Alcohol and Aldehyde Adducts of Zinc Thiolates: Structural Modeling of Alcoholdehydrogenase

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Received October 19, 1998

Bis(pentafluorothiophenolato)zinc (**1**) and bis(2,4,6-triisopropylthiophenolato)zinc (**2**) can be combined with nitrogen-containing derivatives of benzyl alcohol and benzaldehyde to form (N,O-chelate) zinc thiolates. 2-Pyridylmethanol as well as 2-quinolylmethanol (HetMeOH) yield $[(HetMeO)Zn(SR)]_4$ (**3**, **4**) having a cyclo-$Zn_4(\mu\text{-}O)_4$ backbone and only terminal SR. Likewise, thiolate **1** and 2-(dimethylamino)benzyl alcohol form zwitterionic $[(dimethylammoniobenzylato)Zn(SR)_2]_2$ (**5**) with bridging alkoxide and terminal thiolate. In contrast, 6-picolylmethanol (PicMeOH) and thiolate **1** result in $[(PicMeOH)Zn(SC_6F_5)_2]$ (**6**) containing zinc in a tetrahedral $ZnNS_2O$, environment. Simple aromatic aldehydes form polymeric complexes $[(RCHO)Zn(SC_6F_5)_2]$ (**7**: R = *p*-tolyl, **8**: R = mesityl) with a $[Zn-S]_\infty$ backbone. Chelating aldehydes (CA) yield mononuclear complexes with tetrahedral $ZnNS_2O$ coordination $[(CA)Zn(SC_6F_5)_2]$ (**9**, CA = pyridine-2-carbaldehyde; **10**, CA = 6-methylpyridine-2-carbaldehyde; **11**, CA = 6-methoxypyridine-2-carbaldehyde; **12**, CA = quinoline-2-carbaldehyde; **13**, CA = 2-(dimethylamino)benzaldehyde). In contrast, *N*-methylimidazole-2-carbaldehyde (ImA) is coordinated twice in tetrahedral $[(ImA)_2Zn(SC_6F_5)_2]$ (**14**) lacking any Zn−O interactions. Pyridine-2,6-dicarbaldehyde (PDA) forms trigonal bipyramidal $[(PDA)Zn(SC_6F_5)_2]$ (**15**) with $ZnNO_2S_2$ ligation. The structures of **3**, **4**, **6**, **8**, **10**, **11**, **13**, and **14** were determined crystallographically, and the structures of **5** and **15** were deduced from those of the corresponding $ZnBr_2$ complexes. The $ZnNS_2O$ coordination pattern observed for the enzyme has been reproduced to a very good approximation. In complexes **6** and **10**, which are almost superimposable, it is realized for both the corresponding alcohol and aldehyde.

Introduction

Horse liver alcohol dehydrogenase has been very well investigated in terms of both reactivity[1] and structure.[2] It is the prototype of the alcoholdehydrogenases (ADH's) which, depending on the situation, catalyze the dehydrogenation of alcohols by NAD^+ or the hydrogenation of aldehydes by NADH. The catalytic zinc ion in this enzyme has the unusual function of activating a substrate for a redox reaction. It is tuned for this purpose by a $ZnNS_2$ ligand environment composed of one histidine imidazole and two cysteine thiolate ligands inside a hydrophobic pocket. The accumulated evidence indicates that the hydrogen transfer reaction interconverts zinc-bound alkoxide and aldehyde moieties. Thus the inorganic core of the reacting enzyme can be desribed as a $ZnNS_2O$ coordination compound.

Attempts to reproduce this enzymatic environment in zinc complexes by using amine−bisthiols as tridentate NS_2 ligands have invariably resulted in thiolate-bridged oligonuclear compounds.[3−5] Only very recently was a bis(methimazolyl)-(pyrazolyl)borate ligand described that supports tetrahedral $ZnNS_2X$ coordination,[6] but not yet converted to a $ZnNS_2O$ complex, with O representing an alkoxide or aldehyde. Likewise, zinc complexes with terminal monodentate alkoxide ligands are underdeveloped,[7] and prior to our own work,[8] aldehyde complexes of zinc were hardly known. In the course of his studies on low-coordinate zinc thiolates, Bochmann described the first structure of a zinc−aldehyde complex, $Zn(SeR)_2 \cdot R'CHO$,[9] and mentioned a pyridine-2-carbaldehyde·$Zn(SR)_2$ complex assumed to contain the $ZnNS_2O$ coordination pattern.[10] This pattern was verified in aquatris(benzothiazolethiolato)-zincate.[11] But to our knowledge no zinc thiolate with a $ZnNS_2O$ ligand set has been structurally characterized so far.

We have been engaged in studies related to the modeling of ADH for a number of years. We have contributed to the variations of N- and S-containing ligands,[5,12−14] including

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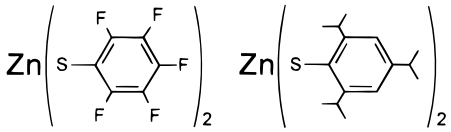
10.1021/ic981227m CCC: $18.00
Published on Web 04/03/1999

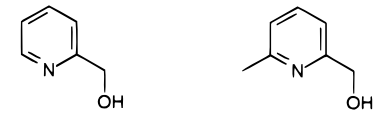
peptides.[15] We have investigated the attachment of alcohols and alkoxides to zinc,[7,16,17] including the chelating 2-pyridylmethanol.[18] We have launched a massive campaign aimed at learning about zinc−aldehyde interactions.[8] Of this, the results on aldehyde complexes of zinc salts with weakly coordinating anions,[19a] of zinc halides,[19b] and on zinc complexes of chelating aldehydes[19c] have been published, being backed up by 40 structure determinations. They have laid the basis for the work described in this paper. Aromatic alcohols and aldehydes were combined with zinc thiolates in the hope to find structural representations of the $ZnNS_2O$ coordination pattern in the enzyme. In most cases stabilization by the chelate effect was sought by using alcohols and aldehydes derived of pyridine. On the side of the thiolates their bridging tendency was reduced by applying steric hindrance (2,4,6-triisopropylthiophenolate) or electronegative substituents (pentafluorothiophenolate). X-ray crystallography again was an indispensable tool to verify the hoped-for and the unexpected results of the investigation.

Results and Discussion

Alcoholic Substrates. The investigations were started by reacting each substrate with both zinc thiolates **1** and **2**. The chelating alcohols used were the 2-methylol derivatives of

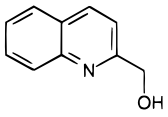


1 **2**

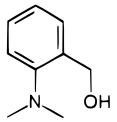


2-pyridylyl-methanol **PyMeOH**

6-picolyl methanol **PicMeOH**



2-quinolyl-methanol **QuiMeOH**



2-dimethylamino-benzylalcohol **DmaMeOH**

pyridine (PyMeOH), picoline (PicMeOH), quinoline (QuiMeOH), and *N*-dimethylaniline (DmaMeOH). While, as a rule, reactions of **1**[20] led to pure products, those of **2**, which itself is difficult to obtain in a pure state,[21] were cumbersome, for which reason the aldehyde reactions described below were performed only with **1**.

