Zinc Complexes of S,N Ligands Derived from Thiazolines

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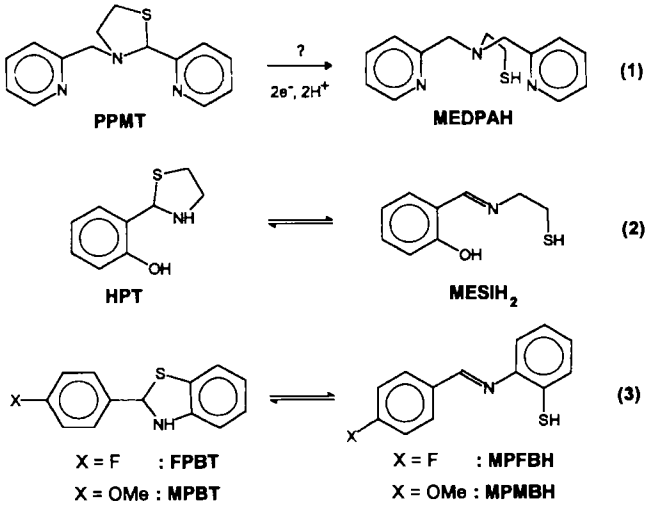
Three different thiazoline derivatives or their tautomeric mercaptoethylamine derivatives were used for the preparation of zinc complexes containing S,N ligands. 2-(2-pyridyl)-3-(2-pyridylmethyl)-1,3-thiazolidine (PPMT) could not be opened reductively but acted as a tridentate nitrogen ligand in (PPMT)ZnX_2 (**1a**, **b**, X = Br, NO_3). The thiazolidine tautomer *N*-(2-mercaptoethyl)salicylideneimine ($MESIH_2$) yielded polymeric (MESI)Zn (**2**) and, after oxidation, monomeric $(MESI)_2Zn$ (**3**) containing a disulfide unit. The 2-aryl-benzo-1,3-thiazoline tautomers *N*-(2-mercaptophenyl)-*p*-fluorobenzylideneimine (MPFBH) and *N*-(2-mercaptophenyl)-*p*-methoxybenzylideneimine (MPMBH) underwent reaction with diethyl zinc resulting in the unstable L · Zn–Et complexes **4a** and **b**, which are probably dimeric and the stable 2:1 complex $(MPFB)_2Zn$ (**5**). The structures of **3** and **5** were determined and were found to exhibit distorted tetrahedral ZnN_2O_2 and ZnN_2S_2 coordinations, respectively.

Metal-sulfur coordination, brought about by the protein constituents cysteine and methionine, is one of the important binding types of metals in biological systems. For the metal zinc it is exclusively realized in the form of zinc-thiolate binding to cysteine, most often in combination with zinc-heterocyclic nitrogen bonding to histidine[1,2]. Zinc complexes with N,S ligands are therefore attractive as models for the biological coordination modes, and they were prepared and structurally characterized by many research groups[2–6] including our own[7–10].

A general problem with zinc complexes containing thiolate ligands is their aggregation via bridging thiolate functions[2,9,11]. The most common approach to reduce aggregation has been the use of sterically demanding thiolates[4,12,13]. A survey of the literature shows that other approaches seem suitable as well. Among these are the use of the less basic aromatic thiolates in place of the aliphatic ones[2,3,9,10] or the encapsulation of the metal ion by increasing the coordination number or by using favourable multi-chelating ligands[4,9,14,15]. In the zinc-protein complexes, of course, encapsulation is the natural situation that inhibits aggregation.

