
Zn4	5000	0	320(1)	41(1)
S2	5304(1)	1008(2)	1512(2)	44(1)
C21	6351(5)	862(7)	1428(7)	54(2)
C22	6582(5)	50(6)	1127(6)	47(2)
N21	6220(4)	−148(5)	299(5)	45(2)
C23	6394(5)	−944(6)	23(8)	51(2)
C24	5904(6)	−1189(6)	−735(7)	48(2)
C25	6153(7)	−1699(6)	−1368(8)	61(3)
C26	5661(10)	−1925(8)	−2008(9)	84(4)
C27	4895(8)	−1637(8)	−2008(9)	76(3)
C28	4706(8)	−1116(9)	−1390(7)	65(3)
N22	5174(4)	−889(5)	−755(6)	49(2)
B1	2898(8)	2699(8)	1757(9)	61(3)
O1	915(5)	2745(5)	688(8)	83(3)
F1	3662(8)	2640(8)	1605(10)	147(4)
F2	2441(11)	2709(12)	1020(12)	187(6)
F3	2657(12)	2848(15)	2561(17)	237(9)
F4	2704(13)	1920(14)	1743(17)	238(9)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **2a**

	x	y	z	U(eq)
Zn	2067(1)	356(1)	2088(1)	32(1)
S	3109(1)	−1384(1)	2937(1)	35(1)
Cl1	1568(1)	−549(1)	2940(1)	44(1)
N2	2439(1)	795(3)	1163(2)	36(1)
N1	1249(1)	−764(3)	853(2)	37(1)
C1	1257(2)	−293(4)	128(2)	41(1)
C6	1827(2)	977(5)	263(2)	48(1)
C5	734(2)	−1818(5)	756(2)	49(1)
C4	197(2)	−2417(5)	−72(3)	59(1)
C2	745(2)	−903(5)	−717(2)	57(1)
C8	3461(1)	−936(4)	2241(2)	41(1)
C3	208(2)	−1936(5)	−813(2)	64(1)
Cl2	386(1)	−6045(2)	−1535(1)	77(1)
C7	2894(2)	−732(4)	1267(2)	43(1)
C9	0	−7390(7)	−2500	58(1)

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **3**

	x	y	z	U(eq)
Zn	1190(1)	800(1)	494(1)	27(1)
S	2147(1)	−392(1)	−1514(1)	31(1)
N1	1732(2)	1358(2)	2180(2)	29(1)
N2	2169(2)	−1546(2)	1734(2)	29(1)
O1	2066(2)	3164(2)	−917(2)	41(1)
O2	1226(2)	3575(2)	−2883(2)	45(1)
C1	2348(2)	147(2)	3152(2)	28(1)
C2	2616(3)	358(2)	4342(2)	37(1)
C3	2208(3)	1857(3)	4534(2)	42(1)
C4	1559(3)	3108(3)	3527(2)	42(1)
C5	1352(3)	2820(2)	2366(2)	38(1)
C6	2805(3)	−1461(2)	2884(2)	34(1)
C7	3573(3)	−2267(2)	705(2)	34(1)
C8	2884(3)	−2389(2)	−452(2)	36(1)
C9	2144(2)	3948(2)	−2278(2)	31(1)
C10	3473(3)	5479(3)	−3195(2)	46(1)

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **4**

	x	y	z	U(eq)
Zn	0	666(1)	7500	36(1)
S(1	1138(1)	−373(1)	8024(1)	47(1)
N1	474(1)	2213(2)	9049(2)	38(1)
N2	−694(1)	4253(3)	8092(2)	54(1)
C1	−681(1)	3310(3)	8979(2)	43(1)
C2	−1292(2)	3123(3)	9219(3)	62(1)
C3	−1932(2)	3945(4)	8519(4)	79(1)
C4	−1959(2)	4936(4)	7625(3)	77(1)
C5	−1329(2)	5068(4)	7428(3)	70(1)
C6	41(1)	2449(3)	9760(2)	47(1)
C7	1260(1)	1700(3)	9909(2)	48(1)
C8	1647(1)	1167(3)	9135(2)	48(1)

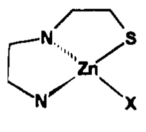
Reaction with CH_2Cl_2. A 66 mg (0.17 mmol) amount of **4** was dissolved in 4 mL of freshly-distilled CH_2Cl_2. After 3 days 49 mg (96%) of crystalline **2a**$\cdot{}^1/_2CH_2Cl_2$ had precipitated, which was filtered off and shortly dried in vacuo.

Reaction with HCl. A 102 mg (0.26 mmol) amount of **4** was dissolved in methanol (15 mL). A 5.0 mL (0.50 mmol) volume of a 0.1 M solution of HCl in methanol was added. After 4 days at −30 °C 35 mg (45%) of **2a** had precipitated, which was filtered off and dried in vacuo.