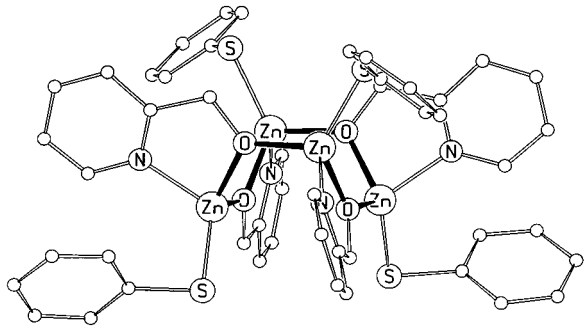


Figure 1. Molecular structure of **3** (isopropyl groups omitted for clarity). Important bond lengths (Å) and angles (deg) (average of four independent values): Zn−O 1.964 ± 0.007(3), Zn−O′ 1.936 ± 0.006(3), Zn−S 2.240 ± 0.007(2), Zn−N 2.069 ± 0.010(3), O−C 1.1398 ± 0.007(5), O−Zn−O′ 99.3 ± 0.9(2), O−Zn−N 81.7 ± 0.3(2), O′−Zn−N 109.0 ± 2.4(2), O−Zn−S 129.1 ± 2.1(2), O′−Zn−S 116.0 ± 1.5(1), N−Zn−S 115.9 ± 0.8(1).

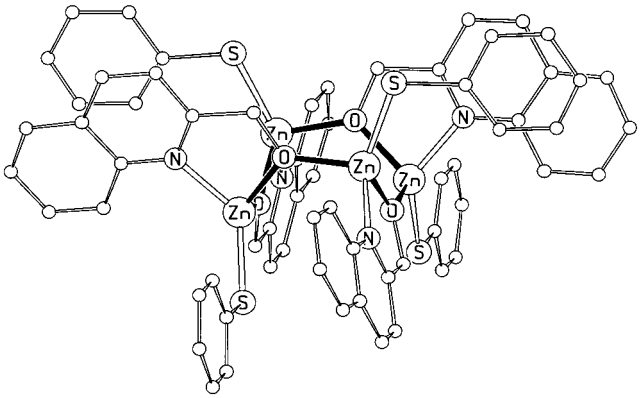


Figure 2. Molecular structure of **4** (all fluorine atoms omitted for clarity). Important bond lengths (Å) and angles (deg) of the tetramer with 4-fold crystallographic symmetry: Zn−O 1.958(3), Zn−O′ 1.964(3), Zn−S 2.253(1), Zn−N 2.048(3), O−C 1.387(5), O−Zn−O′ 104.3(2), O−Zn−N 82.5(2), O′−Zn−N 104.7(2), O−Zn−S 127.3(1), O′−Zn−S 103.9(1), N−Zn−S 130.5(1).

The only crystalline product obtained from **2** was the tetranuclear complex **3**. It resulted from **2** (contaminated with $Zn[N(SiMe_3)_2]_2$) and PyMeOH in hexane. The related tetranuclear complex **4** resulted from treatment of **1** with QuiMeOH in methanol. In both cases deprotonation of the alcohol is facilitated by the presence of the heteroaromatic nitrogen bases and in the first case by the presence of $Zn[N(SiMe_3)_2]_2$. The spectra of **3** and **4** (see Experimental Section) yielded no other information than the 1:1:1 (zinc:thiolate:N,O-ligand) composition.

$[(PyMeO)Zn(SC_6H_2Pr^i_3)]_4$ **3** $\qquad$ $[(QuiMeO)Zn(SC_6F_5)]_4$ **4**

The structure determinations of **3** and **4** (Figures 1 and 2) revealed their tetrameric nature, the presence of alkoxide rather than thiolate bridging, and their overall similarity. The tetramers form boat-shaped Zn_4O_4 rings with a quite symmetrical distribution of Zn−X bond lengths but serious deviations of the bond angles at zinc from the tetrahedral value. Ring shape and ligand distribution are quite similar to those in tetrameric chloro-

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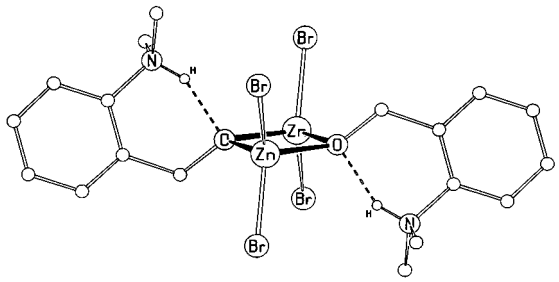
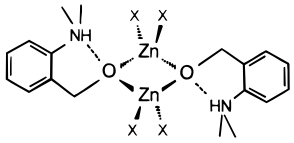


Figure 3. Molecular structure of **5a** (two independent halves of the centrosymmetrical dinuclear complexes per asymmetric unit). Important bond lengths (Å) and angles (deg): Zn−O 2.018 ± 0.008(3), Zn−Br 2.348 ± 0.004(1), O−C 1.428 ± 0.002(5), Zn···Zn 2.97, O−Zn−O 85.4 ± 0.1(1), Br−Zn−Br 122.2 ± 0.1(1).

[(diethylamino)ethanolato]zinc[22] and ethyl(glycineolato)zinc.[23] In contrast, tetrameric Zn(MEMA) (MEMAH$_2$ = (mercaptoethyl)-2-mercaptoaniline)[5] and {[[(trimethylsilyl)methyl]pyridyl]-methanolato}zinc[24] have a chairlike conformation of their Zn_4S_4 and Zn_4O_4 rings. While the structural motif of a single alkoxide bridge between two zinc ions in a dinuclear complex seems to be unknown, the most common motif is $Zn_2(\mu\text{-OR})_2$.[25] It is not immediately obvious that steric hindrance should prevent thiolate bridging in **3** and **4**, but the favorability of Zn−O−Zn ligation can be deduced from the lengths of the Zn−O bonds, which on the average are 0.1 Å shorter than the Zn−N bonds.

The surprising fact that alkoxide bridging is preferred over thiolate bridging in these complexes was underlined by the observation that the same seems to be the case for the adduct between **1** and DmaMeOH, even at the expense of an intramolecular acid−base reaction leading to a zwitterionic product, **5**.



5 : X = SC_6F_5 **5a** : X = Br

5, which was formed by combining the reagents in ether/THF, did not form single crystals. Therefore, the corresponding $ZnBr_2$ complex **5a** was prepared analogously and subjected to a structure determination. The IR and ^{1}H and ^{13}C NMR spectra of **5** and **5a** are almost superimposable (see Experimental Section), indicating a similar structure. The important piece of information concerning the zwitterionic nature is the disappearance of the OH absorption in the IR (cf. **6** below) and the presence of weak to medium and broad IR bands at 2633 cm^{-1} for **5** and at 2657 cm^{-1} for **5a**, which can be assigned to a NH or N−H···O bonding situation.