In this paper we describe some of our attempts to produce low-coordinate and mononuclear zinc complexes with N and S ligands by making use of favorable chelate effects of new polydentate N, S ligands[8–10]. A common feature of the three ligand types described is that their thiolate function was meant to be hidden in ligand precursor molecules in the form of thiazoline or thiazolidine rings. The complexation reaction or a tautomerization under the reaction conditions was then supposed to liberate this function making it available only in the chelated complexes thereby reducing the chances for aggregation and oligomerization. Ring opening of thiazolines generating thiol units is a common reaction in organic chemistry, and its use for the synthesis of metal complexes has also been described in several cases[16–19]. We intended to apply it to zinc complexes of the ligands MEDPAH (unknown), $MESIH_2$, MPFBH, and MPMBH related to their precursors PPMT, HPT[20], FPBT, and MPBT[19] according to the interconversions shown below:



Derivatives of PPMT

The tripod ligand MEDPAH (mercaptoethyl-dipicolylamine) should be a target molecule of high value as its anion should provide a stable multichelating environment for trigonal-bipyramidal zinc complexes in which one ligand position is available for reaction with substrates (cf. similar N_4[21,22] and N_3O[23] chelates). We therefore tried to get access to it via the reductive opening[17,19] of the thiazolidine PPMT [2-(2-pyridyl)-3-(2-pyridylmethyl)-1,3-thiazolidine] according to eqn. (1). This thiazolidine, which to our knowledge has not been described yet, was obtained with-

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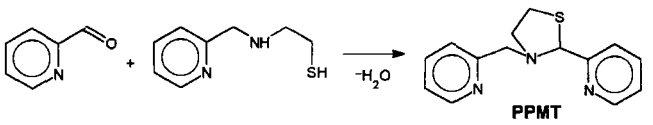
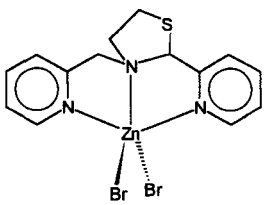
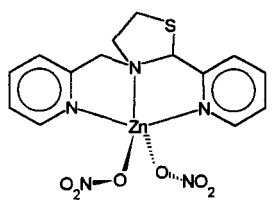
out problems by the following condensation reaction involving mercaptoethyl-picolylamine[9]:



Attempts to reduce PPMT (with $LiAlH_4$, $NaBH_4$ or BH_3 in various solvents or with Na in liquid ammonia) have remained unsuccessful so far. Similarly, the reaction with zinc amalgam in methanol, meant to afford a zinc complex of MEDPA directly, did not take place, leaving MEDPAH to be an elusive compound.



1a



1b

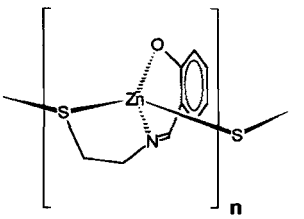
In contrast, it was not difficult to show that PPMT itself acts as a ligand. Its reaction with zinc bromide and zinc nitrate in methanol produced the 1:1 complexes **1a** and **b**. We assign structures with trigonal-bipyramidal coordination to these complexes, according to the structure determinations of similar $LZnX_2$ complexes with tridentate nitrogen ligands[24]. This is supported by their spectral data (see Experimental), specifically the IR bands at 1602 and 1605 cm^{-1} indicating coordinated pyridine rings[9,24], and the low-field shifts of the aliphatic methylidyne ^{1}H-NMR resonances upon coordination. Furthermore, the coordination of the thioether sulfur atoms needs normally not be considered[25].

Derivatives of $MESIH_2$

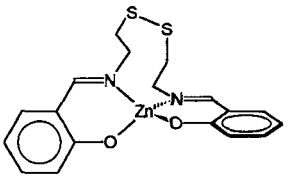
$MESIH_2$ [*N*-(2-mercaptoethyl)salicylideneimine] is the open-chain tautomer of HPT [2-(2-hydroxyphenyl)-1,3-thiazolidine] which, however, exists only in non-measurable quantities in solution[20] according to eqn. (2). It is a diprotonic acid capable of forming the dianionic MESI ligand. So far its ligating properties seem to have been tested only towards copper[26]. We found that protolytic displacement of $HN(SiMe_3)_2$ from $Zn[N(SiMe_3)_2]_2$ or of HOAc from $Zn(OAc)_2$ by $MESIH_2$ resulted in the formation of the 1:1 compound **2**. When solutions containing **2** or its precursors were exposed to air for some days, oxidative interconversion took place precipitating the crystalline 2:1 compound **3**.