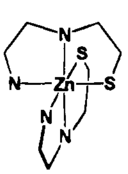
X-ray Crystallography. Crystals of **1a** were obtained by slow evaporation from aqueous solution, those of **2a** from dichloromethane, those of **3** from ethanol, those of **4** from ethanol, and those of **6** from acetonitrile. All crystals were colorless. Diffraction data were recorded with the $\omega/2\Theta$ scan mode in the 2Θ range 5−52° on a Nonius CAD4 diffractometer with molybdenum radiation (λ = 0.710 73 Å) and a graphite monochromator at 294 K. The data were used without an absorption correction. The structures were solved using direct methods (**2a**, **3**, **4**, **6**) or Patterson techniques (**1a**) and refined anisotropically. Hydrogen atoms were included at fixed positions (C−H = 0.96 Å) with a common isotropic temperature factor. Disorder hampered the location of the BF_4 fluorine atoms in **1a**. All crystallographic computing was done with the SHELX program system;[20] the drawings were produced with the SCHAKAL program.[21] Table 1 gives a summary of all crystallographic data: Tables 2−6 list the atomic parameters for the five structures.

Results and Discussion

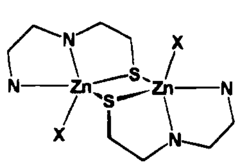
Ligand MEPAH. The aim of the synthesis of *N*-(2-mercaptoethyl)picolylamine (MEPAH) was to obtain a monoanionic N,N,S ligand capable of forming two five-membered chelate rings. Thereby it was expected to obtain stable zinc complexes in which three coordination positions are firmly occupied leaving the fourth and possibly further coordination positions available for coligands or substrates. The main hope was to produce tetrahedral (MEPA)Zn−X complexes which model the environment of zinc in N,S-coordinated active centers of enzymes. It was, however, to be expected that the occurrence of five-membered chelate rings might favor the formation of octahedral complexes or that the coordination number of zinc might rise above 4 due to aggregation via bridging thiolate functions. Thus, exemplified for neutral compounds, complex types **A**−**C** were among those that could be envisaged.



A



B



C

The synthesis of MEPAH was straightforward, following a

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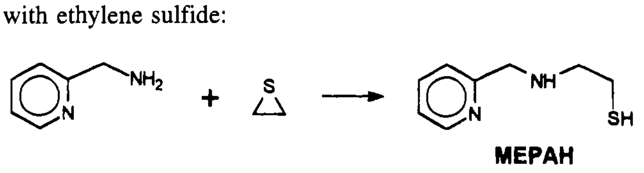
(20) Sheldrick, G. M. SHELXS and SHELXL, Universität Göttingen, 1986 and 1993.

(21) Keller, E. SCHAKAL. Universität Freiburg, 1993.

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (pm^2 $\times$ 10^{-1}) for **6**

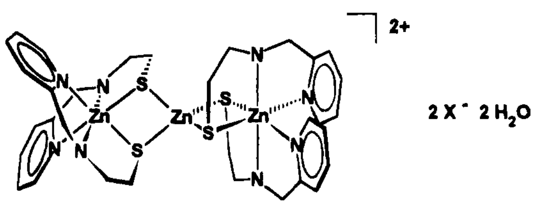
	x	*y*	*z*	*U*(eq)
Zn	2145(1)	2131(1)	8759(1)	31(1)
S1	3231(1)	1580(1)	7917(1)	43(1)
N1	1789(2)	807(3)	9762(2)	34(1)
N2	970(2)	743(3)	7778(2)	32(1)
N3	3112(2)	3698(3)	9800(2)	30(1)
O1	1241(2)	3875(2)	8420(2)	39(1)
O2	1299(2)	6224(2)	8451(2)	50(1)
C1	2021(3)	1051(4)	10722(2)	43(1)
C2	1735(3)	145(4)	11317(3)	45(1)
C3	1204(3)	−1083(4)	10926(3)	47(1)
C4	965(3)	−1343(4)	9943(3)	41(1)
C5	1261(2)	−372(3)	9373(2)	32(1)
C6	1029(3)	−602(3)	8297(2)	40(1)
C7	1209(3)	595(4)	6870(2)	41(1)
C8	2361(3)	329(4)	7075(3)	48(1)
C9	2719(2)	4985(3)	9568(2)	30(1)
C10	3230(3)	6218(3)	10031(2)	36(1)
C11	4168(3)	6083(4)	10774(2)	38(1)
C12	4608(2)	4745(4)	11053(2)	35(1)
C13	5571(3)	4527(4)	11827(3)	45(1)
C14	5951(3)	3205(5)	12049(3)	54(1)
C15	5425(3)	2022(4)	11521(3)	52(1)
C16	4493(3)	2194(4)	10774(3)	42(1)
C17	4067(2)	3558(3)	10536(2)	32(1)
C18	1660(3)	5057(3)	8747(2)	32(1)

procedure by Reynolds et al.[22] for mercaptoethylations of amines with ethylene sulfide:



MEPAH is a colorless liquid of unpleasant odor which is oxidized by access of air. One of its advantages is that it is miscible with water and all common organic solvents. Its NMR data are given in the Experimental Section. Its characteristic IR bands (pure liquid film) are 3309 (m, NH), 2540 (w, SH), 1589 (vs) and 1568 (s, pyridine ring vibrations) cm^{-1}. These IR bands are of simple diagnostic value for the formation of the complexes of MEPAH. The ^{1}H and ^{13}C-NMR data of the ligand and the complexes are of little information other than showing the presence of the constituents. They are all given in the Experimental Section and will not be discussed in detail. One reason for their limited value lies in the fact that most of the complexes required the highly polar DMSO as a solvent. This solvent has the disadvantage that it obscures the information obtainable from signal splittings or multiplet patterns by causing broad NMR resonances.