The structure of **5a** is displayed in Figure 3. The molecules are centrosymmetrical; i.e., they contain planar Zn_2O_2 rings. The noninvolvement of the amine nitrogen in zinc coordination, unlike the situation in the corresponding aldehyde complex (see **13**, below, and ref 19c), is obvious. It corresponds to N

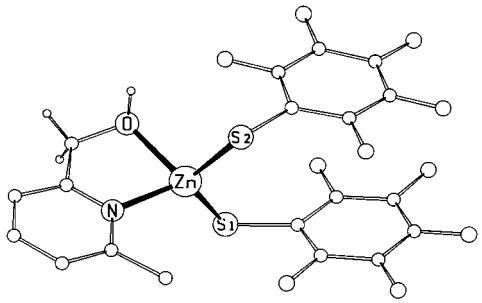


Figure 4. Molecular structure of **6**. Important bond lengths (Å) and angles (deg): Zn−O 2.123(3), Zn−N 2.048(3), Zn−S1 2.249(1), Zn−S2 2.290(1), O−C 1.435(4), O−Zn−N 80.1(1), O−Zn−S1 109.2(1), O−Zn−S2 106.2(1), N−Zn−S1 120.1(1), N−Zn−S2 112.4(1), S1−Zn−S2 120.1(1).

protonation verified by localization of the NH hydrogen (N−H = 0.9(1) Å), and the short N···O distance of 2.65(1) Å. Applied to **5** this means that the coordination pattern of zinc is ZnS_2O_2 rather than the desired $ZnNS_2O$.

A complex with this desired coordination was obtained by combining **1** and PicMeOH in chloroform. It is not quite obvious which subtle difference betweeen PicMeOH on one side and PyMeOH or QuiMeOH on the other side explains the preference for either mononuclear alcohol or polynuclear alkoxide complexes. Complex **6** resulted in good yields. Its lower nuclearity was indicated by its higher solubility, compared to that of **3** and **4**. Its intact alcohol function could be deduced from the IR band at 3265 cm^{-1}. The bonding of its alcohol function to zinc was obvious from the OCH_2 ^{1}H NMR signal (see Experimental Section), which is shifted downfield by 0.48 ppm relative to that of free PicMeOH.

$$[\text{PicMeOH}\cdot\text{Zn}(SC_6F_5)_2]$$
6

At first glance the structure of **6** confirms the expected tetrahedral environment of zinc in its NS_2O donor set; see Figure 4. The bond lengths and angles of **6**, however, reveal very characteristic deviations. Thus the Zn−O bond is much longer than those in **3**, **4**, or **5a**, indicating its weakness, while the Zn−N bond length agrees with those in **3** and **4**. All three O−Zn−X angles are narrow, and the three other angles are wide, indicating a distortion of the $ZnNS_2O$ tetrahedron such that a trigonal $ZnNS_2$ coordination is approximated. The bonding features of this $ZnNS_2$ unit can actually be compared with those of purely tricoordinate and planar L·Zn(SR)$_2$ complexes.[10,26] In the case of **6** the weak interaction with the alcohol function lifts the zinc ion 0.35 Å out of the NS_2 plain, about half the amount for pure tetrahedral coordination.

Aldehydic Substrates. Plain Aldehydes. Simple aromatic aldehydes (A) were found to form two basic types of zinc halide complexes, A_2ZnHal_2 and halide-bridged $[A\cdot ZnHal_2]_\infty$.[19b] One should have expected similar findings for the aldehyde/**1** combination. It seems, however, that a bridging thiolate ligand is always preferred by zinc over a second aldehyde ligand here, making the $[A\cdot Zn(SR)_2]_x$ combination the only one that is realized. Two representatives of it, polymeric **7** and **8**, were isolated in a pure form after dissolving **1** in *p*-tolylaldehyde and mesitylaldehyde and precipitating the adducts with petroleum ether. Similar 1:1 adducts, but of a dimeric rather than polymeric nature, were obtained by Bochmann from benzalde-

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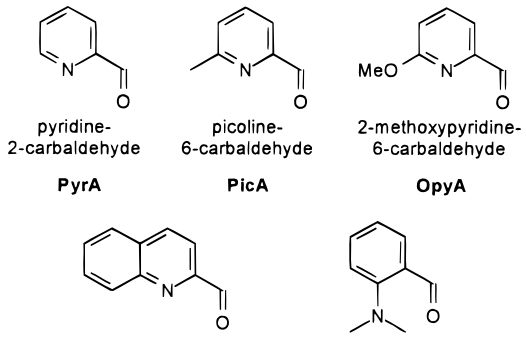
hyde or anisaldehyde and tri(*tert*-butyl)benzenethiolate or -selenolate.[9]

$$[(RCHO)Zn(SC_6F_5)_2]_\infty$$
7: R = *p*-tolyl
8: R = mesityl

The aldehyde coordination in these complexes is evident from the ν(CO) bands in the IR spectra, which are shifted 65 and 60 cm^{-1} to lower wavenumbers compared to those of the free aldehydes, which are typical values for the A·ZnX_2 composition.[19b] **7** and **8** dissolve readily in donor solvents such as acetone or acetonitrile, indicating breakdown of the polymers. Solution spectra give no clear information about the nature of the species in solution. While the ν(CO) IR bands are hidden under solvent bands, all NMR signals (^{1}H, ^{13}C, ^{19}F) are close to those of the individual components. This, however, is a common feature of most zinc complexes and cannot be taken as evidence for a release of the aldehydes from zinc in donor solvents.

The structure of **8** (see Figure 5) confirms the polymeric nature of the complexes but cannot be discussed in detail due to the low quality of the data set. As previously observed for zinc halide complexes of *p*-tolylaldehyde and *o*-chlorobenzaldehyde,[19b] the backbone of the polymer is a zigzag chain oriented along a glide plane. All aromatic residues are roughly parallel, indicating that their stacking shapes the structure. The coordination pattern is ZnS_3O, which is quite unusual in zinc chemistry.

Chelating Aldehydes. From our work on aldehyde complexes of zinc salts[19] we knew that aldehyde ligands enabling N,O chelation greatly enhance the stability of the complexes. With this in mind we chose the following aldehydes, which are derivatives of either pyridine or aniline and which allow the formation of either five- or six-membered N,O chelate rings, for reactions with $Zn(SR)_2$.



All five aldehydes underwent facile reactions with stoichiometric amounts of **1** in ether, forming complexes **9**−**13** in very good yields after precipitation with petroleum ether. The integrity of the complexes not only in the solid state but also in solution is evident from their spectra (see Experimental Section). In the IR spectra the ν(CO) bands are shifted by 30−50 cm^{-1} to lower wavenumbers and the intense heteroaromatic ring vibrations near 1600 cm^{-1} are shifted by 10−20 cm^{-1} to higher wavenumbers in comparison to the absorptions of the free aldehydes. The NMR spectra, unlike those for the alcohol or plain aldehyde complexes, contain a sensitive indicator of aldehyde coordination in the form of the CHO resonances.[19] The ^{1}H resonances of the aldehyde proton are shifted by 0.05−0.77 ppm to lower fields, the ^{13}C resonances for the aldehyde carbon are shifted by 0.9−4.4 ppm to higher fields, compared to the free aldehydes.