(MESI)Zn (MESI)$_2$Zn
2 **3**

Compound **2** which is partly soluble only in DMSO and DMF seems to be a polymer. Its IR spectrum shows the band of the C=N moiety at 1621 cm^{-1}, thereby indicating that MESI is present as a ligand and coordinated via the imine nitrogen[27]. This is supported by the absence of a N–H band in the IR, and similarly the absence of O–H and S–H bands indicates O and S coordination. The ligand MESI therefore must be tridentate, and assuming polymerization via bridging thiolate functions, we can deduce the following structure for **2**:



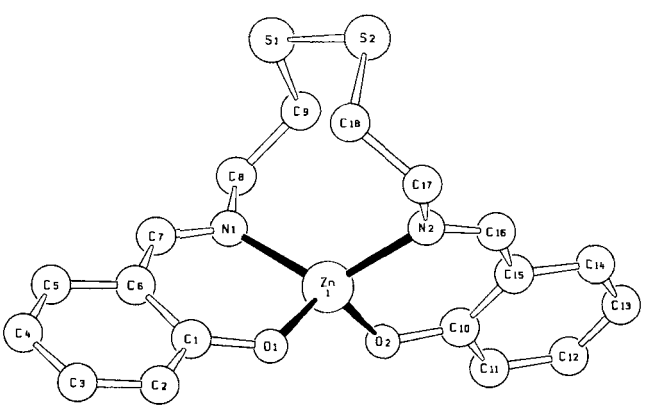
2



3

The IR spectrum of **3** is quite similar to that of **2**. Its C=N band at 1616 cm^{-1} which appears 5 cm^{-1} at lower field than that of **2** gave the misleading clue that the imine nitrogen might not coordinate. The absence of O–H, N–H, and S–H bands in the IR spectrum seemed to indicate that there were two excessive negative charges in a compound of composition $(MESI)_2Zn$ or, alternatively, ligand dimerization had taken place. The latter was proven to be the case by a structure determination of **3**, yielding the constitution given in the formula and the geometry of the complex given in Figure 1. The ease of disulfide formation leading to **3** parallels the observation that the corresponding ligand in complex **3a** (see below) could not be reduced electrolytically to the thiolate fragments in the presence of zinc[27].

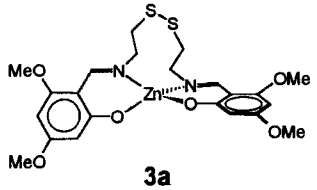
Figure 1. Molecular structure of **3**



Selected bond lengths [Å] and angles at zinc [°]: Zn1–O1 1.897(3), Zn1–O2 1.905(3), Zn1–N1 1.996(3), Zn1–N2 1.995(3), S1–S2 2.006(2); O1–Zn1–O2 121.8(2), N1–Zn1–N2 121.7(1), O1–Zn1–N1 97.1(1), O2–Zn1–N2 97.1(1), O1–Zn1–N2 112.0(1), O2–Zn1–N1 108.9(2).

The new ligand $(MESI)_2^{2-}$ seems to create a rather strain-free environment for tetrahedral zinc in a N_2O_2 coordination sphere (cf. bond lengths and angles). As salicylideneimine ligands are quite common in zinc chemistry[2], several structure determinations exist for similar ZnN_2O_2 complexes[27–30]. Most similar is complex **3a** obtained from the corresponding disulfide[27]. In all cases there is a close correspondence with the atomic distances and bond angles around zinc. The disulfide unit in **3** has a normal S–S distance and a dihedral angle of 95° showing that it is strain-

free as well. Its sulfur atoms are well outside the bonding range for zinc (4.20 and 4.25 Å).