Complexes with $Zn(BF_4)_2$, $Zn(ClO_4)_2$, and $Zn(NO_3)_2$. When ligand MEPAH, which was always converted to its anionic form by NaOH, was reacted with zinc salts of noncoordinating anions, it was hoped for that a tetrahedral species L·Zn−X of type **A** would form. Such a species which was successfully produced with L = pyrazolylborate[10] or dipicolylglycinate[11] and in which X is derived from the solvent (X = OH, H_2O, ROH) would be the simplest model of the active center of a N,N,S-coordinated zinc enzyme. Alternatively, it was feared that an octahedral complex of type **B** would result. Neither was the case. Irrespective of the stoichiometric ratio of the reactants the compounds **1a-c** were precipitated which all contain the same trinuclear complex cation. This cation can be formulated as a Zn^{2+} ion coordinated by two octahedral Zn(MEPA)$_2$ units of type **B**.



1a: X = BF_4, **1b:** X = ClO_4, **1c:** X = NO_3

The 4:3 (ligand:zinc) composition of the complexes could be deduced from the elemental analyses. Their constitution became only clear after the structure determination. The IR spectra of **1a−c** point to the tridentate attachment of the ligand by the absence of the SH band and by the shift of the higher pyridine ring vibration band from 1589 cm^{-1} in the free ligand to ca. 1605 cm^{-1} in the complexes.[23] They provide no clue to the nuclearity of the complexes. As all four MEPA ligands are symmetry equivalent in **1a−c**, the NMR spectra which show only one set of MEPA resonances provide neither structural information on the trinuclear complexes **1** nor an answer to the question whether the complexes have a different constitution of possibly lower nuclearity in solution.

The crystal structure determination of **1a** has shown the trinuclear complex cations to possess S_4 symmetry. Two independent cations exist in the crystal lattice of space group $I\bar{4}$ with the central zinc atoms located at 0, 0, 0 and $^1/_2$, 0, $^1/_4$. Thereby the (MEPA)$_4$Zn$_3$ units are fully described by the positions of one of the outer zinc atoms and one of the MEPA ligands. The crystal water molecules and the BF_4 anions are located on general positions. Figure 1 shows one of the trinuclear complex cations; Table 7 gives some bond lengths and angles.

While there are some significant differences between the two independent trinuclear complexes, cf. all distances related to Zn2, their overall similarities are dominant, and they will be discussed together. The main feature of the trinuclear species is the occurrence of tetrahedral and octahedral zinc bound to the same ligand. The central zinc atom has a severely distorted tetrahedral ZnS_4 environment. The reason for this distortion is the S1−Zn1−S1′ angle which itself is enforced by the typical valence angle near 90° at S1 in the Zn_2S_2 rectangle. The central Zn−S bond lengths of 2.35 Å are normal, cf. ZnS_4 units in bridged,[24] nonbridged,[25] or protein-bound[26] zinc/sulfur species. For the octahedrally coordinated Zn2 atoms the Zn−N bond lengths (2.11−2.26 Å) are in the expected range;[1] the Zn−S distances (average 2.58 Å) seem rather long, however. This may have to do with the fact that octahedral zinc complexes with Zn−S coordination are rare and that Zn−S bonding may be weak in such somplexes. Material for comparison exists in the form of three octahedral complexes with chelating N,S

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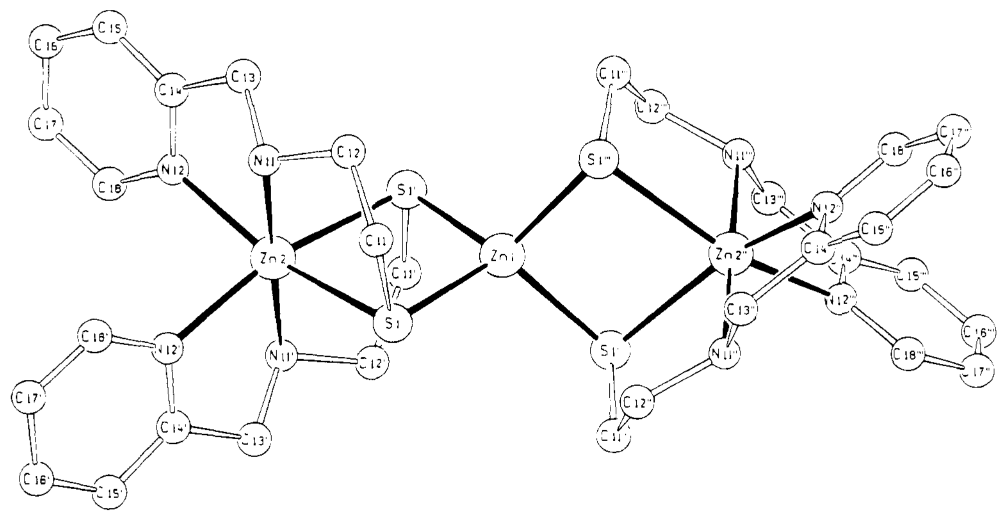


Figure 1. View of the trizinc cation of **1a**.

