Zinc Complexes of Aldehydes and Ketones, 4[+]
Zinc Complexes of Chelating Aldehydes

Bodo Müller[a] and Heinrich Vahrenkamp*[a]

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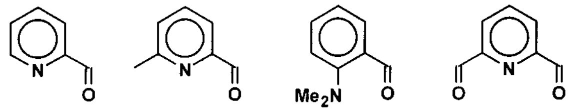
The reactions of various zinc salts with the chelating aromatic aldehydes pyridine-2-carbaldehyde, 6-methylpyridine-2-carbaldehyde, pyridine-2,6-dicarbaldehyde, and 2-dimethylaminobenzaldehyde were studied. The monoaldehydes and zinc halides yielded the tetrahedral chelate complexes $ZnHal_2$·aldehyde. Pyridine-2-carbaldehyde also formed the octahedral bis-chelate complexes $ZnHal_2$·2 aldehyde. The octahedral tris-chelate complexes $[Zn(aldehyde)_3]^{2+}$ were obtained from $[Zn(CH_3CN)_6](SbCl_6)_2$. Pyridine-2,6-dicarbaldehyde was found to be tridentate in the trigonal-bipyramidal complexes $ZnHal_2$·aldehyde. The structural variability in this system was underlined by the identification of the two unusual complexes $[(pyridine\text{-}2\text{-}carbaldehyde)_2(H_2O)Zn–Cl–ZnCl_3]$ and $[ZnI(pyridine\text{-}2\text{-}carbaldehyde)_2]_2[ZnI_4]$.

The importance of metal catalysis for reactions of organic carbonyl compounds in chemistry and biology, specifically by zinc compounds, has motivated us to undertake a systematic study of the interactions between the zinc ion and carbonyl-containing species. We started this study with an investigation of zinc−aldehyde complexes. The justification and scope of our work, as well as the relevant information from the literature, are summarized in our first full paper on this subject[2]. It can be stated that, to date, surprisingly little is known about the composition, structure, and bonding of metal-aldehyde adducts, be it in solution or in the solid state.

Our investigations with various zinc salts and plain aldehydes[1][2] gave rise to the conclusion that many complexes can be isolated and that they have a very rich structural chemistry, but that they are of low stability, very labile, and do not persist in solution in the presence of water or solvents of even low donor ability. We therefore sought to improve the situation by ligand design in terms of the aldehydes as well as of the coligands. Complex stabilization by chelation could be predicted to be advantageous for this purpose. We therefore used aldehydes bearing an additional nitrogen donor function, suitable for N,O chelation. A second motivation for this choice came from our attempts to model the structure and function of the enzyme alcohol dehydrogenase, in which the reacting aldehyde or alkoxide are attached to zinc as part of a ZnS_2NO donor set[3].

A search of the literature revealed that, just as for the plain aldehydes, there is very little information on the metal complexation of N,O chelating aldehydes. The only reported structural study showed that pyridine-2-carbaldehyde coordinates to CuCl only through the nitrogen atom[4]. For zinc the complex types $ZnBr_2$•2 aldehyde[5] and $Zn(SR)_2$•aldehyde[6] were described for pyridine-2-carbaldehyde, but these compounds were not structurally characterized. Structural information exists only for the somewhat related zinc halide complexes of pyridine-2-carboxylic acid esters, which contain N,O chelate rings[7]. Some work from a mechanistic point of view was reported for the zinc salt-catalyzed reduction of acyl-substituted pyridines and isoquinolines by hydride donors of the NADH type[8−10].

In order to provide a basis of isolated and structurally characterized complexes we investigated the coordinating abilities of the four typical chelating aldehydes PA, MPA, ABA, and PDA towards zinc salts. We found all four of these compounds to be suitable ligands for zinc, making ZnL, ZnL_2, and ZnL_3 complexes accessible. A small number of these results have already been described briefly[11].



2-pyridine-carbaldehyde **PA** | 6-methylpyridine-2-carbaldehyde **MPA** | 2-dimethylamino benzaldehyde **ABA** | 2,6-pyridine-dicarbaldehyde **PDA**

Preparations

The zinc halides formed 1:1 as well as 1:2 complexes with the chelating aldehydes. When a solution of the zinc halide in diethyl ether was treated dropwise with an ethereal solution of one equivalent of the aldehyde, the 1:1 complexes **1**−**3** precipitated. With pyridine-2-carbaldehyde it could be shown that the accessibility of the 1:1 complexes depends on the presence of sub-stoichiometric amounts of the aldehyde in solution and on its removal by precipitation. However, when the zinc halide and the aldehyde were dissolved simultaneously in the better solvent acetonitrile, the sub-

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[a] Institut für Anorganische und Analytische Chemie der Universität Freiburg,
Albertstr. 21, D-79104 Freiburg, Germany

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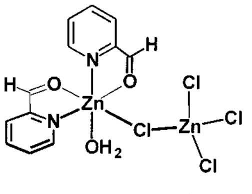
sequent crystallization yielded the 1:2 complexes **4a−c** regardless of the stoichiometric ratio of the reagents. Near quantitative conversion to **4a−c** occurred when the required 1:2 ratio was employed. Complexes **1−4** are stable enough to be recrystallized from organic donor solvents. Complex **4b** is the only zinc complex of a chelating aldehyde that has been described before[5].