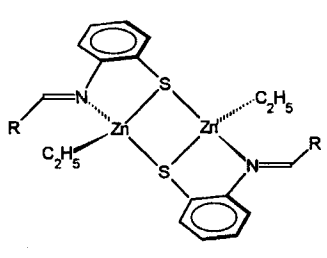


3a

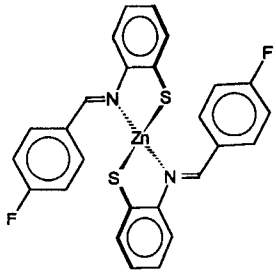
Derivatives of FPBT and MPBT

The tautomerization of the 2-aryl-benzo-1,3-thiazolines FPBT and MPBT to the *N*-(2-mercaptophenyl)-benzylideneimines MPFBH and MPMBH [cf. eqn. (3)] should produce ligands of lower functionality as compared to $MESIH_2$. We hoped that, in their anionic form, these ligands would form zinc complexes in which one additional reactive function, i.e. the positive charge or a labile ligand in the 1:1 compounds, would be available for further studies. We therefore carried out some reactions with MPBT[19] and the new thiazoline FPBT which are both accessible by condensation of *o*-aminothiophenol with the *p*-substituted benzaldehydes, and which, according to our NMR observations, exist only in the thiazoline form in solution.

Under protic conditions (water, methanol) reactions of zinc salts with the thiazolines afforded product mixtures which were difficult to separate. We therefore made use of the acidity of the ligands to cleave diethylzinc into hydrocarbons and Zn^{II}. From 1:1 reactions the two 1:1 complexes **4a** and **b** were obtained. These complexes have the advantage that they contain a reactive site in the form of the ethylzinc groups. However, this advantage is outbalanced by the high lability of the compounds which can be handled only in the solid state. In solution they decompose so quickly that NMR spectra could not be recorded. Solid-state ^{13}C-NMR spectra were measured to verify the presence of the MPFB and MPMB ligands and the zinc-bound ethyl groups. Furthermore the C=N bands in the IR spectra at 1599 (**4a**) and 1605 cm^{-1} (**4b**), as above, indicate coordination of the imine nitrogen atoms. Thus, three coordination positions on each zinc atom are accounted for. It seems therefore likely that the complexes are dimeric as shown by the formulas. This would give each zinc ion a tetrahedral environment and correspond to the situation in similar zinc-alkyl complexes with amine-thiolato ligands[31].



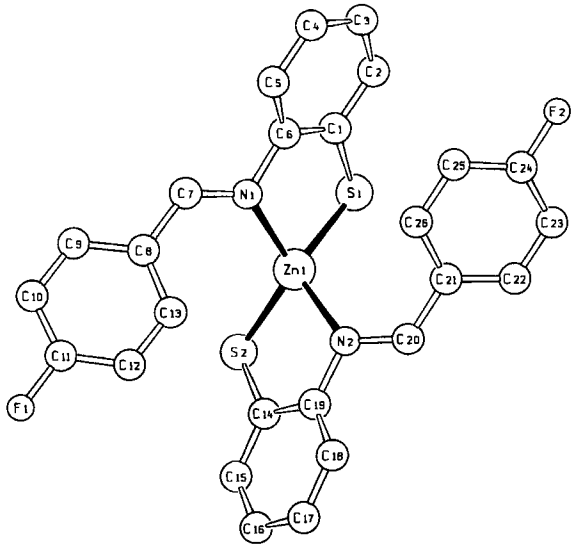
4a: R = FC_6H_4
4b: R = $MeOC_6H_4$



5

One of the decomposition products of **4a** which crystallized from a toluene solution was the 2:1 complex **5**. This complex could more conveniently be obtained by reaction of FPBT with $ZnEt_2$ in a 2:1 ratio. The ^1H-NMR spectrum of **5** shows nothing but the presence of the ligand MPFB, and the IR band at 1598 cm^{-1} again indicates coordination with the imine nitrogen atoms. Thus, **5** can be assumed to be a tetrahedral ZnN_2S_2 complex.

Figure 2. Molecular structure of **5**



Selected bond lengths [Å] and angles at zinc [°]: Zn–N1 2.105(4), Zn–N2 2.118(4), Zn–S1 2.238(2), Zn–S2 2.261(2); N1–Zn–N2 115.1(2), N1–Zn–S1 89.4(1), N2–Zn–S2 88.0(1), N1–Zn–S2 123.8(1), N2–Zn–S1 120.0(1), S1–Zn–S2 123.6(1).