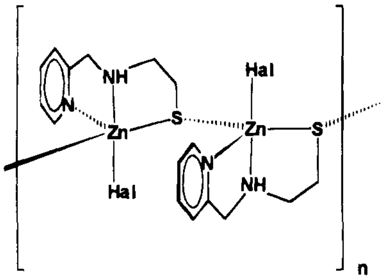
Table 7. Selected Bond Lengths (Å) and Angles (deg) for **1a**

	molecule 1	molecule 2
Zn1···Zn2	3.419(1)	3.324(1)
Zn1−S1	2.347(3)	2.355(3)
Zn2−S1	2.602(3)	2.564(3)
Zn2−N11	2.133(8)	2.112(7)
Zn2−N12	2.182(8)	2.259(8)
S1−Zn1−S1′	98.9(1)	100.5(1)
S1−Zn1−S1″	115.0(1)	114.2(1)
S1−Zn2−S1′	86.6(1)	89.8(1)
S1−Zn2−N11	82.8(2)	83.7(1)
S1−Zn2−N12	160.7(2)	160.6(2)
S1−Zn2−N11′	97.3(2)	97.6(2)
S1−Zn2−N12′	94.9(2)	94.8(2)
N11−Zn2−N12	77.9(3)	77.1(3)
N11−Zn2−N11′	179.8(4)	178.2(4)
N11−Zn2−N12′	102.0(3)	101.6(3)
N12−Zn2−N12′	90.1(4)	87.1(5)
Zn1−S1−Zn2	87.2(1)	84.9(1)

ligands,[27] in which the Zn−S distances range from 2.47 to 2.63 Å. It is interesting to note that in a similar trinickel complex of a N_2S_2 ligand the central nickel ion in the $(NiN_2S_2)Ni(S_2N_2Ni)$ core has a square planar NiS_4 environment.[28]

The S_4 symmetry of the whole trinuclear cations goes along with their characteristic features. Thus the three zinc ions are exactly colinear and the two Zn_2S_2 planes are exactly perpendicular. The three donor atoms of the MEPA ligands occupy meridional positions at Zn2. The resulting mer(cis, trans, cis) arrangement of the two MEPA units which is enforced by the bridging positions of the sulfur atoms represents one of eleven possible isomeric forms. At the same time the two chiral $(MEPA)_2Zn$ units in the trinuclear complex are mirror images although the central Zn1 atom lies neither on a mirror plane nor on an inversion center.

Zinc Halide Complexes. When solutions of MEPAH, deprotonated by NaOH, were treated with $ZnCl_2$ or $ZnBr_2$, the polymeric complexes **2** were precipitated. In the case of $ZnCl_2$ the precipitate was not pure, probably due to the facile hydrolysis or alcoholysis of $ZnCl_2$, and it could not be purified due to its insolubility. However, the interconversions of complex **4** (see below) produced pure **2a**. In the case of $ZnBr_2$ the precipitate from the reaction mixture contained pure **2b**. Both compounds **2** were not soluble enough in standard solvents for recrystallization, but crystalline **2a** resulted from the reaction of **4** with CH_2Cl_2. The trigonal-bipyramidal coordination of zinc in **2a**,**b** can be related to type **C** (see above, polymer rather than dimer).



2a: Hal = Cl, **2b**: Hal = Br

The IR data of **2a**,**b** prove the tridentate nature of MEPA again by the absence of a S−H band and by the high-frequency position of the pyridine bands at 1607 and 1605 cm^{-1}, respectively. A constitution like that of complexes **1** which might be represented by a composition $[(MEPA)_4Zn_3]ZnHal_4$ could be excluded (i) by the ^{1}H-NMR spectra (see Experimental Section) which are too different from those of complexes **1** and (ii) by Raman spectra which fail to show the characteristic bands[29] of $ZnCl_4^{2-}$ and $ZnBr_4^{2-}$ in the 200 cm^{-1} range. No clue as to the nature of complexes **2** in DMSO solution (oligonuclear, dinuclear, solvated mononuclear) could be obtained from the spectra.

The information on the solid state nature of complexes **2** was obtained from the structure determination of the CH_2Cl_2 solvate of **2a**; see Figure 2 and Table 8. The complex units are linked by the sulfur atoms generating a chainlike polymer, the backbone of which consists of Zn−S bonds. The single units are related to one another by the 2-fold screw axis making all polymeric chains run parallel to the crystallographic *b* axis and making the Zn−Cl bonds alternatively pointing up and down.