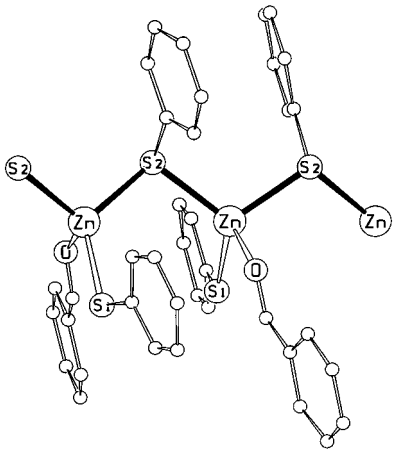


Figure 5. Structure of polymeric **8** (all substituents on the aromatic rings omitted for clarity). Important bond lengths (Å) and angles (deg): Zn−O 2.084(7), Zn−S1 2.294(3), Zn−S2 2.336(3), Zn−S2′ 2.342(3), O−C 1.22(1), O−Zn−S1 94.8(2), O−Zn−S2 92.8(2), O−Zn−S2′ 119.7(2), S1−Zn−S2 125.1(1), S1−Zn−S2′ 116.7(1), S2−Zn−S2′ 105.8(1), Zn−S2−Zn′ 101.2(1).

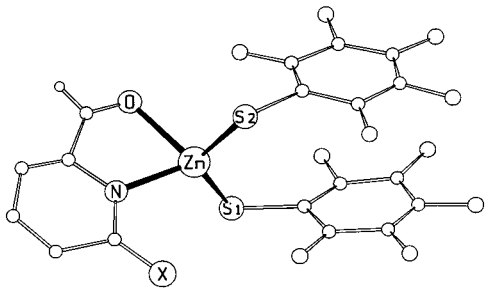


Figure 6. Molecular structure of complexes **10** (X = CH_3) and **11** (X = OCH_3). Important bond lengths (Å) and angles (deg) for **10**: Zn−O 2.24(1), Zn−N 2.07(1), Zn−S1 2.256(7), Zn−S2 2.250(8), O−C 1.20(2), N−Zn−O 73.4(7), N−Zn−S1 113.2(6), N−Zn−S2 117.4(5), O−Zn−S1 112.8(5), O−Zn−S2 103.4(5), S1−Zn−S2 123.9(2). For **11**: Zn−O 2.165(2), Zn−N 2.059(2), Zn−S1 2.274(1), Zn−S2 2.261(1), O−C 1.218(3), N−Zn−O 77.85(6), N−Zn−S1 115.16(5), N−Zn−S2 115.43(5), O−Zn−S1 102.63(5), O−Zn−S2 113.06(5), S1−Zn−S2 122.47(3).

$$[(CA)Zn(SC_6F_5)_2]$$

	9	10	11	12	13
CA:	PyrA	PicA	OpyA	QuiA	DmaA

The molecular structures of **10** and **11** can be discussed together and represented by one figure (Figure 6). Both share the distorted tetrahedral coordination of zinc, characterized by the narrow bite angle of the chelate ligand and the characteristically wide S−Zn−S angle. In both cases the coordination pattern and the nature of the ligands imply that the three aromatic ring systems of the complex are coplanar. The distortion of the coordination toward a trigonal $ZnNS_2$ environment is equally pronounced as in **6**, as evidenced by the bond angles and the distance of the zinc ion from the NS_2 plane (0.30 Å in **10**, 0.34 Å in **11**). In addition, the Zn−O bonds are significantly longer than the Zn−O (alcohol) bond in **6**, in accordance with the still lower donor quality of the aldehydes. The Zn−O distances correspond with those for our other zinc−aldehyde complexes,[19] and they are characteristically different from those for zinc complexes of the corresponding aldimine ligands.[27]

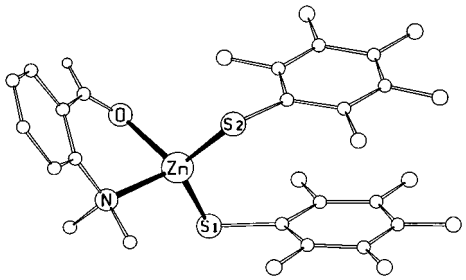
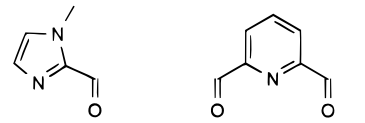


Figure 7. Molecular structure of **13**. Important bond lengths (Å) and angles (deg): Zn−O 2.10(1), Zn−N 2.10(1), Zn−S1 2.255(4), Zn−S2 2.254(4), O−C 1.22(2), O−Zn−N 86.0(4), O−Zn−S1 108.0(3), O−Zn−S2 111.9(3), N−Zn−S1 110.0(3), N−Zn−S2 110.4(3), S1−Zn−S2 124.0(2).

The structure of complex **13** is displayed in Figure 7. While its $Zn(SR)_2$ part looks the same as in all other complexes described here, the different chelate ring size and the different kind of the nitrogen donor cause some structural variations in comparison to **10** and **11**. Thus the whole (N,O) ligand system is not coplanar but folded across the chelate ring, and this time the Zn−N and Zn−O bond lengths are virtually identical. In addition, the $ZnNS_2O$ coordination geometry is closest to purely tetrahedral in this case. Three factors seem to combine to cause this: smaller angular strain at the chelate angle N−Zn−O, lower donor quality of the N atom (aliphatic amine rather than heteroaromatic imine), and better donor quality of the O atom (due to the more electron rich aromatic substituent). There are no comparable complexes in the literature other than our own zinc halide complexes,[19c] for which a comparison of the donor qualities of DmaA and PyrA led to the same observations. The most important feature of all complexes **9**−**13**, which is proved by these structure determinations, is the presence of the "enzymatic" coordination pattern $ZnNS_2O$ for aldehyde ligands.

Nonbidentate Chelating Aldehydes. To approximate the enzymatic situation a little better, the pyridine part of the chelating aldehydes was exchanged for the *N*-methylimidazole unit, having in mind that in the ADH enzyme the N donor of the $ZnNS_2O$ ligand set is the imidazole unit of histidine. Accordingly, the aldehyde MimA was considered a minimal



representation of the corresponding aldehyde ligation. On the other hand, it seemed suitable to find out whether the attachment of two aldehyde donors to the $Zn(SR)_2$ unit might be possible by making them part of the same chelating ligand, specifically PDA, again derived from pyridine.

No 1:1 complex could be isolated from mixtures of **1** and MimA. The 1:2 complex **14** obtained is another example of the highly dominant ZnN_2S_2 ligation in the field of zinc/sulfur/nitrogen complexes. By its very composition complex **14** indicated that the MimA ligands are bound to zinc solely with their N atoms. The IR spectrum of **14** showing two intense carbonyl bands shifted by −3 and +8 cm^{-1} relative to those of

(27) The average value for the Zn−N distance of all tetrahedral Zn−aldimine and Zn−ketimine complexes in the Cambridge Crystallographic Data File is 2.02 Å.