The structure determination of **5** confirmed the structural assignment (cf. Figure 2). Compound **5** belongs to the large class of ZnN_2S_2 complexes which contains several of the L_2Zn type with five-membered chelate rings[32,33] or with chelating mercaptoimine ligands[6,34,35], and to which belong important ones of the zinc finger proteins[36]. For all those complexes that contain two five-membered N,S-chelate rings, the bond lengths and angles about the zinc ion are very close to those observed for **5**. Therefore, the observed values can be used for structural assignments or molecular mechanics calculations of biological ZnN_2S_2 systems. It should be noted, however, that this is valid only for the ZnN_2S_2 situation, and that already the homologous ZnN_2O_2 situation, as described above for **3**, provides Zn–N distances which are about 0.11 Å shorter.

The present work has shown that the original strategy of using thiazolines and thiazolidines as precursors of chelating N,S ligands may still be applied. With the systems employed, however, the control of the outcome of the reactions is still rather limited. This is most typically revealed by the $MESIH_2$ derivatives whose thiolate function ends up either in a bridging position (**2**) or as part of a disulfide linkage (**3**). While this is not too unexpected in the light of many other attempts to modify the structure of zinc-thiolate complexes, it still poses the challenge of obtaining better results

by proper modifications of the starting materials. A particular challenge in this context is the synthesis of the elusive tripod ligand MEDPAH into which we plan to invest increased efforts.

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Experimental

The general experimental techniques and the measuring instruments were as described before[37]. Starting materials were obtained commercially. All reactions were performed under nitrogen.

Synthesis of the ligand precursors: HPT[20] and MPBT[19] were prepared as described.

PPMT: 10.2 g of pyridine-2-carbaldehyde (95.7 mmol) was treated dropwise with 16.0 g (95.7 mmol) of 2-mercaptoethyl-2-picolylamine[9]. The mixture was stirred for 30 min, 100 ml of ethanol was added and the solution was refluxed for 2 h. The solvent was removed in vacuo and the remaining oil treated five times with 10 ml of benzene, stirred, and evaporated to dryness again. 24.5 g (99%) of PPMT remained as a yellowish viscous oil which was pure according to its ^{1}H-NMR analysis. – $C_{14}H_{16}N_3S$ (257.3): calcd. C 65.85, H 5.13, N 16.46; found C 64.33, H 5.72, N 16.09. – Selected IR bands (film, cm^{-1}): 1588 vs, 1569 s, 1468 s, 1433 vs, (pyridine bands). – ^{1}H NMR ([D$_6$]DMSO, δ): 2.95–3.09 (m, 2H, NCH$_2$C*H*$_2$S), 3.17–3.37 (m, 2H, NC*H*$_2$CH$_2$S), 3.76 (d, *J* = 13.1 Hz, 1H, NC*H*HPy), 3.89 (d, *J* = 13.1 Hz, 1H, NCH*H*Py), 5.43 (s, 1H, methyne-CH), 7.16–7.32 (m, 2H, py), 7.46–7.60 (m, 2H, py), 7.66–7.82 (m, 2H, py), 8.42–8.55 (m, 2H, py). – ^{13}C NMR ([D$_6$]DMSO, δ): 30.8 (NCH$_2$*C*H$_2$S), 56.7 (N*C*H$_2$CH$_2$S), 59.1 (NCH$_2$py), 76.3 (methyne-C), 119.6, 122.1, 122.5, 136.5, 136.7, 148.7, 158.5, 161.5 (pyridine-C).