	$ZnHal_2$•A Hal	A
1a	Cl	PA
1b	Br	PA
2a	Cl	MPA
2b	Br	MPA
2c	I	MPA
3a	Cl	ABA
3b	Br	ABA
3c	I	ABA

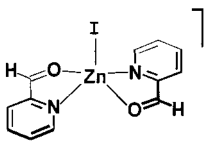
	$ZnHal_2$•2 PA Hal
4a	Cl
4b	Br
4c	I

Two unexpected results pointed to the subtleties inherent in these reaction systems, despite the higher stabilities of the chelating aldehyde complexes in comparison to those of the plain aldehydes. When water was accidentally present in the reaction solution for the preparation of **1a**, complex **5** was isolated instead. **5** was subsequently prepared from $ZnCl_2$, PA, and H_2O in the ratio 2:2:1. Just like complexes **4** in comparison to complex **1**, complex **5** shows a preference for higher coordination numbers in the presence of oxygen-containing ligands. In a similar fashion complex **6**, which was isolated instead of the expected yet elusive ZnI_2•PA, shows the PA ligands to be part of the five-coordinate $[ZnL_2I]^+$ cation. In both **5** and **6** the bonding preferences of the hard and soft ligands are realized by dismutation into an N,O-coordinated zinc cation and a halide-coordinated zincate anion, albeit in quite different ways and yet different from the way chosen by the compound of composition $ZnBr_2(4\text{-fluorobenzaldehyde})_2$[1].



$(PA)_2(ZnCl_2)_2 \cdot H_2O$

5



$[(PA)_2ZnI]_2\ (ZnI_4)$

6

Exclusive coordination of zinc by the chelating aldehydes could be achieved when starting with zinc compounds with weakly coordinating anions. After some futile attempts with fully dehydrated zinc nitrate, tetrafluoroborate, or perchlorate[2] or the hexaethanol zinc complex, it was found that hexa(acetonitrile)−zinc−bis(hexachloroantimonate)[12] is a suitable starting material. Treatment of this compound with the aldehydes PA and MPA resulted in the formation of the 1:3 complexes **7** and **8**. Although **7** and **8** could not be obtained as X-ray quality crystals, their constitution is confirmed by the spectra (see below), which indicate coordination of all N and O donors to zinc, thus implying octahedral ZnL_3 cations.

$[Zn(A)_3][SbCl_6]_2$

7: A = PA; **8**: A = MPA

As expected, the doubly chelating bis-aldehyde ligand PDA formed 1:1 complexes with the zinc halides. Complexes **9a−c** resulted from adding a solution of the ligand to a solution of the halide in ether. While we are aware of no other metal complex of PDA, the corresponding Schiff bases are popular ligands, and some zinc halide complexes are known from them[13]. As could be predicted, such complexes, like **9a−c**, are trigonal-bipyramidal with the halide ligands in equatorial positions.

$ZnHal_2$•PDA

9a: Hal = Cl; **9b**: Hal = Br; **9c**: Hal = I

Structures

The simplest complex type, $ZnHal_2$•aldehyde, was characterized by the structure determinations of **2b** and **2c**. Figure 1 shows that the aldehyde acts as a symmetrically chelating ligand with similar Zn−N and Zn−O bond lengths. The chelate ring is planar and is also coplanar with the aromatic ring. The $ZnHal_2$ plane is perpendicular to the ZnNO plane, i.e. tetrahedral coordination is realized to a good approximation. However, as is usual due to the geometrical restraints of the chelate ring, the N−Zn−O angle has a typically small value, which is compensated by a rather large Hal−Zn−Hal angle.

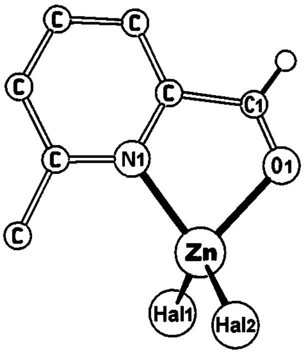


Figure 1. Molecular structure of complexes **2b** and **2c**
Relevant bond lengths [Å] and angles [°] (**2c** has two independent molecules in the asymmetric unit for which average values are given): Z−N1 2.05(2)/2.06(1), Zn−O1 2.10(1)/2.11(1), Zn−Hal1 2.334(4)/2.530(2), Zn−Hal2 2.314(3)/2.513(1), O1−C1 1.18(3)/1.21(1), N1−Zn−O1 80.3(6)/80.2(6), Hal1−Zn−Hal2 119.1(1)/122.8(3.0).

Complex **3c** shares the basic structural features of **2b** and **2c**, i.e. similar Zn−N and Zn−O bond lengths and the symmetrically distorted tetrahedral coordination of zinc (Figure 2). The six-membered chelate ring allows a larger N−Zn−O angle that is still considerably smaller than the tetrahedral angle. The six-membered chelate ring is characteristically folded along the N−O line, allowing the aromatic ring and the aldehyde function to be coplanar. This situation, however, means that unlike in all other aldehyde complexes characterized by us in this study[1][2], the zinc ion is displaced from this plane by the considerable distance of 1.1 Å. Compared to the tetrahedral zinc halide complexes of plain aldehydes[1] the Zn−Hal distances in **2b**, **2c**, and **3c** are in the normal range, but the Zn−O distances are elongated by roughly 0.05 Å. This must be related to the presence of N donors in the molecules, which serve to better satisfy the electron-acceptor properties of the zinc ions.

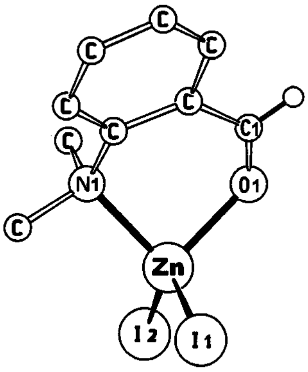


Figure 2. Molecular structure of complex **3c**
Relevant bond lengths [Å] and angles [°]: Zn−N1 2.099(4), Zn−O1 2.051(3), Zn−I1 2.518(1), Zn−I2 2.518(1), O1−C1 1.222(6), N1−Zn−O1 89.3(1), I1−Zn−I2 122.07(2).