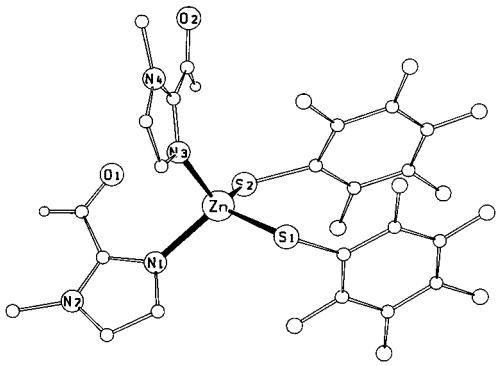


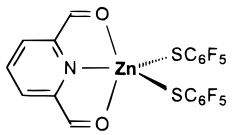
Figure 8. Molecular structure of **14**. Important bond lengths (Å) and angles (deg): Zn−N1 2.048(3), Zn−N3 2.055(3), Zn−S1 2.313(1), Zn−S2 2.288(1), Zn···O1 3.061(3), O1−C 1.217(4), O2−C 1.211(4), N1−Zn−N3 97.2(1), S1−Zn−S2 118.77(4).

free MimA indicated a different bonding situation of the two aldehydic functions. The ^1H NMR spectrum showing small coordination shifts for all MimA resonances gave no further information. They do not exclude the possibility that donor solvents replace MimA from zinc upon dissolution.

$$[(MimA)_2Zn(SC_6F_5)_2]$$
14

The molecular structure of **14** (see Figure 8) seems to be in accord with the IR data: there may be one weak Zn−O interaction. **14** basically is a normal ZnN_2S_2 complex with the typically narrow N−Zn−N angle and the typically wide S−Zn−S angle. But one of the two aldehyde units is oriented such that its O atom occupies a position trans to a sulfur atom (S1−Zn−O1 angle 168°), reminiscent of the beginning of nucleophilic attack at a tetrahedral center. But the Zn−O distance (3.06 Å) is so long and the deformations of the ZnN_2O_2 polyhedron are so insignificant that the Zn−O interaction cannot be but very weak. It remains to be found out why the imidazole ring unlike the pyridine ring does not support good (hetero-N, aldehyde-O) chelation.

Combining **1** and PDA produced, as expected, the 1:1 complex **15** in very good yield. **15** did not form single crystals, and its structural assignment therefore rests on spectra and



15

analogies. Reference points are the zinc halide complexes of PDA of which the $ZnCl_2$ and $ZnBr_2$ complex had their structures determined.[19c] The coordination shifts of **15** for the aldehyde function in the ^1H and ^{13}C NMR spectra (+0.11 and −0.7 ppm, respectively, in acetone-d_6) as well as the coordination shift of the pyridine ring vibration in the IR spectrum (+24 cm^{-1}) agree very closely with those of the $ZnHal_2$ complexes of PDA. Some uncertainty is caused by the ν(CO) IR data. **15** shows a band shifted by −40 cm^{-1} compared to that of free PDA, again in excellent agreement with the data of the PDA·$ZnHal_2$ complexes. There is, however, another band, shifted by −24 cm^{-1}. This may be an indication of PDA being only bidentate and having one uncoordinated aldehyde function. But it may also be a solid-state phenomenon, as we have observed similar band splittings for other aldehyde complexes whose structures were

known not to contain different bonding modes of the aldehyde function. We therefore weigh the positive evidence higher and assign the given structure with tridentate PDA to complex **15**, making ligand PDA the third kind of donor among the heteroaromatic aldehydes after monodentate MimA and the majority of bidentate donors.

Structural Comparisons. Of the 13 zinc thiolate complexes described here, 6 contain the $ZnNS_2O$ coordination pattern present in the enzymatic model ADH. For one case of an alcohol complex (**6**) and for three cases of aldehyde complexes (**10**, **11**, **13**) it was verfied by structure determinations. Thus there is a good basis for structural comparisons. Table 1 summarizes the data to be compared. The reference is the structure of the enzyme complexed with the inhibitor pentafluorobenzyl alcohol.[2c] The closest relative is **6** ($Zn(SR)_2$·alcohol). Distant relatives are the three complexes **10**, **11**, and **13**, whose structural data are averaged under "$Zn(SR)_2$−aldehyde".

Table 1. Comparison of the $ZnNS_2O$ Coordinations of ADH and the Alcohol and Aldehyde Complexes Described Here

	ADH·alcohol	$Zn(SR)_2$·alcohol	$Zn(SR)_2$·aldehyde
Zn−O (Å)	2.0	2.12	2.17
Zn−N (Å)	2.2	2.05	2.08
Zn−S (Å)	2.23	2.27	2.26
O−Zn−N (deg)	93	80	79
O−Zn−S (deg)	106	107	109
N−Zn−S (deg)	110	116	112
S−Zn−S (deg)	126	120	123

The structural similarities between the enzyme and the model complexes are evident. The distortions of the tetrahedral symmetry, most visible in the small N−Zn−O and large S−Zn−S angles, are the same in all compounds. The Zn−S bond lengths are reproduced very well. The only significant difference concerns the Zn−N and Zn−O bond lengths. Zn−O is shorter than Zn−N in the enzyme, but in all complexes this is the other way round. While in the complexes it reflects the low donor quality of the alcohol and aldehyde functions, in the enzyme−inhibitor adduct it may reflect the basic feature of the inhibitor, i.e., that of being too good a ligand.

The very close relation between the alcohol complex **6** and the aldehyde complex **10** also calls for a closer comparison of their structures. In Figure 9 the superimposed chelate rings of both complexes are projected parallel and perpendicular to the Zn−N bonds. While the overall similarity between the two chelate rings is documented, some typical differences are also visible. One of them is the smaller bite angle at zinc for the aldehyde complex, mainly caused by the shorter C−C and C−O bonds. Another is the more noticeable folding of the ring for the alcohol complex, mainly caused by the sp^3 configuration of the alcohol carbon atom. On the other hand the significant difference of the Zn−O bond lengths is hardly noticeable with this kind of view, making it visually inducive that the proton and hydride transfers interconverting alcohol and aldehyde in the enzyme proceed with low activation barriers.

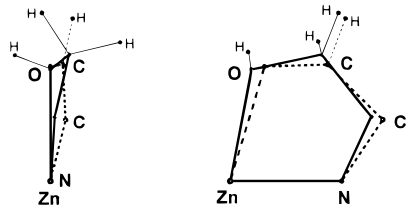


Figure 9. Superpositions of the chelate rings in **6** (solid lines) and **10** (dashed lines).

