Zinc Complexes of Aldehydes and Ketones, 2[+]
Zinc-Aldehyde Complexes with Weakly Coordinating Anions

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Keywords: Zinc / Aldehyde ligands / Weakly coordinating anions / Structural chemistry

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Zinc salts of low or zero water content were obtained from the hexahydrates of zinc nitrate, zinc perchlorate, and zinc tetrafluoroborate by dehydration with triethoxymethane or by solvation with acetonitrile or nitromethane. The compounds incorporated aldehydes as ligands when treated with an excess of the aromatic aldehydes benzaldehyde, mesitylaldehyde, 2-chlorobenzaldehyde, and 4-fluorobenzaldehyde. Eighteen zinc-aldehyde complexes were isolated and identified by crystal structure determinations. All contain octahedral zinc to which 2, 3, 4, 5, or 6 aldehyde ligands are bound. Water, ethanol, and acetonitrile molecules act as coligands. Of the anions employed, BF_4^- and $SbCl_6^-$ were found to be only noncoordinating and NO_3^- only coordinating, whereas complexes with one or two perchlorate ligands were obtained in addition to perchlorate salts.

It is widely known that countless reactions of organic carbonyl compounds (esters, amides, aldehydes, ketones, etc.) can be catalyzed by metal salts or complexes. Zinc species play a dominant role in this context for preparative organic chemistry[2] as well as for enzyme-catalyzed transformations[3]. The basic function of the metal ion in these reactions is its attachment to the carbonyl oxygen to induce Lewis-acidic activation. However, since carbonyl compounds are only weak donors and since the important reactions are catalytic, metal complexes of organic carbonyl compounds are rarely isolated. Therefore, in sharp contrast to the many mechanistic proposals involving metal activation of the carbonyl function, the coordination chemistry of this function is rather underdeveloped[4].

We became interested in zinc coordination of CO-containing species during our model studies and mechanistic interpretations of zinc enzyme-catalyzed hydrolyses of esters, amides, and CO_2 by Zn−OH complexes[5]. Our attention focused on aldehydes and alkoxides as ligands when trying to reproduce the biological function of zinc-containing alcohol dehydrogenase[6] by stepwise reactions with zinc complexes[7]. We therefore set out to undertake a comprehensive study of zinc complexation by aldehydes, which led to the results presented in this and the two succeeding[8][9] papers.

The literature on metal complexation of plain aldehydes contains a few papers describing zinc complexes, i.e. hexaaldehyde solvates of zinc salts[10][11], the benzaldehyde adduct of zinc chloride[12], mono- and bis-aldehyde adducts of zinc chalcogenolates[13], chelate complexes of pyridine-2-carbaldehyde[14−16], and two zinc porphyrin complexes with η^1-coordinated benzaldehyde[17][18]. Of these examples only the latter two[17][18] and the $Zn(SeR)_2$(anisaldehyde) dimer[13] were characterized by structure determinations. Likewise, for all other metals the number of well-characterized aldehyde complexes is small, and the level of information is noteworthy only for complexes of salicylic aldehyde and its derivatives as well as for organometallic complexes of η^2 (side-on)-coordinated simple aldehydes[4]. A search of the Cambridge Crystallographic Data File has yielded just six further structures of classical metal complexes with monodentate O-coordinated aldehyde ligands.

Our systematic approach to the chemistry of zinc aldehyde complexes followed four lines: (a) monodentate plain aldehydes and zinc salts of weakly coordinating anions; (b) monodentate plain aldehydes and zinc halides; (c) chelating aldehydes derived from nitrogen heterocycles; (d) aldehyde complexes of zinc thiolates. The aims of this study were: (a) to obtain as many different compound types as possible; (b) to confirm their composition and constitution by structure determinations; (c) to elucidate the donor qualities of the aldehydes as compared to those of competing ligands like water and anions; (d) to find relationships between the complex properties and catalytic phenomena; (e) to model the structure and function of the active site of horse liver alcohol dehydrogenase. We have published a short communication describing the initial stages of this work[1]. This manuscript is the first in a series of full papers describing zinc complexes with predominant or exclusive aldehyde coordination.

Preparations and Structures

It was clear after our preliminary studies[1] that water, donor solvents, and anions with donor properties, like halides, are better ligands for the zinc ion than aldehydes. Furthermore, aliphatic aldehydes were preferentially condensed, polymerized, or underwent disproportionation to carboxylic esters rather than being incorporated into stable