The $ZnHal_2$•2 aldehyde complexes **4a−c** crystallize with unusual molecular shapes (Figure 3). These compounds are not octahedral, as can be seen from the severe angular distortions, but their oxygen atoms are visibly oriented towards the zinc ions despite their extremely long Zn−O distances. In addition, the oxygen atoms are positioned cleanly in *trans*-positions opposite to the halide ligands such that they cannot be excluded from the ligand sphere, a situation that would render the complexes tetrahedral. Tetrahedral ZnN_2Hal_2 complexes are commonplace and, just like the tetrahedral ZnN_2S_2 complexes, define a highly preferred coordination mode. Thus it must again be concluded that the good donor qualities of the pyridine nitrogens saturate the electronic demands of the zinc ions and render further coordination by the aldehyde oxygens almost unnecessary. A similar situation was observed for zinc halide complexes of pyridine-2-carboxylic esters[7] with Zn−O distances ranging from 2.38 to 2.50 Å as compared to 2.48−2.54 Å seen here. In the pyridine-ester complexes, just as in our pyridine-aldehyde complexes, the zinc−halide distances are characteristically longer than in the tetrahedral zinc halide complexes, e.g. of the plain aldehydes[1], in accord with the higher coordination number of zinc.

The weak N−O coordination characteristic of **4a−c** is not observed in the unique complexes **5** and **6**, see Figures 4 and 5. Both **5** and **6** contain cationic units bearing two chelating aldehyde ligands attached to zinc of coordination number 5 or 6 together with anionic $ZnHal_4$ units. In **5** cation and anion are halide bridged, in **6** the ZnI_4 anions are isolated. The Zn−O distances in **5** and **6**, with an average length of 2.25 Å, are longer than those in the tetrahedral complexes **2** and **3** (see above) and also those in octahedral complexes of the plain aldehydes[2], but they are not significantly outside the range for octahedral zinc. Thus, although the weakening of the Zn−O bonds due to the presence of the Zn−N bonds is observed, it is less pronounced because the zinc ions, due to the cationic nature of the complexes, are better electron acceptors than those in complexes **2**, **3**, or **4**. Although complexes **5** and **6** are both the first examples of their kind, their structural patterns are not singular. Both halide bridging between octahedral and tetrahedral zinc[14] and bis(chelate)-mono(halide)-zinc cations of square-pyramidal geometry[15] have been observed before.

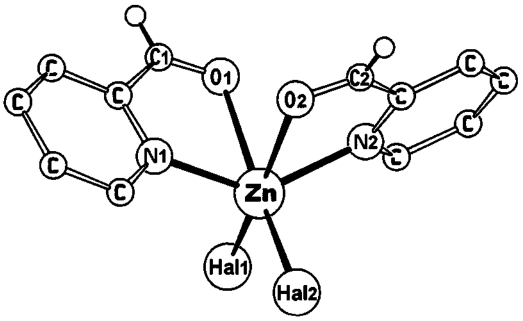


Figure 3. Molecular structures of complexes **4a−c**
Relevant bond lengths [Å] and angles [°] for **4a**/**4b**/**4c**: Zn−N1 2.108(7)/2.102(15)/2.102(5), Zn−N2 2.108(7)/2.111(14)/2.117(4), Zn−O1 2.481(6)/2.498(14)/2.483(4), Zn−O2 2.544(7)/2.525(14)/2.532(4), Zn−Hal1 2.301(3)/2.450(3)/2.661(1), Zn−Hal2 2.300(3)/2.441(3)/2.665(1), O1−C1 1.20(1)/1.19(3)/1.21(1), O2−C2 1.22(1)/1.20(2)/1.21(1), N1−Zn−N2 137.7(3)/135.9(6)/136.8(2), O1−Zn−O2 80.8(2)/83.3(5)/85.8(2), Hal1−Zn−Hal2 130.7(1)/102.9(1)/101.92(3), N1−Zn−O1 72.2(2)/71.7(5)/72.1(2), N2−Zn−O2 71.0(2)/70.9(5)/71.6(2).

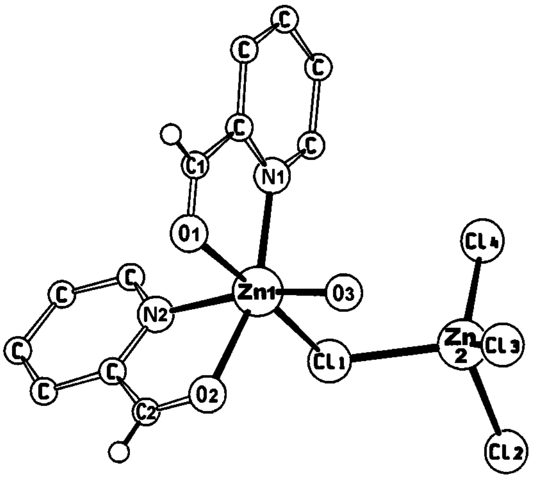


Figure 4. Molecular structures of complex **5**
Relevant bond lengths [Å] and angles [°]: Zn1−N1 2.087(3), Zn1−N2 2.108(3), Zn1−O1 2.244(3), Zn1−O2 2.267(3), Zn1−O3 2.024(3), Zn1−Cl1 2.394(1), Zn2−Cl1 2.366(1), Zn2−Cl2 2.258(1), Zn2−Cl3 2.259(1), Zn2−Cl4 2.202(1), O1−C1 1.201(5), O2−C2 1.209(5), N1−Zn1−O1 77.1(1), N2−Zn1−O2 75.3(1), N1−Zn1−O2 156.7(1), N2−Zn1−O3 163.8(1), O1−Zn1−Cl1 176.0(1).