The coordination of the zinc ion in **2a** is trigonal-bipyramidal to a reasonably good approximation. This demonstrates the flexibility of the MEPA ligand which adopts a facial arrangement here (N1−Zn−S angle 118°) as compared to the meridional one in **1a** (N12−Zn2−S1 angle 161°). The Zn−N bond lengths in **2a** show the characteristic difference which is observed for axial versus equatorial coordination. This and the characteristically long Zn−Cl distance can be compared with

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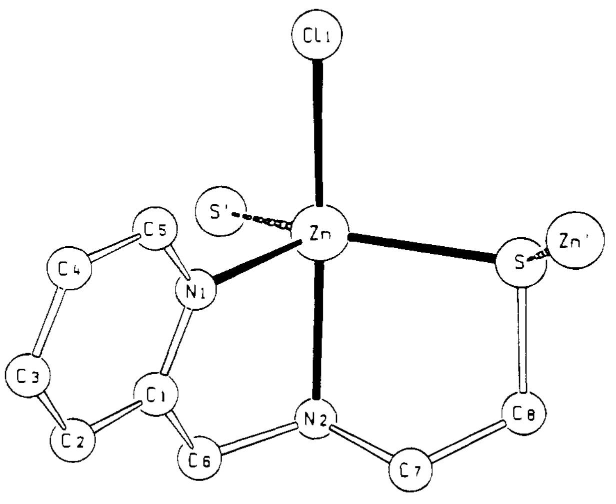


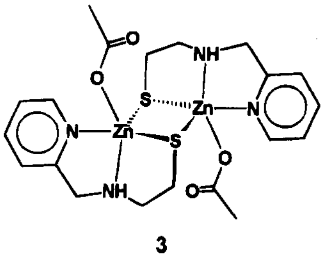
Figure 2. Coordination of one zinc ion in polymeric **2a**.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for **2a**

Zn−N1	2.138(2)	N1−Zn−S	118.26(7)
Zn−N2	2.235(2)	N1−Zn−S′	108.16(6)
Zn−S	2.385(1)	S−Zn−N2	84.22(6)
Zn−S′	2.403(1)	S−Zn−Cl1	95.91(3)
Zn−Cl1	2.418(1)	S−Zn−S′	129.52(2)
Zn••Zn	4.023(1)	N2−Zn−Cl1	170.70(6)
Zn−S−Zn′	114.37(3)	N2−Zn−S′	88.31(6)
N1−Zn−N2	76.65(8)	Cl1−Zn−S′	98.66(2)
N1−Zn−Cl1	95.23(6)		

the situation in the $[(\text{tren})\text{ZnCl}]^+$ cation.[30] The Zn−S distances in **2a** are intermediate between those for the tetrahedral and the octahedral zinc ions in **1a**. Their value (average 2.39 Å) as well as the Zn••Zn distance of 4.02 Å can be compared with those in other singly sulfur bridged dizinc units in complexes[14,24] or in Zn_2Cd_5 metallothioneine.[31]

Zinc Acetate Complex. As the acetate ligand is similar to the halide ligands in its bonding tendency toward zinc, it could be expected that zinc acetate might form a complex with MEPAH which is similar to the zinc halide complexes. This was, in principle, observed but only as far as the composition of the product is concerned. Zinc acetate and the ligand, without the aid of an additional base, form the soluble 1:1 complex species in ethanol which is precipitated with less polar organic solvents as the dinuclear complex **3**. The constitution of **3** corresponds to type **C** (see above).



3

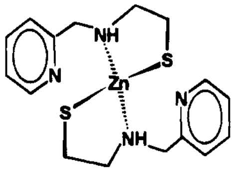
The constitution of **3** in solution, whether mononuclear or dinuclear, cannot be deduced from the NMR data (see Experimental Section) which merely show the presence of the coordinated ligands. For the solid compound the IR band at 1605 cm^{-1} and the missing SH band confirm the tridentate nature of MEPA while the two acetate bands at 1562 and 1408 cm^{-1} point to a monodentate acetate coordination.[32]

In crystalline **3** the complex exists in the form of centrosymmetrical dinuclear molecules; see Figure 3 and Table 9. The similarity with polymeric **2a** is limited to the pentacoordination of the metal; the major differences lie in the acute bond angles at the bridging sulfur atoms and the square pyramidal coordination of zinc in **3**. For both complex halves the apex of the square pyramid is the sulfur atom of the other (MEPA)Zn(OAc) unit. Unlike the situation in **2a** the two Zn−N bonds in **3** are of similar length, and the apical bond (Zn−S1′) is shorter than the corresponding basal bond (Zn−S1), as might be expected for square pyramidal complexes. In accordance with the acute Zn−S-Zn angle in **3** the Zn••Zn distance is 1 Å shorter than that in **2a**.