FPBT: A mixture of 5.79 g (46.6 mmol) of *p*-fluorobenzaldehyde and 5.85 g (46.7 mmol) of 2-mercaptoaniline was stirred. It became hot and solidified within a few minutes. After 4 h the solid was recrystallized from ethanol. After filtration, washing with cold ethanol and drying in vacuo 8.51 g (79%) of FPBT remained as yellowish crystals of m.p. 60°C. – $C_{13}H_{10}FNS$ (231.3): calcd. C 67.51, H 4.36, N 6.06; found C 67.59, H 4.32, N 6.05. – Selected IR bands (KBr, cm^{-1}): 3317 s (NH), 1601 s, 1580 s, 1506 vs, 1472 s, 1461 vs (aromatic), 1227 vs (CF). – ^{1}H NMR ([D$_6$]acetone, δ): 6.01 (s, br., 1H, NH), 6.48 (d, *J* = 2.8 Hz, 1H, methyne-CH), 6.63–6.70 (m, 2H, phenyl), 6.91 (dt, *J* = 8.2 and 1.4 Hz, 1H, phenyl), 6.99 (dd, *J* = 7.8 and 1.4 Hz, 1H, phenyl), 7.10 (dd, *J* = 8.8 and 8.8 Hz, 2H, fluorophenyl), 7.59 (dd, *J* = 8.6 and 5.5 Hz, 2H, fluorophenyl). – ^{13}C NMR ([D$_6$]acetone, δ): 69.7 (methyne-C), 109.9 (phenyl), 115.9 (d, *J* = 22 Hz, fluorophenyl), 120.4, 122.0, 126.3, 127.3 (phenyl), 129.3 (d, *J* = 9 Hz, fluorophenyl), 139.9, 148.2 (phenyl), 163.4 (d, *J* = 245 Hz, fluorophenyl). – ^{19}F NMR ([D$_6$]acetone): δ = −114.5 ppm vs. $CFCl_3$.

Zinc Complexes

1a: A solution of 96 mg (0.38 mmol) of PPMT in 4 ml of ethanol was stirred and treated dropwise with a solution of 83 mg (0.38 mmol) of $ZnBr_2$ in 10 ml of ethanol. After stirring for 1 h the precipitate was filtered off, washed with ethanol and dried in vacuo to yield 133 mg (73%) of **1a** as a colorless powder of m.p. 255°C (dec.). – $C_{14}H_{15}Br_2N_3SZn$ (482.6): calcd. C 34.85, H 3.13, N 8.79; found C 34.63, H 3.09, N 8.48. – Selected IR bands (KBr, cm^{-1}): 1602 vs, 1572 m, 1482 s, 1471 s, 1439 vs (pyridine bands). – ^{1}H NMR ([D$_6$]DMSO, δ): 2.63–3.25 (m, 4H, NC*H*$_2$C*H*$_2$S), 4.21 (s, 2H, NCH$_2$Py), 5.84 (s, 1H, methyne-CH), 7.62–7.94 (m, 4H, py), 8.05–8.17 (m, 2H, py), 8.77–8.92 (m, 2H, py). – ^{13}C NMR ([D$_6$]DMSO, δ): 29.8 (NCH$_2$*C*H$_2$S), 55.6 (N*C*H$_2$CH$_2$S and NCH$_2$Py), 74.9 (methyne-C), 124.4, 124.9, 140.2, 140.4, 147.2, 147.8, 154.0, 157.0 (pyridine-C).

1b: A solution of 33 mg (0.13 mmol) of PPMT in 4 ml of ethanol was stirred at treated dropwise with a solution of 34 mg (0.13 mmol) of $Zn(NO_3)_2 \cdot 4\ H_2O$ in 4 ml of ethanol. After stirring for 30 min the precipitate was filtered off, washed with ethanol and dried in vacuo to yield 45 mg (78%) of **1b** as a colorless powder of m.p. 270°C (dec.). – $C_{14}H_{15}N_5O_6SZn$ (446.8): calcd. C 37.63, H 3.38, N 15.67; found C 37.62, H 3.33, N 15.65. – Selected IR bands (KBr, cm^{-1}): 1605 s, 1468 vs, 1459 vs (pyridine bands), 1384 vs, 1337 m, 1307 vs, 1292 vs (nitrate bands). – ^{1}H NMR ([D$_6$]DMSO, δ): 2.56–3.36 (m, 4H, NCH$_2$CH$_2$S), 4.17–4.34 (m, 2H, NCH$_2$py), 5.78 (s, 1H, methyne-CH), 7.62–7.87 (m, 4H, py), 8.08–8.28 (m, 2H, py), 8.54–8.73 (m, 2H, py). – ^{13}C NMR ([D$_6$]DMSO, δ): 30.0 (NCH$_2$*C*H$_2$S), 55.6 (N*C*H$_2$CH$_2$S), 56.1 (NCH$_2$py), 75.4 (methyne-C), 124.7, 124.9, 125.4, 140.6, 140.9, 146.6, 147.5, 154.3, 157.1 (pyridine-C).