Complexes **9a** and **9b** belong to the group of trigonal-bipyramidal $LZnX_2$ complexes in which L represents a doubly chelating tridentate ligand. Close relatives of **9a** are $LZnCl_2$ with L = terpyridyl[16] and L = 2,6-diacetylpyridinedioxime[17]. These complexes share the coplanar nature of the whole ligand L and the severe deviation of the axial

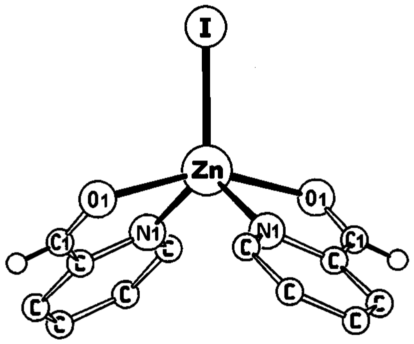


Figure 5. Structure of the cations of compound **6**
Relevant bond lengths [Å] and angles [°]: Zn−N1 2.06(1), Zn−O1 2.25(1), Zn−I 2.515(4), O1−C1 1.19(2), N1−Zn−O1 76.8(5), N1−Zn−N1′ 116.5(8), O1−Zn−O1′ 154.6(8), N1−Zn−O1′ 89.8(5), N1−Zn−I 121.8(4), O1−Zn−I 102.7(4).

ligand arrangement from linearity. However, while in the latter two complexes the axial zinc-ligand bonds (in both cases Zn−N) are not significantly longer than the equatorial Zn−N bond, the opposite is the case for **9a** and **b** (Figure 6). The Zn−O bonds are, on average, 2.34 Å long and are therefore halfway between those in tetrahedral **2** or **3** and octahedral **4**. As in complex **2** or **3** only a single nitrogen donor is present, but as is the case in **4** two aldehyde oxygen donors compete for the remaining acceptor strength of the zinc ion. Like in all other complexes described in this paper, the aldehyde C=O bond lengths do not reflect the variable strength of the Zn−O interactions. They all have lengths of around 1.21 Å with very little variation.

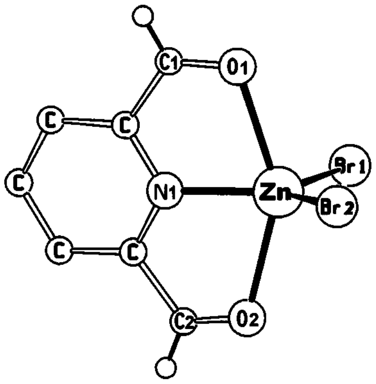


Figure 6. Molecular structure of complexes **9a** and **9b**
Relevant bond lengths [Å] and angles [°] for **9a**/**9b**: Zn−N1 2.046(4)/2.043(4), Zn−O1 2.336(4)/2.348(4), Zn−O2 2.322(4)/2.327(4), Zn−Hal1 2.198(2)/2.337(1), Zn−Hal2 2.189(2)/2.322(1), O1−C1 1.213(7)/1.210(6), O2−C2 1.214(7)/1.218(6), O1−Zn−O2 148.0(2)/148.2(1), N1−Zn−O1 74.0(2)/74.2(1), N1−Zn−O2 74.3(2)/74.3(1), Hal1−Zn−Hal2 121.33(6)/120.91(3).

Spectroscopy

Upon coordination to transition metals, the intense IR ν(CN) band of pyridine-derived ligands is shifted by about 10 to 50 cm^{-1} to higher wavenumbers[18][19]. This shift is observed in the +20 cm^{-1} category here, proving the expected Zn−N coordination of the pyridine-derived aldehydes (Table 1). Conversely, the aldehyde-ν(CO) band is shifted by about 50 cm^{-1} to lower wavenumbers in zinc complexes of the plain aldehydes[1][2]. Shifts to lower wavenumbers are also observed here. They are in the 40−50 cm^{-1} range for those complexes (**1**−**3**, **5**, **6**) in which, according to the structure determinations, the Zn−O interactions are strong or medium. The shifts are typically smaller when the Zn−O interactions are known to be weak (complexes **4**, **9**). For the presumably octahedral ZnN_3O_3 complexes **7** and **8** there seem to be good interactions according to the IR data. Some spectra are further complicated as far as this interpretation is concerned by showing ν(CO) bands that are split into two maxima. As this occurs irregularly and the intensity of the second band varies significantly we refrain from interpreting this observation in terms of structural details or crystal packing phenomena.

Table 1. Relevant IR data (KBr, cm^{-1}) of the complexes

	ν(CN)	$\Delta\nu$	ν(CO)	$\Delta\nu$
1a	1603	+18	1669	−44
1b	1600	+15	1679	−34
2a	1606	+13	1666	−46
2b	1604	+11	1652	−60
2c	1603	+10	1652/1675	−60/−37
3a	1208	+20	1638	−47
3b	1207	+19	1633	−52
3c	1205	+17	1630	−55
4a	1600	+15	1682/1702	−32/−11
4b	1600	+15	1679/1697	−34/−16
4c	1599	+14	1674	−39
5	1615	+30	1663/1680	−50/−33
6	1601	+16	1658	−55
7	1605	+20	1666	−47
8	1607	+22	1666	−47
9a	1597	+18	1687	−31
9b	1596	+17	1684	−34
9c	1594	+15	1680	−38