A Zn_2S_2 quadrangle with similar dimensions as in **3** has been observed for dimeric (piperidinium thiolato)zinc dichloride.[33] The only other complex with a ZnS_2N_2O coordination of which a structure has been determined is bis(6-amino-2-thiouracilato)-aquazinc.[34] But the small bite of the N,S chelate ligand prevents a comparison of the coordination in this complex with that in **3**.

There is no obvious reason why compound **3** should be dimeric while **2a** is polymeric. The difference in electronegativity between O and Cl should not be able to account for this. It is also not striking to us that the higher sterical demands of the acetate ligand should cause the lower nuclearity of **3**. Thus the sum of several subtle differences seems to cause the change which will be subtle on the energy scale as well. Not the least of these differences may be two intramolecular hydrogen bridges in **3** which link N2 and O2′ and its counterpart N2′ and O2.

Binary Compound Zn(MEPA)$_2$. Only by avoidance of the use of zinc salts could the bis(ligand) complex **4** be obtained. It was formed by the proteolytic cleavage of $Zn[N(SiMe_3)_2]_2$ by 2 equiv of the "acid" MEPAH. The type of ligand binding in **4** could in part be deduced from its IR spectrum which by the missing SH band indicates coordination of the sulfur and by the unshifted pyridine band at 1591 cm^{-1} indicates noncoordination of the pyridine nitrogen. While the resulting ZnN_2S_2 coordination is not unusual for zinc thiolate complexes, it was surprising in the context of the other zinc complexes of MEPAH and by the fact that it corresponds to neither of the structural types **A**, **B**, or **C** (see above).



4

The X-ray analysis of **4** revealed that the specific type of coordination is indeed unusual; see Figure 4 and Table 10. The zinc atom of **4** is located on a 2-fold axis relating both ligand molecules to one another. The MEPA ligands are wrapped around the zinc such that nearly the whole volume of the ligands is on one side of the complex. This leaves the sulfur atoms bare and exposed, and there cannot be a steric reason why they should not be bridging or why the pyridine nitrogen atoms should not coordinate as they do in complexes **1**. The reason

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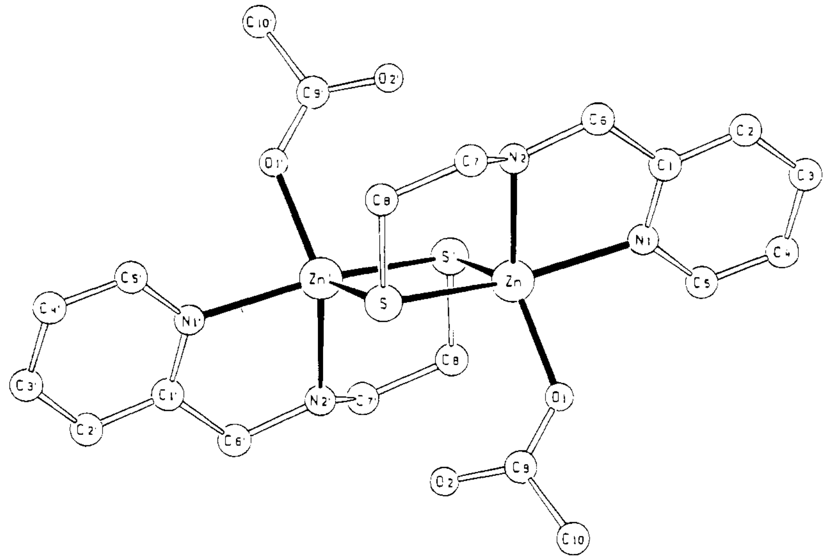

Figure 3. View of the dinuclear complex **3**.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **3**

Zn–N1	2.155(2)	N1–Zn–S1′	103.32(5)
Zn–N2	2.183(2)	N1–Zn–O1	86.89(6)
Zn–S1	2.485(1)	N2–Zn–S1	82.47(5)
Zn–S1′	2.378(1)	N2–Zn–S1′	104.90(6)
Zn–O1	2.001(2)	N2–Zn–O1	142.01(6)
Zn••Zn	3.065(1)	S1–Zn–S1′	101.89(3)
Zn–S1–Zn′	78.11(3)	S1–Zn–O1	96.85(5)
N1–Zn–N2	77.17(6)	S1′–Zn–O1	112.30(6)
N1–Zn–S1	150.87(4)	Zn–O1–C9	129.7 (1)

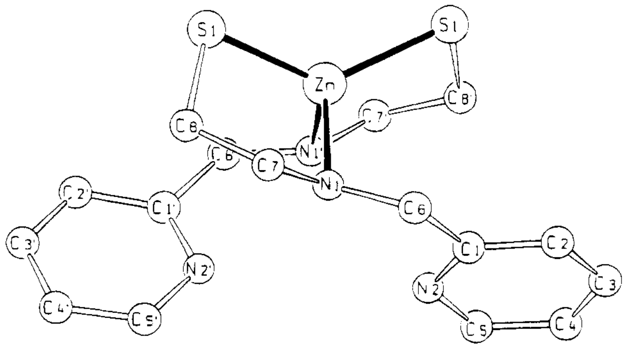

Figure 4. Molecular structure of complex **4**.