2: A solution of 289 mg (2.27 mmol) of HPT and 0.63 ml (460 mg, 4.5 mmol) of triethylamine in 2 ml of acetonitrile was stirred and treated dropwise with a solution of 498 mg (2.27 mmol) of $Zn(OAc)_2 \cdot 2\ H_2O$ in 10 ml of acetonitrile. After stirring for 1 h the precipitate was filtered off, washed with acetonitrile and dried in vacuo to yield 189 mg (34%) of **2** as an off-white powder of m.p. 250°C (dec.). – $C_{18}H_{18}N_2O_2S_2Zn_2$ (489.2): calcd. C 44.19, H 3.71, N 5.73; found C 44.45, H 4.13, N 5.09. – Selected IR bands (KBr, cm^{-1}): 1621 vs, 1599 s (C=N), 1535 s, 1466 s, 1446 vs, 1401 s (aromatic). – ^{1}H NMR ([D$_6$]DMSO, δ): 2.59–2.69 (br., 2H, NCH$_2$C*H*$_2$S), 3.52–3.63 (br., 2H, NC*H*$_2$CH$_2$S), 6.48 (t, *J* = 7.4 Hz, 1H, phenyl), 6.71 (d, *J* = 8.1 Hz, 1H, phenyl), 7.09–7.20 (m, 2H, phenyl), 8.32 (s, 1H, N=CH). – ^{13}C NMR ([D$_6$]DMSO, δ): 22.9 (NCH$_2$*C*H$_2$S), 59.2 (N*C*H$_2$CH$_2$S), 112.8, 119.6, 122.6, 132.9, 134.8, 136.3 (aromatic). 166.6 (C=N).

3: In dry air a solution of 780 mg (4.30 mmol) of HPT in 30 ml of toluene was stirred and treated dropwise with a solution of 1.66 g (4.30 mmol) of $Zn[N(SiMe_3)_2]_2$ in 20 ml of toluene. After 2 h the precipitate, consisting of 0.30 g (29%) of **2**, was filtered off. The mother liquor was allowed to stand for a week during which time a few mg of **3** (m.p. 212°C) were precipitated as a yellowish powder containing a few single crystals. – $C_{18}H_{18}N_2O_2S_2Zn \cdot 1/2\ C_7H_8$ (423.9 + 46.1) calcd. C 54.95, H 4.72, N 5.96; found C 54.91, H 4.86, N 5.72. – Selected IR bands (KBr, cm^{-1}): 1616 vs, 1603 s (C=N), 1534 s, 1464 s, 1445 s, 1401 s (aromatic). – The amount of **3** was not sufficient for recording NMR spectra.

4a: A suspension of 2.75 g (11.9 mmol) of FPBT in 30 ml of hexane was stirred and treated dropwise with 12.2 ml (12.2 mmol) of a 1 M solution of $ZnEt_2$ in hexane. The resulting orange suspension was stirred for 1 d. Then the precipitate was filtered off, washed with hexane, and dried in vacuo yielding 3.51 g (91%) of **4a** as a yellow powder of m.p. 170°C (dec.). – $C_{30}H_{28}F_2N_2S_2Zn_2$ (649.5): calcd. C 55.48, H 4.35, N 4.31, Zn 20.1; found C 53.56, H 4.00, N 4.24, Zn 20.2. – Selected IR bands (KBr, cm^{-1}): 1599 vs (C=N), 1587 s, 1572 s, 1561 s, 1508 vs (aromatic), 1239 vs (CF). – ^{13}C NMR (MAS, δ): 3.2 (Zn*C*H$_2$CH$_3$), 13.1 (ZnCH$_2$*C*H$_3$), 112.2, 119.5, 126.3, 130.3, 132.4, 136.6 (aromatic), 163.9 (C=N).