Conclusions

Zinc thiolates, specifically $Zn(SC_6F_5)_2$, have been found to be good bonding partners for alcohols, alkoxides, and aldehydes. Mono-, di-, tetra-, and polynuclear complexes were obtained. The alcohol function could be attached as a donor when part of a (N,O) chelate ligand. Alkoxide was always found in the bridging mode. Aldehydes were attached as plain monodentate ligands, but in a more stable fashion in the form of (N,O) five- or six-membered chelate rings. The coordination patterns $ZnNSO_2$, ZnS_2O_2, $ZnNS_2O$, ZnS_3O, ZnN_2S_2, and $ZnNS_2O_2$ were realized. Of these, the pattern $ZnNS_2O$, which represents the enzyme−substrate complex of alcoholdehydrogenase, was realized and structurally charaterized for the first time for zinc−alcohol as well as for zinc−aldehyde ligation. The high structural similarity within the pair of $Zn(SC_6F_5)_2$ complexes of picoline-2-methanol and picoline-2-carbaldehyde points to facile interconversions between corresponding alcohols and aldehydes in the ligand sphere of zinc.

Experimental Section

General Information. All reactions were carried out in an atmosphere of 99.99% nitrogen using carfefully dried solvents. The general working techniques were as described previously.[28] All organic reagents were obtained commercially or prepared according to established procedures. The zinc thiolates **1**[20] and **2**[21] were synthesized as described. The term hexanes is used for petroleum ether boiling between 60 and 70 °C.

Spectra. IR spectra were obtained from KBr pellets on a Bruker IFS-25 spectrometer. The spectra of the complexes in essence are superpositions of the spectra of their free organic constituents. For this reason only those bands that shift upon complexation are reported here.

NMR spectra (^1H, ^{13}C, ^{19}F) were recorded on a Bruker AC 200-FL machine, normally (for reasons of solubility and comparability) from solutions in $(CD_3)_2CO$ and from the same sample. For the larger part of the organic molecules they are similar to the spectra of the free ligands, and only groups close to the donor atoms show significantly shifted signals. Therefore, for the ^{13}C NMR spectra only these signals are listed here. The ^{19}F NMR spectra of all $Zn(SC_6F_5)_2$ complexes show a doublet near 133 ppm (vs $CFCl_3$) for 2 F, a triplet near 164 ppm for 1 F, and a multiplet near 165 ppm for 2 F. All NMR data are given in ppm and Hz.

Complex 3. The compound $Zn_3(SC_6H_2Pr^i_3)_4[N(SiMe_3)_2]_2$[21c] (194 mg, 0.24 mmol $Zn(SC_6H_2Pr^i_3)_2$) was dissolved in hexanes (5 mL). PyMeOH (22 mg, 0.21 mmol) was added. Within 12 h the product had precipitated. The solvent was removed with a syringe; the precipitate was washed with hexanes (1 mL) and dried in vacuo. **3** (38 mg, 25%) remained as colorless crystals, mp 241 °C. IR: 1609 (m) (ring), 1073 (m), 1048 (m) (CO). ^1H NMR ($CDCl_3$): 0.77−1.52 [m, 18H, CH_3], 2.75 [m, 1H, $CHMe_2$], 3.78 [m, 1H, $CHMe_2$], 4.09 [m, 1H, $CHMe_2$], 4.93 [br, 1H, CH_2], 5.42 [br, 1H, CH_2], 6.62 [s,1H, phenyl], 6.68 [s, 1H, phenyl], 6.79 [m, 1H, pyridyl], 7.23 [m, 2H, pyridyl], 7.58 [m, 1H, pyridyl].

Anal. Calc for $C_{21}H_{29}NOSZn$ (M_r = 408.9): C, 61.68; H, 7.15; N, 3.43; Zn, 15.99. Found: C, 61.30; H, 7.06; N, 3.71; Zn, 14.94.

Complex 4. A solution of QuiMeOH (69 mg, 0.43 mmol) in methanol (5 mL) was slowly added to a solution of **1** (200 mg, 0.43 mmol) in methanol (10 mL) with stirring. After 2 h the solvent was removed in vacuo, the residue picked up in a minimum amount of dichloromethane, and this was layered with hexanes (10 mL). Complex **4** (32 mg, 16%) was precipitated as big yellow crystals, mp 211 °C. IR: 1608 (m) (ring), 1125 (m), 1079 (s) (CO). ^1H NMR ($CDCl_3$): 5.52 [d, J = 17.8, 1H, CH_2], 5.99 [d, J = 17.8, 1H, CH_2], 7.45 [m, 2H, quinolyl], 7.61 [m, 2H, quinolyl], 7.82 [m, 2H, quinolyl].

Anal. Calc for $C_{16}H_8F_5NOSZn·{}^1/_2CH_2Cl_2$ (M_r = 422.7 + 42.5): C, 42.61; H, 1.95; N, 3.01; Zn, 14.06. Found: C, 42.17; H, 1.87; N, 2.82; Zn 13.88.

(28) Förster, M.; Burth, R.; Powell, A. K.; Eiche, T.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 2643−2648.

Table 2. Crystallographic Data

	3	**4**	**5a**	**6**	**8**	**10**	**11**	**13**	**14**
formula	$C_{84}H_{116}N_4O_4S_4Zn_4 \cdot C_6H_{14}$	$C_{64}H_{32}F_{20}N_4O_4S_4Zn_4 \cdot 2\ CH_2Cl_2$	$C_{18}H_{26}Br_4N_2O_2Zn_2$	$C_{19}H_9F_{10}NOS_2Zn$	$C_{22}H_{12}F_{10}OS_2Zn$	$C_{19}H_7F_{10}NOS_2Zn$	$C_{19}H_7F_{10}NO_2S_2Zn$	$C_{21}H_{11}F_{10}NOS_2Zn$	$C_{22}H_{12}F_{10}N_4O_2S_2Zn$
MW	1721.9	1860.6	752.8	586.8	611.8	584.8	600.8	612.8	683.8
space group	$P2(1)/c$	$I4(1)/a$	$P\bar{1}$	$P2(1)/n$	$Pbca$	$Pca2_1$	$P\bar{1}$	$P2_1$	$P\bar{1}$
Z	4	4	2	4	8	4	2	2	2
a (Å)	18.571(4)	13.806(2)	8.115(1)	13.887(3)	15.591(4)	12.763(8)	8.746(2)	11.064(4)	7.712(2)
b (Å)	28.138(6)	13.806(2)	11.237(1)	10.562(2)	7.227(2)	14.058(7)	8.777(2)	7.510(2)	11.702(2)
c (Å)	20.567(9)	36.254(7)	13.852(1)	15.353(3)	40.355(5)	11.602(8)	13.782(3)	13.779(3)	15.247(3)
α (deg)	90	90	92.81(1)	90	90	90	100.22(3)	90	81.94(3)
β (deg)	119.14(2)	90	91.32(1)	115.46(3)	90	90	92.17(3)	90.60(2)	78.75(3)
γ (deg)	90	90	95.04(1)	90	90	90	95.12(3)	90	73.50(3)
V (Å^3)	9386.8(8)	6910.2(5)	1256.3(2)	2033.2(7)	4547.3(2)	2081.6(8)	1035.5(4)	1144.8(6)	1288.7(5)
d(calc) (g cm^{-3})	1.22	1.79	1.99	1.92	1.79	1.87	1.93	1.78	1.76
μ(Mo Kα) (mm^{-1})	1.15	1.75	8.29	1.52	1.36	1.48	1.50	1.35	1.22
R1 (obs reflns)[a]	0.037	0.041	0.033	0.054	0.129	0.065	0.025	0.058	0.037
wR2 (all reflns)[b]	0.105	0.113	0.086	0.149	0.346	0.194	0.069	0.188	0.106