Table 10. Selected Bond Lengths (Å) and Angles (deg) for **4**

Zn–N1	2.114(2)	S1–Zn–S1′	132.18(4)
Zn–S1	2.255(1)	S1–Zn–N1	92.09(5)
Zn–S1–C8	92.82(7)	S1–Zn–N1′	119.03(5)
SZnS/NZnN	71.3 (1)	N1–Zn–N1′	99.87(10)

for the preferred occurrence of a ZnS_2N_2 (and not ZnS_2N_{2+x} or $ZnS_2N_2O_x$) coordination must therefore be strictly electronic.

The bond lengths and angles of **4** are normal, compared to the large number of ZnN_2S_2 complexes[35] or the recently identified zinc finger proteins with $ZnHis_2Cys_2$ coordination.[36] The closest relation in all geometrical details exists between **4** and the three other structurally characterized ZnL_2 complexes of the five-membered ring chelate ligands (2-methyl-2-mercaptopropyl)amine and *N,N*-dimethyl-(2-mercaptoethyl)amine.[37,38]

The unusual stoichiometry, bonding pattern, and structure of **4** did point to an "unsaturation" of the complex which might be relieved by making use of the remaining donor capacity of the sulfur atoms or the pendant pyridine rings. Experimental verification of this was found in the reactions of **4** with the zinc salts $Zn(BF_4)_2$, $Zn(ClO_4)_2$, and $Zn(NO_3)_2$ which produced good yields of the above-described complexes **1a–c**. It seems that withdrawal of electron density from **4** by coordination of the sulfur to another metal ion liberates sufficient acceptor capacity on its zinc atom for pyridine coordination. This way two molecules of **4** become ligands for the central zinc ion in **1a–c** thereby changing their own coordination environment at the same time.

A similar interconversion of **4** was achieved by treatment with HCl. As a result of this treatment about 50% of the complex and about 75% of the total content of MEPA were lost, and the remaining constituents were recovered as the polymeric (MEPA)Zn chloride complex **2a**. The most noticeable demonstration of the structural and chemical unsaturation of **4** was found fortuitously upon attempts to recrystallize **4** from CH_2Cl_2: an almost quantitative interconversion occurred using the chloride content of CH_2Cl_2 to precipitate polymeric **2a** which was used for the structure determination of this compound. On the basis of these findings it seems attractive to further exploit the hidden donor and acceptor properties of **4** and similar complexes by preparative and mechanistic studies.

Mixed-Ligand Complexes. If ligand MEPAH is to be used for model studies related to zinc-containing enzymes, it has to be incorporated in complexes together with coligands which represent substrates of the enzymes or the remainder of the biological coordination sphere. Two such coligands were used in this study. 2-(Hydroxymethyl)benzenethiol was tested for its ability to create a NS_2(alcohol) coordination around zinc as it is supposed to occur in the active state of the enzyme alcohol dehydrogenase.[4] Quinoline-2-carboxylic acid was expected to create, together with MEPA, a N_3OS coordination around zinc as it has been proposed for bovine 5-aminolaevulinate dehydratase.[6]

2-(Hydroxymethyl)benzenethiol could be incorporated by reacting it and an equivalent amount of MEPAH with $Zn[N(SiMe_3)_2]_2$ in toluene. The resulting complex **5** could not be obtained in the form of single crystals. Its NMR data (see Experimental Section) prove the presence of both ligands; its

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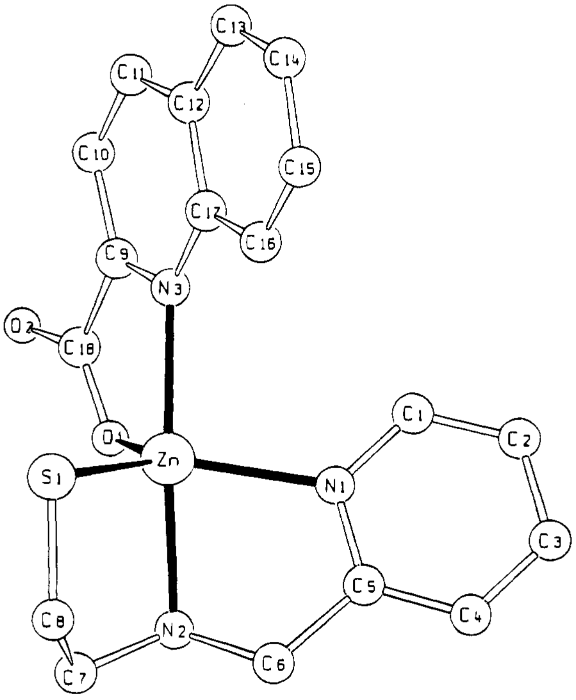
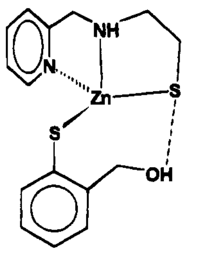


Figure 5. Molecular structure of complex **6**.