4b: Like **4a** from 1.44 g (5.92 mmol) of MPBT and 8.2 mmol of $ZnEt_2$. Yield 1.94 g (97%) of **4b** as a greenish-yellow powder of m.p. 230°C (dec.). – $C_{32}H_{34}N_2O_2S_2Zn_2$ (673.2): calcd. C 57.07, H 5.09, N 4.16, Zn 19.4; found C 55.59, H 4.99, N 3.98, Zn 19.7. – Selected IR bands (KBr, cm^{-1}): 1605 s (C=N), 1593 vs, 1566 s, 1554 s, 1514 vs (aromatic), 1267 vs (C–O). – ^{13}C NMR (MAS, δ):

2.1 ($ZnCH_2CH_3$), 13.8 ($ZnCH_2CH_3$), 54.7 (OCH_3), 111.2, 118.0, 123.7, 126.6, 129.7, 133.4, 135.4, 138.7, 147.6 (aromatic), 164.1 (C=N).

5: Solutions of 850 mg (3.67 mmol) of FPBT in 30 ml of toluene and of 1.84 mmol (1.84 ml of 1 M in hexane) of $ZnEt_2$ in 30 ml of toluene were mixed. After a few minutes a precipitate started forming which after 2 h was filtered off, washed with toluene, and dried in vacuo yielding 947 mg (97%) of **5** as an orange powder of m.p. 210°C (dec.). – $C_{26}H_{18}F_2N_2S_2Zn$ (525.9): calcd. C 61.94, H 3.88, N 4.90; found C 60.90, H 3.74, N 4.87. – Selected IR bands (KBr, cm^{-1}): 1598 vs (C=N), 1584 s, 1571 s, 1561 m, 1543 m, 1508 s (aromatic), 1243 s (CF). – ^1H NMR ([D$_6$]acetone, δ): aromatic multiplets at 6.38 (4H), 7.01 (2H), 7.16 (2H), 7.32 (2H), 7.44 (2H), 7.99 (4H), methyne singlet (2H) at 8.92. – The poor ^{13}C-NMR spectrum ([D$_6$]acetone) due to the low concentration showed only aromatic signals. – ^{19}F NMR ([D$_6$]acetone): δ = −105.2 ppm vs. $CFCl_3$.

Structure Determinations[38]: Crystals of **3** and **5**, both containing solvent of crystallization, were obtained from toluene. All crystallographic details are given in Table 1. Data were obtained with a Nonius CAD4 diffractometer using Mo-K_α radiation and the ω/2Θ technique. The structures were solved with direct methods and refined anisotropically without an absorption correction. In both cases a distorted toluene molecule was found to be located around an inversion center. In the crystals of **3** there is some disorder in the disulfide group which can be accounted for by splitting the S2 position into two with occupancy factors of 0.89 and 0.11. Hydrogen atoms were included with fixed C–H distances of 96 pm and a common isotropic temperature factor. Calculations were done with the SHELX programs[39], the drawings were produced using SCHAKAL[40].

Table 1. Crystallographic details

	3	**5**
formula	$C_{18}H_{18}N_2O_2S_2Zn \cdot \frac{1}{2}C_7H_8$	$C_{26}H_{18}F_2N_2S_2Zn \cdot \frac{1}{2}C_7H_8$
mol. wt.	423.9+46.1	525.9+46.1
crystal size [mm]	0.4·0.4·0.15	0.5·0.5·0.7
cryst. from	toluene	toluene
colour	yellow	red
space group	P-1	$P2_1/c$
Z	2	4
a [Å]	10.361(1)	13.766(1)
b [Å]	10.587(1)	13.899(1)
c [Å]	11.796(1)	14.304(2)
α [°]	107.15(1)	90
β [°]	95.92(1)	105.09(1)
γ [°]	116.74(1)	90
V [nm³]	1.0612(1)	2.6425(5)
$d_{calc.}$ [gcm^{-1}]	1.47	1.44
$d_{obs.}$ [gcm^{-1}]	1.45	1.38
μ(Mo-K$_\alpha$) [mm^{-1}]	1.37	1.12
2Θ range [°]	5 - 52	5 - 52
hkl range	±h, +k, ±l	-h, +k, ±l
ind. refln. measd.	4009	5158
refln. used [I>2σ(I)]	3112	2275
parameters	289	361
R-value	0.047	0.049
residual el.density, [e. Å³]	+0.9 / -0.8	+0.3 / -0.4

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