The NMR data of the complexes (see Tables 2 and 3) are characteristically different from those of the zinc complexes of plain aldehydes[1][2]. Whereas the latter show NMR spec-

Table 2. Typical ^{1}H-NMR data (in [D_6]acetone, δ) of the complexes

	δ(CHO)	$\Delta\delta$	δ(H6)	$\Delta\delta$
1a	10.25	+0.24	9.15	+0.39
1b	10.35	+0.34	9.24	+0.48
2a	10.25	+0.31	2.85[a]	+0.27
2b	10.33	+0.39	2.92[a]	+0.34
2c	10.31	+0.37	2.91[a]	+0.33
3a	10.15	−0.08	2.96[b]	+0.11
3b	10.14	−0.09	2.95[b]	+0.10
3c	10.10	−0.13	2.96[b]	+0.11
4a	10.17	+0.16	9.03	+0.27
4b	10.22	+0.21	9.09	+0.33
4c	10.26	+0.25	9.09	+0.33
5	10.27	+0.26	9.19	+0.43
6	10.40	+0.39	9.22	+0.46
7	10.29	+0.28	9.25	+0.49
8	10.27	+0.34	3.11[a]	+0.53
9a	10.22	+0.11	−	−
9b	10.30	+0.19	−	−
9c	10.34	+0.23	−	−

[a] Methyl group on C6. − [b] NMe_2 signal.

Table 3. Typical ^{13}C-NMR data (in [D$_6$]acetone, δ) of the complexes

	δ(CHO)	Δδ	δ(C2/C6)	Δδ
1a	193.2	−0.7	150.6/151.3	−2.9/+0.5
1b	193.5	−0.4	149.0/151.4	−4.5/+1.1
2a	196.9	+2.8	148.0/161.1	−5.2/+1.1
2b	197.2	+3.1	146.5/161.1	−6.7/+1.1
2c	197.5	+3.4	146.4/161.1	−6.8/+1.1
3a	193.8	+3.2	46.1[a]	+0.5
3b	194.4	+3.8	46.2[a]	+0.6
3c	196.7	+6.1	46.7[a]	+1.1
4a	193.5	−0.4	152.5/151.3	−1.0/+0.5
4b	193.7	−0.2	150.3/151.3	−3.2/+0.5
4c	194.1	+0.2	150.3/151.2	−3.2/+0.4
5	193.1	−0.9	150.2/151.4	−3.3/+0.6
6	194.1	+0.2	148.9/151.2	−4.6/+0.4
7	193.4	−0.50	150.8/148.6	−2.7/−2.2
8	194.2	+0.07	151.6/160.6	−1.6/+0.6
9a	192.5	−0.6	151.5	−2.5
9b	192.0	−1.1	149.7	−4.3
9c	191.6	−1.5	148.7	−5.3

[a] NMe$_2$ signal.

tra that are almost identical to those of the free aldehydes, thereby supporting the suspicion that the complexes dissociate in solution, all pyridine-aldehyde complexes display significant coordination shifts for the signals of the groups in the vicinity of the donor atoms N and O. In particular, the proton resonances of the aldehyde CHO groups and the ^{13}C resonances of the pyridine-C$_\alpha$ carbon atoms provide important evidence that the aldehyde function is coordinated to zinc in all cases, even in solution.

Discussion

The results of this work have verified the assumption that the chelate effect will lead to more stable and more inert zinc−aldehyde complexes. Unlike the complexes of the plain aldehydes, compounds **1**−**9** do not require a large excess of the aldehyde to be isolable, they result from stoichiometric amounts of the reagents in solution, they can be recrystallized from donor solvents (e.g. THF), and their NMR spectra indicate the persistence of the zinc-aldehyde binding in solution. With the exception of **5** and **6** their structures can be deduced from their compositions by assuming coordination of all donor groups. Accordingly, the structure proposed for **4b**, the only previously reported zinc complex of a pyridine aldehyde[5], was confirmed.

While the Zn−N coordination is essential for the existence of the complexes, it is also the reason for weaker Zn−aldehyde interactions. Only in the 1:1 complexes **1**−**3** are the Zn−O bonds as strong (i.e. short) as in the Zn-aldehyde complexes without N-donor ligands[1][2]. These complexes can, however, only be isolated by precipitation from solutions with low pyridine aldehyde concentrations, and when dissolved complexes **1** undergo dismutation with formation of complexes **4**. Similarly, compound **6**, having a 1:2 (zinc/aldehyde) composition in its complex cation, was the only isolable product in attempts to prepare the elusive ZnI$_2$•PA. This preference for the 1:2 over the 1:1 composition is a reflection of the high stability of ZnN$_2$X$_2$ species, where N represents a heteroaromatic nitrogen donor and X e.g. a halide, in zinc complex chemistry.

By adjusting the reaction conditions and the nature of the coligands, zinc complexes with one, two, or three chelating aldehydes were accessible, e.g. **1a**, **4a**, and **7** for pyridine-2-carbaldehyde. Tetrahedral, square-pyramidal, and octahedral coordination of zinc has been observed. Most typical for the chelating aldehydes are the distorted coordination geometries between tetrahedral and octahedral, as exemplified by complexes **4**, and this phenomenon is caused by the strong Zn−N and weak Zn−O interactions. The distortion is most pronounced for complexes **4** because without Zn−O interactions these complexes would be very stable tetrahedral complexes of the ZnN$_2$Hal$_2$ type. On the other hand, the absence of a second nitrogen donor makes Zn−O binding stronger and hence complexes **1**−**3** are less distorted, and likewise complexes like **5** or **7**, bearing the chelating aldehyde bound to a cationic ZnL$_6$ species, have stronger Zn−O interactions and hence more symmetrical coordinations due to the higher electron acceptor strength of the zinc ion. Similar observations have been made for zinc halide complexes of pyridine-2-carboxylic esters[7].