Complex 5. 1 (0.98 g, 2.11 mmol) was dissolved in diethyl ether (45 mL) and a few drops of THF. A solution of DmaMeOH (0.32 g, 2.12 mmol) in diethyl eyther (5 mL) was added dropwise with stirring. Upon addition of hexanes (200 mL) the product was precipitated, which was filtered off, washed with hexanes, and dried in vacuo. **5** (0.50 g, 38%) remained as a colorless powder, mp 133 °C. IR: 2633 (w), 2517 (w), (NH), 1083 (s), 1006 (s) (CO). ^{1}H NMR [$(CD_3)_2CO$]: 3.02 [s, 6H, NMe_2], 5.07 [s, 2H, OCH_2], 7.19 [dd, J = 7.3 Hz, 1H, phenyl], 7.30−7.40 [m, 2H, phenyl], 7.46 [d, J = 7.3 Hz, 1H, phenyl]. ^{13}C NMR: 46.5 (NMe_2), 65.1 (OCH_2).

Anal. Calc for $C_{21}H_{13}F_{10}NOS_2Zn$ (M_r = 609.8): C, 41.02; H, 2.13; N, 2.28; Zn, 10.64. Found: C, 40.23; H, 2.11; N, 2.61; Zn, 10.50.

Complex 5a. Like **5** from $ZnBr_2$ (1.12 g, 4.97 mmol) and DmaMeOH (0.75 g, 4.96 mmol). Yield: 1.67 g (90%) of **5a** as a corlorless powder, mp 150 °C (dec). IR: 2567 (m), 2510 (m) (NH), 1045 (s), 1012 (s) (CO). ^{1}H NMR [$(CD_3)_2CO$]: 3.08 [s, 6H, NMe_2], 5.15 [s, 4H, OCH_2], 7.27−7.32 [m, 2H, phenyl], 7.45 [dd, J = 7.0 Hz, 1H, phenyl], 7.59 [d, J = 8.0 Hz, 1H, phenyl], 9.03 [br, 1H, OH]. ^{13}C NMR: 47.4 (NMe_2), 65.8 (OCH_2).

Anal. Calc for $C_9H_{13}Br_2NOZn$ (M_r = 376.4): C, 28.72; H, 3.48; N, 3.72; Zn, 17.37; Br, 42.46. Found: C, 28.65; H, 3.41; N, 3.67; Zn, 17.43; Br, 42.52.

Complex 6. 1 (0.28 g, 0.60 mmol) was dissolved in chloroform (10 mL). PicMeOH (74 mg, 0.60 mmol) was added with stirring. After 30 min the volume of the solution was reduced to 3 mL in vacuo. Addition of hexanes (10 mL) produced a precipitate, which was filtered off, washed with hexanes, and dried in vacuo. **6** (0.34 g, 97%) remained as a colorless powder, mp 108 °C. IR: 3256 (br) (OH), 1610 (m) (ring). ^{1}H NMR ($CDCl_3$): 2.73 [s, 3H, CH_3], 5.17 [s, 2H, CH_2], 7.19 [m, 2H, pyridyl], 7.83 [m, 1H, pyridyl]. ^{13}C NMR: 23.2 (CH_3), 62.9 (CH_2).

Anal. Calc for $C_{19}H_9F_{10}NOS_2Zn$ (M_r = 586.8): C, 38.89; H, 1.55; N, 2.39; Zn, 11.14. Found: C, 39.01; H, 1.59; N, 2.39; Zn 11.57.

Complex 7. 1 (0.18 g, 0.39 mmol) was dissolved upon warming in 3.00 mL (3.06 g, 8.32 mmol) of *p*-tolylaldehyde. After cooling to room temperature, the solution was diluted with dichloromethane (2 mL). Dropwise addition of hexanes (30 mL) produced a precipitate, which was filtered off, washed with hexanes, and dried in vacuo. **7** (0.17 g, 75%) was obtained as a colorless powder, mp >320 °C (dec). IR: 1639 (s), 1602 (s) (CO). ^{1}H NMR [$(CD_3)_2CO$]: 2.41 [s, 3H, Me], 7.38 [d, J = 7.7 Hz, 2H, phenyl], 7.78 [d, J = 7.7 Hz, 2H, phenyl], 9.96 [s, 1H, CHO]. ^{13}C NMR: 21.8 (Me), 192.5 (CHO).

Anal. Calc for $C_{20}H_8F_{10}OS_2Zn$ (M_r = 583.8): C, 41.15; H, 1.38; Zn, 11.20. Found: C, 40.18; H, 1.37; Zn, 11.07.

Complex 8. Like **7** from 0.38 g (0.82 mmol) of **1** and 10.00 mL (10.05 g, 67.8 mmol) of mesitylaldehyde. Yield: 0.35 g (70%) of **8** as a colorless powder, mp 144 °C. IR: 1630 (s), 1608 (s) (CO). ^{1}H NMR [$(CD_3)_2CO$]: 2.28 [s, 3H, Me], 2.53 [s, 6H, Me], 6.94 [s, 2H, CH], 10.53 [s, 1H, CHO]. ^{13}C NMR: 20.4, 21.3 (Me), 193.4 (CHO).

Anal. Calc for $C_{22}H_{12}F_{10}OS_2Zn$ (M_r = 611.8): C, 43.19; H, 1.98; Zn, 10.69. Found: C, 43.11; H, 2.54; Zn, 10.63.

Complex 9. A solution of PyrA (0.15 g, 1.40 mmol) in diethyl ether (10 mL) was added dropwise with stirring to a solution of **1** (0.64 g, 1.38 mmol) in diethyl ether (40 mL). Precipitation started, which was completed by addition of hexanes (75 mL). Filtration, washing with hexanes, and drying in vacuo yielded 0.68 g (86%) of **9** as a pale yellow powder, mp 110 °C (dec). IR: 1719 (m), 1685 (s) (CO), 1607 (s), 1573 (m) (ring). ^{1}H NMR [$(CD_3)_2CO$]: 8.16 [t, J = 4.3 Hz, 1H, pyridyl], 8.48−8.56 [m, 2H, pyridyl], 9.15 [d, J = 4.3 Hz, 1H, pyridyl], 10.24 [s, 1H, CHO]. ^{13}C NMR: 194.8 (CHO).

Anal. Calc for $C_{18}H_5F_{10}NOS_2Zn$ (M_r = 570.8): C, 37.88; H, 0.88; N, 2.45; Zn, 11.46. Found: C, 38.67; H, 1.09; N, 2.73; Zn, 11.53.