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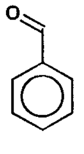
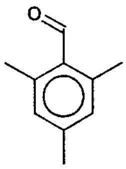
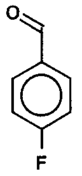
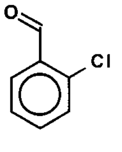
complexes. This fact dictated the working procedures and the choice of aldehydes. All reactions were carried out in water-free nonpolar solvents containing high concentrations of the aldehydes or using the neat aldehydes as solvents. The water content of the zinc salts was controlled by using triethoxymethane as a dehydrating agent[19] or by starting from water-free zinc hexachloroantimonate solvates[20][21]. Thus the starting zinc compounds were $[Zn(H_2O)_6]X_2$ (X = ClO_4, BF_4, NO_3), $[Zn(CH_3CN)_6](SbCl_6)_2$, and $[Zn(CH_3NO_2)_6](SbCl_6)_2$. These compounds were treated with various aromatic aldehydes of which the following allowed the isolation of pure complexes:


benz-aldehyde
BA


mesityl-aldehyde
MA


4-fluoro-benzaldehyde
FA


2-chloro-benzaldehyde
CA

The hydrated zinc salt was always first dissolved in triethoxymethane before the reaction was started. For each water molecule to be removed, one equivalent of triethoxymethane was applied, plus one additional equivalent for completion of the dehydration. After drying the (partially) dehydrated zinc salt in vacuo it was treated with a large excess of the aldehyde. The resulting clear solutions were diluted with petroleum ether, which caused the aldehyde-containing zinc salts to precipitate. This process worked in all cases. However, the precipitates were never crystalline (e.g. oily) or pure when the precipitation was performed by adding petroleum ether. It was therefore essential to prepare the products by slow crystallization. This was achieved by layering the neat or dichloromethane-diluted aldehyde solutions with petroleum ether and keeping the mixture in a vibration-free place at or slightly below room temperature. In this way all products that could be obtained pure were crystalline and immediately suitable for X-ray crystallography. Due to their extremely hygroscopic nature, all handling of the compounds required the rigorous exclusion of water.

Tetraaqua-bisaldehyde complexes were obtained from zinc perchlorate and tetrafluoroborate with mesitylaldehyde. Compounds **1** and **2** were originally believed to be tetraaldehyde complexes, and only the structure determinations revealed that they contain, in the solid state, two non-coordinating aldehyde molecules that are linked by hydrogen bridges to water ligands.

$[Zn(MA)_2(H_2O)_4]X_2 \bullet 2$ MA
1: X = ClO_4, **2**: X = BF_4

Figure 1 shows the coordination pattern of **1** and **2**. In both cases the two aldehyde ligands are in *trans* positions, and the Zn−O(aldehyde) bonds are longer than the Zn−O(water) bonds.

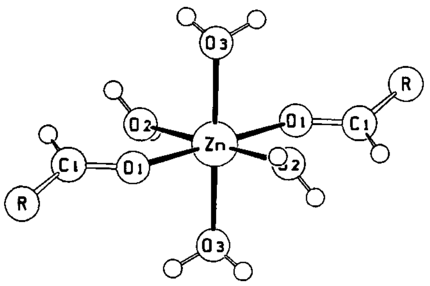


Figure 1. Zinc coordination in **1** and **2**. Bond lengths [Å] and angles [°] for **1**/**2**: Zn−O1 2.125(1)/2.129(2), Zn−O2 2.069(1)/2.052(2), Zn−O3 2.053(1)/2.075(2), O1−C1 1.227(2)/1.227(3), Zn−O1−C1 135.2(1)/135.5(2), O−C−C 126.0(1)/125.4(2).

Diaqua-tetraaldehyde complexes were again obtained only from $Zn(ClO_4)_2$, $Zn(BF_4)_2$ and mesitylaldehyde. Of these complexes, compound **3** again contains two aldehyde molecules in the second coordination sphere, while **4** has only zinc-coordinated aldehyde. The structure determinations showed that zinc is again *trans*-configured in both compounds (Figure 2). In these cases the Zn−O(aldehyde) and Zn−O(water) bond lengths are spread irregularly over their range from 2.04 to 2.13 Å.

$[Zn(MA)_4(H_2O)_2](ClO_4)_2 \bullet 2$ MA
3

$[Zn(MA)_4(H_2O)_2](BF_4)_2$
4

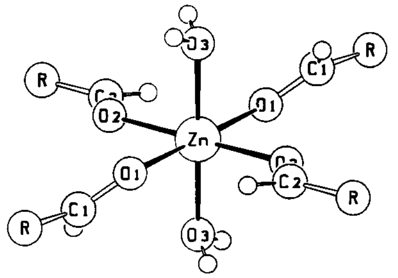


Figure 2. Zinc coordination in $[Zn(MA)_4(H_2O)_2](ClO_4)_2 \bullet 2$ MA (**3**) and $[Zn(MA)_4(H_2O)_2](BF_4)_2$ (**4**). Bond lengths [Å] and angles [°] for **3**/**4**: Zn−O1 2.061(3)/2.128(1), Zn−O2 2.086(2)/2.102(1), Zn−O3 2.109(2)/2.036(1), O1−C1 1.225(3)/1.233(2), O2−C2 1.226(4)/1.225(2), Zn−O1−C1 130.7(2)/122.6(1), Zn−O2−C2 132.7(2)/129.3(1), O1−C−C 125.9(3)/126.5(2), O2−C−C 125.1(3)/125.1(2).