The structural variability of the complexes reported here is much greater than that of the complexes of the plain aldehydes[1][2]. The latter invariably form octahedral complexes in the absence of halide and tetrahedral complexes with halides as coligands. In the compounds reported here, halide can be coligand in tetrahedral (**1**−**3**), five-coordinate (**6**), and octahedral (**5**) complexes. As discussed above, the composition of the compounds as well as the reaction conditions influence the specific geometry. The subtleties governing this are demonstrated by the formation of **6** instead of the elusive ZnI$_2$•PA as well as the fact that 2-dimethylaminobenzaldehyde forms only the 1:1 complexes **3** but not 1:2 complexes like **4**. A variation of this theme concerns the dismutation reactions of some of the zinc halide complexes into cationic zinc-aldehyde and anionic zinc halide constituents, of which the latter again show structural variability by existing as isolated ZnHal$_4^{2-}$ (**6**), halide bridged ZnHal$_4^{2-}$ (**5**) or even isolated Zn$_2$Hal$_6^{2-}$ [together with a Zn(aldehyde)$_6^{2+}$ cation][1].

In terms of activation of the carbonyl function for catalytic reactions, the complexes described here offer important information by their variable Zn−O (aldehyde) interactions. In the complexes of the plain aldehydes, octahedral coordination agrees with Zn−O distances close to the average of 2.09 Å[2] and tetrahedral coordination with Zn−O distances averaging 2.04 Å[1]. In contrast, in the compounds reported here Zn−O bond lengths ranging from 2.05 to 2.54 Å are observed with no systematic correlation between distance and coordination number. There is, however, a correlation between Zn−O bond length and the donor/acceptor situation at the zinc ion. In complexes **1**−**3** a single nitrogen donor provides the zinc ion with insufficient electron density and hence the Zn−O bonds are short (ca. 0.05 Å above the tetrahedral reference value). On the other hand complexes **4** would be able to exist as four-coordinated ZnN_2Hal_2 species, i.e. Zn−O coordination is not required and hence is weak (Zn−O distances ca. 0.40 Å above the octahedral reference value). Complexes **5** and **6**, as discussed above, are intermediate cases (with Zn−O distances ca. 0.15 Å above average). Complexes **9** can be referenced against complexes **1**−**3**. In the latter compounds one nitrogen and one oxygen donor both experience good Zn−O(N) interactions, while in **9** two oxygen donors have to share the remaining bonding capacity, resulting in clearly weaker Zn−O interactions (bond lengths ca. 0.25 Å above average). These variations in the Zn−O interactions are in part reflected by the IR data, which demonstrate a congruous variation of the C=O bond strengths. Thus the electronic situation of the "catalytic" zinc ion visibly influences the electronic modification of the aldehydic C=O functions, which should become effective in terms of reaction rates or reaction pathways.

In terms of modelling the enzyme alcohol dehydrogenase, complexes **1**−**3** represent an advancement as they contain Zn−O(aldehyde) together with Zn−N(heteroaromatic) coordination in the tetrahedral $ZnHal_2NO$ pattern. The realization of the enzyme-like ZnS_2NO pattern with the pyridine-aldehyde ligands calls for a replacement of the halide ligands by thiolate ligands. This has already been reported by Bochmann[6], yet without the support of a structure determination. Our own work using the chelating aldehydes and $Zn(SC_6F_5)_2$, including X-ray structural studies, will be published shortly[20].

Experimental Section

The general working and measuring conditions were as in ref.[21], the specific conditions as in ref.[2]. The aldehydes were obtained commercially and distilled or recrystallized prior to use. The anhydrous zinc halides were prepared from zinc and HHal or Hal_2, respectively, in diethyl ether[22][23], $[Zn(CH_3CN)_6]$ $[SbCl_6]_2$ was prepared according to the published procedure[12]. The new complexes were prepared following the general procedure below, details for which are given in Table 4. Table 5 gives details of the analytical characterizations.

Table 4. Reaction details

Compl.	Solvent[a]	zinc salt				aldehyde					yield		m.p.
			g	mmol	mL solv.		mL	g	mmol	mL solv.	g	%	°C
1a	E	$ZnCl_2$	1.03	7.56	40	PA	0.72	0.81	7.56	10	1.76	96	211
1b	E	$ZnBr_2$	0.83	3.69	40	PA	0.355	0.40	3.73	10	1.07	87	162 (dec.)
2a	E	$ZnCl_2$	0.64	4.70	60	MPA	−	0.57	4.70	15	1.09	90	192 (dec.)
2b	E	$ZnBr_2$	0.71	3.15	100	MPA	−	0.38	3.14	20	0.90	82	182 (dec.)
2c	E	ZnI_2	1.08	3.38	150	MPA	−	0.41	3.39	20	1.17	79	158
3a	E	$ZnCl_2$	2.12	15.60	100	ABA	−	2.32	15.60	100	3.66	82	154 (dec.)
3b	E	$ZnBr_2$	1.12	4.97	40	ABA	−	0.74	4.96	10	1.73	93	160 (dec.)
3c	E	ZnI_2	0.76	2.38	100	ABA	−	0.35	2.35	10	0.89	81	170 (dec.)
4a	A	$ZnCl_2$	1.36	9.98	40	PA	1.90	2.14	19.98	10	2.88	82	164 (dec.)
4b	A	$ZnBr_2$	0.80	3.55	40	PA	0.675	0.76	7.10	10	1.18	76	173 (dec.)
4c	A	ZnI_2	2.84	8.90	40	PA	1.70	1.91	17.83	10	4.50	95	172 (dec.)
5	E	$ZnCl_2$	3.50	25.68	50[b]	PA	2.44	2.75	25.68	50	5.94	92	200 (dec.)
6	E	ZnI_2	1.58	4.95	100	PA	0.471	0.53	4.95	10	1.71	99	178 (dec.)
7	E/D	$Zn(MeCN)_6(SbCl_6)_2$	1.74	1.77	40[c]	PA	0.506	0.57	5.32	10	1.76	94	82 (dec.)
8	E/D	$Zn(MeCN)_6(SbCl_6)_2$	1.73	1.76	40[c]	MPA	−	0.64	5.28	10	1.66	86	105 (dec.)
9a	E	$ZnCl_2$	1.13	8.29	80	PDA	−	1.12	8.29	20	2.08	93	202
9b	E	$ZnBr_2$	1.27	5.64	80	PDA	−	0.76	5.63	20	1.83	90	182 (dec.)
9c	E	ZnI_2	0.80	2.51	80	PDA	−	0.34	2.52	20	0.96	84	198 (dec.)