IR data document the attachment of both ligands as thiolates by the lack of SH bands and the tridentate nature of MEPA by the pyridine band at 1604 cm^{-1}. The spectroscopic information on the bonding situation of the alcoholic function is limited. Its very broad IR band with a maximum at 3380 cm^{-1} indicates its involvement in a hydrogen bridge. We therefore assume a constitution for **5** as given in the formula, with zinc being tetrahedrally N_2S_2 coordinated and the OH group not bound to zinc but attached via a hydrogen bridge to sulfur. This way **5** would be a representative of type **A** (see above).



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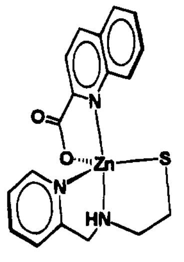

6

Quinoline-2-carboxylic acid was incorporated by combining it with MEPAH, NaOH, and $Zn(ClO_4)_2$ in aqueous methanol. The resulting soluble complex was shown to contain both ligands by its NMR spectra (see Experimental Section) and to have them both bound via their heterocyclic nitrogen atoms by the very strong IR band at 1604 with a shoulder at 1611 cm^{-1}. The bonding situation of the carboxylate group could not be assigned because only one of its IR bands could be identified at 1635 cm^{-1} while the other occurs within a group of bands between 1460 and 1290 cm^{-1}.

The crystal structure determination of **6** (see Figure 5 and Table 11) proved ligand MEPA to be tridentate as usual and the quinoline carboxylate to be bidentate, giving the zinc ion a trigonal-bipyramidal coordination once again. There is a general similarity between complexes **2a** and **6**, with all zinc-to-MEPA bond lengths in **6** being shorter and the bond angles in **6** being a bit closer to those in the ideal trigonal bipyramid. There are two structure determinations of Zn complexes with a N_3OS coordination in the literature, one with a tridentate ONS ligand and bipyridine[39] and the other with a tetradentate N_3S ligand and acetate.[40] Both are trigonal bipyramidal like **6**, both have oxygen and sulfur in the equatorial plane like **6**, and both have a similar distribution of bond lengths, though not bond angles, as **6**. Thus the most remarkable feature in the constitution and structure of complex **6** is the fact that it is the only one of the complexes of ligand MEPAH which has the zinc ion coordinated to only one sulfur atom.

Table 11. Selected Bond Lengths (Å) and Angles (deg) for **6**

Zn–O1	2.015(2)	O1–Zn–N3	77.9(1)
Zn–N1	2.104(3)	N1–Zn–S1	125.8(1)
Zn–S1	2.285(1)	N1–Zn–N2	78.7(1)
Zn–N2	2.180(3)	N1–Zn–N3	98.5(1)
Zn–N3	2.220(4)	S1–Zn–N2	88.7(1)
O1–Zn–N1	112.9(1)	S1–Zn–N3	100.3(1)
O1–Zn–S1	120.6(1)	N2–Zn–N3	170.5(1)
O1–Zn–N2	94.7(1)		

Conclusions

The N,N,S ligand MEPAH forms stable zinc complexes in which it is bound in its anionic form. Its main property is the great variability of its coordinative behavior toward the zinc ion. It is able to provide two (**4**), three (**5**, **6**), and four (**1**–**3**) donor bonds. It forms 1:1 (**2**, **3**, **5**, **6**), 2:1 (**4**), and 4:3 (**1**) complexes. It goes along with a tetrahedral (**1**, **4**, **5**), trigonal-bipyramidal (**2**, **6**), square-pyramidal (**3**), and octahedral (**1**) geometry around zinc. It gets engaged in complexes in which zinc is bound to one (**6**), two (**1**–**5**), and four (**1**) sulfur atoms. And finally it has an equally pronounced tendency to use (**1**–**3**) or not to use (**4**–**6**) the thiolate sulfur as a briding ligand. Due to this flexibility the zinc complexes of MEPAH can mimic virtually any type of zinc–sulfur coordination that occurs in biological systems.

As was demonstrated by the chemistry of the binary compound $(MEPA)_2Zn$ (**4**), there is an intriguing interplay between the donor capacity of the zinc-bound sulfur and the acceptor capacity of the metal. It seems attractive to us to exploit the consequences of this interplay by learning more about stabilities, structures, and (possibly catalytic) reactions of zinc complexes derived from **4** by utilizing the unused donor abilities of its sulfur and pyridine nitrogen atoms with hard and soft Lewis acids.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. We thank Dr. W. Deck for NMR spectra, Dr. H. Rotter for Raman spectra, and Mr. M. Ruf for help during the structure determinations.

Supplementary Material Available: Tables containing the details of data acquisition and refinement, complete interatomic distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated parameters of hydrogen atoms and thermal ellipsoid (ORTEP) plots for all five structure determinations (22 pages). Ordering information is given on any current masthead page.

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