Complex 10. Like **9** from PicA (0.18 g, 1.49 mmol) and **1** (0.70 g, 1.51 mmol). Yield: 0.79 g (91%) of **10** as a pale yellow powder, mp 135 °C (dec). IR: 1703 (w), 1663 (s) (CO), 1609 (s) (ring). ^{1}H NMR [$(CD_3)_2CO$]: 2.96 [s, 3H, Me], 8.09 [t, J = 4.5 Hz, 1H, pyridyl], 8.47 [d, J = 4.5 Hz, 2H, pyridyl], 10.26 [s, 1H, CHO] ^{13}C NMR: 24.2 (Me), 197.4 (CHO).

Anal. Calc for $C_{19}H_7F_{10}NOS_2Zn$ (M_r = 584.8): C, 39.03; H, 1.21; N, 2.40; Zn, 11.18. Found: C, 39.04; H, 1.18; N, 2.40; Zn, 10.80.

Complex 11. Like **9** from OpyA (93 mg, 0.68 mmol) and **1** (314 mg, 0.68 mmol). Yield: 315 mg (77%) of **11** as a pale yellow powder, mp 127 °C. IR: 1659 (s) (CO), 1611 (s) (ring). ^{1}H NMR [$(CD_3)_2CO$]: 3.87 [s, 3H, OMe], 7.01 [d, J = 8.2 Hz, 1 H, pyridyl], 7.49 [d, J = 7.5 Hz, 1H, pyridyl], 7.81 [dd, J = 8.2 Hz, 7.5 Hz, 1H, pyridyl], 9.82 [s, 1H, CHO].

Anal. Calc for $C_{19}H_7F_{10}NO_2S_2Zn$ (M_r = 600.8): C, 37.99; H, 1.17; N, 2.33; Zn, 10.88. Found: C, 37.28; H, 1.11; N, 2.14; Zn, 10.69.

Complex 12. Like **9** from QuiA (72 mg, 0.46 mmol) and **1** (215 mg, 0.46 mmol). Yield: 205 mg (74%) of **12** as a orange powder, mp 145 °C (dec). IR: 1621 (s) (CO), 1607 (s) (ring). ^{1}H NMR [$(CD_3)_2CO$]: 7.17−8.17 [m, 6H, quinolyl], 10.10 [s, 1H, CHO].

Anal. Calc for $C_{22}H_7F_{10}NOS_2Zn$ (M_r = 620.8): C, 42.56; H, 1.14; N, 2.26; Zn, 10.53. Found: C, 42.12; H, 1.44; N, 2.78; Zn, 10.50.

Complex 13. Like **9** from DmaA (0.18 g, 1.21 mmol) and **1** (0.56 g, 1.21 mmol). A few drops of acetone were added to improve the miscibility of the reagents. Yield: 0.66 g (89%) of **13** as an orange powder, mp 110 °C (dec). IR: 1644 (s) (CO). ^{1}H NMR [$(CD_3)_2CO$]: 2.99 [s, 6H, NMe_2], 7.20 [dd, J = 7.8 Hz, 1H, phenyl], 7.36 [d, J = 8.0 Hz, 1H, phenyl], 7.64 [dd, J = 7.8 Hz, 1H, phenyl], 7.84 [d, J = 7.5 Hz, 1H, phenyl], 10.11 [s, 1H, CHO]. ^{13}C NMR: 46.4 (NMe_2), 195.0 (CHO).

Anal. Calc for $C_{21}H_{11}F_{10}NOS_2Zn$ (M_r = 612.8): C, 41.16; H, 1.81; N, 2.29; Zn, 10.67. Found: C, 40.35; H, 1.76; N, 2.17; Zn, 10.70.

Complex 14. A solution of MimA (200 mg, 1.80 mmol) in THF (5 mL) was added dropwise with stirring to a solution of **1** (420 mg, 0.90 mmol) in diethyl ether (5 mL). After stirring overnight the precipitate was filtered off, washed with hexanes, and dried in vacuo. **14** (410 mg, 71%) remained as a colorless powder, mp 166 °C. IR: 1696 (s), 1685 (s) (CO), 1510 (vs), 1477 (vs) (ring). ^{1}H NMR [$(CD_3)_2CO$]: 4.01 [s, 3H, Me], 7.38 [s, 1H, CH], 7.55 [s, 1H, CH], 10.03 [s, 1H, CHO].

Anal. Calc for $C_{22}H_{12}F_{10}N_4O_2S_2Zn$ (M_r = 683.8): C, 38.64; H, 1.77; N, 8.19; Zn, 9.56. Found: C, 38.02; H, 1.84; N, 7.80; Zn, 9.28.

Complex 15. Like **9** from PDA (0.18 g, 1.33 mmol) and **1** (0.62 g, 1.34 mmol). Yield: 0.62 g of **15** as a yellow powder, mp 135 °C (dec).

IR: 1694 (m), 1678 (s) (CO), 1603 (s) (ring). ^{1}H NMR [$(CD_3)_2CO$]: 8.66 [s, 3H, pyridyl], 10.22 [s, 2H, CHO]. ^{13}C NMR: 192.4 (CHO).

Anal. Calc for $C_{19}H_5F_{10}NO_2S_2Zn$ (M_r = 598.8): C, 38.11; H, 0.84; N, 2.34; Zn, 10.92. Found: C, 37.88; H, 0.94, N, 2.28; Zn, 10.87.

Structure Determinations. Crystals of **3**, **4**, and **8** were grown directly from the reaction solutions, those of **6** from a solution in CCl_4/CH_2Cl_2, those of **5a** and **10** from a solution in THF/CH_2Cl_2, those of **11**, **13**, and **14** from a solution in CH_2Cl_2, each time by layering with hexanes. They were sealed in glass capillaries. Diffraction data were recorded at room temperature except for **5a**, **8**, and **11** which were cooled to ca. −100 °C, on a Nonius CAD4 diffractometer (exception is **8**, for which the data set was obtained by the image plate technique on a Stoe IPDS diffractometer) with graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å). Absorption corrections based on ψ scans were applied for **5a**, **10**, and **13**. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.[29] The NH hydrogen atom in **5a** was located and refined freely. Otherwise hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. For complex **6** consideration of a 9:1 disorder of the picolylmethanol ligand (180° rotation about the Zn−N line) by using split positions for Zn and all PyMeOH atoms except N reduced the R value from 10.2 to 5.3%. For complex **8** the hairlike shape of the crystals and the 40 Å crystallographic axis resulted in a low-quality data set, which caused an only mediocre R value. Complex **10** formed crystals that were inversion twins, which was accommodated in the computations by refining the Flack parameter to a final value of x = 0.41. Drawings were produced with SCHAKAL.[30] Table 2 lists the crystallographic data.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are indebted to Prof. H. Grützmacher for a sample of 2,4,6-triisopropylthiophenol and to Prof. D. Fenske for obtaining the X-ray data set of complex **8**. Dr. U. Brand helped with the structure determinations.

Supporting Information Available: Fully labeled ORTEP plots for all nine structure determinations (9 pages). Nine crystallographic files, in CIF format, are available on the Internet only. This information is available free of charge via the Internet at http://pubs.acs.org.

IC981227M

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