[a] A = acetonitrile; D = dichloromethane; E = diethyl ether. − [b] + 0.23 mL (0.23 g, 12.80 mmol) H_2O. − [c] + 2 mL tetrahydrofuran.

Table 5. Analytical characterization

	formula mol. wt.	Analyses calcd./found C	H	N	Zn	Hal
1a	$C_6H_5Cl_2NOZn$	29.61	2.07	5.76	26.86	29.13
	243.4	29.59	2.16	5.66	26.89	29.02
1b	$C_6H_5Br_2NOZn$	21.69	1.52	4.22	19.68	48.09
	332.3	21.72	1.59	4.17	19.81	48.16
2a	$C_7H_7Cl_2NOZn$	32.66	2.74	5.44	25.40	27.54
	257.4	32.54	2.75	5.37	25.33	27.61
2b	$C_7H_7Br_2NOZn$	24.28	2.04	4.04	18.88	46.14
	346.3	24.42	2.10	3.97	18.95	46.22
2c	$C_7H_7I_2NOZn$	19.09	1.60	3.18	14.85	57.64
	440.3	19.30	1.64	3.15	14.77	57.78
3a	$C_9H_{11}Cl_2NOZn$	37.87	3.88	4.91	22.91	24.84
	285.5	35.78	3.72	4.58	22.99	24.96
3b	$C_9H_{11}Br_2NOZn$	28.87	2.96	3.74	17.47	42.69
	374.4	28.18	2.94	3.59	17.58	42.38
3c	$C_9H_{11}I_2NOZn$	23.08	2.37	2.99	13.96	54.19
	468.4	23.83	2.90	2.92	14.03	54.08
4a	$C_{12}H_{10}Cl_2N_2O_2Zn$	41.12	2.88	7.99	18.66	20.23
	350.5	40.89	2.86	8.08	18.71	20.16
4b	$C_{12}H_{10}Br_2N_2O_2Zn$	32.80	2.29	6.38	14.88	36.37
	439.4	32.77	2.28	6.48	14.92	36.41
4c	$C_{12}H_{10}I_2N_2O_2Zn$	27.02	1.89	5.25	12.26	47.58
	533.4	27.11	1.92	5.30	12.18	47.63
5	$C_{12}H_{12}Cl_4N_2O_3Zn_2$	28.55	2.40	5.55	25.91	28.09
	504.8	28.29	2.22	5.41	25.90	28.02
6	$C_{24}H_{20}I_6N_4O_4Zn_3$	20.80	1.45	4.04	14.15	54.94
	1386.0	20.22	1.38	3.96	14.30	54.81
7	$C_{18}H_{15}Cl_{12}N_3O_3Sb_2Zn$	20.48	1.43	3.98	6.19	40.30
	1055.7	19.93	1.35	3.85	6.32	40.08
8	$C_{21}H_{21}Cl_{12}N_3O_3Sb_2Zn$	22.98	1.93	3.83	5.96	38.76
	1097.7	21.76	1.97	3.44	6.03	38.84
9a	$C_7H_5Cl_2NO_2Zn$	30.98	1.86	5.16	24.09	26.12
	271.4	29.71	1.81	4.84	24.24	25.83
9b	$C_7H_5Br_2NO_2Zn$	23.33	1.40	3.89	18.15	44.35
	360.3	21.19	1.37	3.36	18.28	44.09
9c	$C_7H_5I_2NO_2Zn$	18.51	1.11	3.08	14.39	55.87
	454.3	18.57	1.13	3.12	14.22	55.98

Preparation of the Complexes: The zinc salt was dissolved in the organic solvent. The chelating aldehyde was added as a solution in diethyl ether with stirring. The resulting complex either precipitated immediately or after cooling the hot solutions to room temperature. After filtration the product was washed with petroleum ether (b.p. 60−70°C) and dried in vacuo.

Structure Determinations[24]: Crystals of **3a**−**c** were obtained by dissolution in CH_2Cl_2, all others by dissolution in THF/CH_2Cl_2

Table 6, part 1. Crystallographic details

	2b	**2c**	**3c**	**4a**	**4b**
formula	$C_7H_7Br_2NOZn$	$C_7H_7I_2NOZn$	$C_9H_{11}I_2NOZn$	$C_{12}H_{10}Cl_2N_2O_2Zn$	$C_{12}H_{10}Br_2N_2O_2Zn$
mol. mass	346.33	440.31	468.36	350.49	439.41
crystal size [mm]	0.4 × 0.03 × 0.03	0.5 × 0.5 × 0.2	0.3 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.4 × 0.2 × 0.2
space group	*Fdd2*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*1
Z	16	8	4	4	2
a [Å]	23.075(9)	16.043(1)	7.788(1)	7.716(1)	7.687(5)
b [Å]	23.351(6)	9.140(1)	9.555(1)	13.801(3)	7.726(2)
c [Å]	7.785(7)	16.610(1)	17.805(3)	12.809(2)	12.513(4)
α [°]	90	90	90	90	97.17(2)
β [°]	90	109.03(1)	92.25(1)	100.99(1)	101.26(4)
γ [°]	90	90	90	90	94.65(4)
V [Å^3]	4195(4)	2302.5(3)	1323.9(3)	1339.0(3)	718.8(6)
d(calc.) [g·cm^{-3}]	2.19	2.54	2.35	1.74	2.03
d(obs.) [g·cm^{-3}]	−	2.50	2.26	1.71	1.97
temp. [K]	183(2)	183(2)	183(2)	293(2)	293(2)
μ(Mo-*Kα*) [mm^{-1}]	9.92	7.46	6.49	2.23	7.26
hkl range	*h*: −27 to 0	*h*: −19 to 0	*h*: −9 to 9	*h*: 0 to 8	*h*: −9 to 8
	k: −27 to 27	*k*: 0 to 11	*k*: −11 to 0	*k*: 0 to 16	*k*: −9 to 9
	l: 0 to 9	*l*: −19 to 20	*l*: −21 to 0	*l*: −14 to 14	*l*: 0 to 15
refl. measd.	1969	4665	2676	2398	1678
indep. refl.	1000	4497	2591	2221	1678
obs. refl. [*I*>2σ(*I*)]	561	3965	2406	1279	1678
parameters	103	217	127	172	172
refl. refined	1000	4497	2591	2221	1678
R_1 (obs. refl.)	0.048	0.056	0.026	0.059	0.087
wR_2 (all refl.)	0.122	0.159	0.080	0.183	0.266
residual el. density [e/Å^{-3}]	+1.0 −1.1	+2.8 −1.5	+0.8 −0.8	+3.3 −0.7	+3.3 −1.1

Table 6, part 2. Crystallographic details

	4c	**5**	**6**	**9a**	**9b**
formula	$C_{12}H_{10}I_2N_2O_2Zn$	$C_{12}H_{12}Cl_4N_2O_3Zn_2$	$C_{24}H_{20}I_6N_4O_4Zn_3$	$C_7H_5Cl_2NO_2Zn$	$C_7H_5Br_2NO_2Zn$
mol. mass	533.39	504.78	1385.95	271.39	360.31
crystal size [mm]	0.3 × 0.2 × 0.03	0.6 × 0.5 × 0.5	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
space group	*P*1	*P*1	*I*42*d*	*P*2$_1$/*n*	*P*2$_1$/*c*
Z	2	2	4	4	4
a [Å]	7.739(1)	7.997(1)	11.746(1)	7.236(2)	7.395(2)
b [Å]	7.879(1)	7.875(1)	11.746(1)	9.398(2)	9.965(2)
c [Å]	13.031(1)	15.573(1)	28.259(2)	14.382(4)	14.436(4)
α [°]	100.79(1)	100.69(1)	90	90	90
β [°]	93.79(1)	101.73(1)	90	103.37(2)	104.67(2)
γ [°]	95.08(1)	101.40(1)	90	90	90
V [Å^3]	774.7(1)	914.9(1)	3898.9(4)	951.5(4)	1029.1(4)
d(calc.) [g·cm^{-3}]	2.29	1.83	2.36	1.89	2.326
d(obs.) [g·cm^{-3}]	2.17	1.82	2.23	1.88	2.287
temp. [K]	293(2)	293(2)	293(2)	183(2)	183(2)
μ(Mo-*Kα*) [mm^{-1}]	5.57	3.22	6.61	3.10	10.12
hkl range	*h*: 0 to 9	*h*: −9 to 0	*h*: −15 to 0	*h*: −7 to 7	*h*: −9 to 0
	k: −9 to 9	*k*: −9 to 9	*k*: −15 to 0	*k*: 0 to 10	*k*: 0 to 12
	l: −16 to 16	*l*: −19 to 19	*l*: −36 to 0	*l*: 0 to 14	*l*: −17 to 17
refl. measd.	3283	3978	2282	1097	2168
indep. refl.	3045	3701	1197	1097	2007
obs. refl. [*I*>2σ(*I*)]	2411	3056	642	1096	1558
parameters	172	216	94	118	118
refl. refined	3045	3701	1197	1097	2007
R_1 (obs. refl.)	0.032	0.034	0.043	0.038	0.028
wR_2 (all refl.)	0.086	0.099	0.150	0.101	0.078
residual el. density [e/Å^{-3}]	+0.8 −0.6	+0.8 −0.4	+1.6 −0.9	+0.6 −0.5	+0.5 −0.7

(1:1). Careful layering with petroleum ether (b.p. 70−90°C) and storage of the sample in a vibration-free place yielded well-shaped crystals. These crystals were immersed in perfluorinated polyether oil for protection and attachment to the goniometer head and immediately subjected to the nitrogen flow of the diffractometer's cooling system. Diffraction data were recorded at low temperatures with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube ($K_α$, λ = 0.7107 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved by direct methods and refined anisotropically with the SHELX program suite[25]. The aldehyde C−H hydrogen atoms were located and refined freely. All other hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma F_o - F_c / \Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL[26]. Table 6 lists the crystallographic data.

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