In order to make these partially solvated zinc salts available for a wider range of aldehydes, two equivalents of ethanol were added to solutions of the bis-hydrates in various aldehydes. However, in only two cases did this lead to pure compounds, and these products were **5** and **6**. In all other cases the precipitates were non-crystalline and non-uniform. The structure determinations (Figure 3) showed that the two aldehyde, alcohol, and water ligands are each bound to zinc in an all-*trans* fashion. There is no noteworthy distinction between the Zn−O bond lengths for the aldehyde, alcohol, or water ligands.

$[Zn(A)_2(EtOH)_2(H_2O)_2]\ (ClO_4)_2$
5: A = MA; **6**: A = CA

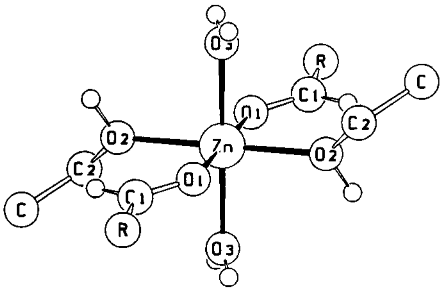


Figure 3. Zinc coordination in $[Zn(A)_2(EtOH)_2(H_2O)_2](ClO_4)_2$ (**5**: A = MA, **6**: A = CA). Bond lengths [Å] and angles [°] for **5**/**6**: Zn−O1 2.083(5)/2.098(3), Zn−O2 2.080(5)/2.057(4), Zn−O3 2.079(5)/2.011(4), O1−C1 1.230(8)/1.225(5), O2−C2 1.440(9)/1.496(9), Zn−O1−C1 130.1(5)/135.1(3), Zn−O2−C2 128.0(4)/127.0(4), O1−C−C 125.4(7)/122.1(4).

Further removal of water allowed the isolation of monoaqua complexes. In the case of 2-chlorobenzaldehyde, four aldehyde molecules and one perchlorate ion were the other ligands in complex **7**. **7** has the water and perchlorate ligands *trans* to each other (Figure 4). Although the Zn−O(aldehyde) bonds are of average length, there is a *trans* effect for the two other Zn−O bonds: the weak (long) Zn−perchlorate interaction has a strong (short) Zn−water interaction *trans* to it.

$[Zn(CA)_4(H_2O)(ClO_4)]ClO_4$
7

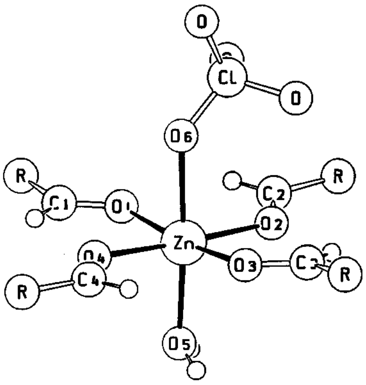


Figure 4. Zinc coordination in $[Zn(CA)_4(H_2O)(ClO_4)]ClO_4$ (**7**). Bond lengths [Å] and angles [°]: Zn−O1 2.078(4), Zn−O2 2.093(5), Zn−O3 2.068(4), Zn−O4 2.095(4), Zn−O5 2.032(6), Zn−O6 2.188(5), O1−C1 1.203(7), O2−C2 1.218(7), O3−C3 1.201(7), O4−C4 1.214(7), Zn−O1−C1 127.8(4), Zn−O2−C2 127.8(4), Zn−O3−C3 127.2(4), Zn−O4−C4 130.0(4), O1−C−C 123.8(6), O2−C−C 123.2(6),O3−C−C 123.4(6), O4−C−C 123.1(6), Zn−O6−Cl 132.4(3).

Five benzaldehyde ligands are present in complex **8**. This time there is no *trans* effect associated with the water ligand, but the average Zn−O(aldehyde) bond length of 2.09 Å is significantly longer than the average Zn−O(water) bond length of 2.02 Å (Figure 5).

$[Zn(BA)_5(H_2O)](BF_4)_2$
8

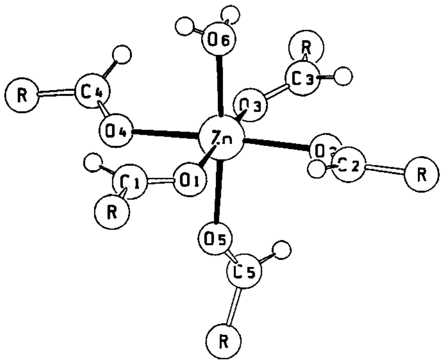


Figure 5. Zinc coordination in $[Zn(BA)_5(H_2O)](BF_4)_2$ (**8**). Bond lengths [Å] and angles [°] in the two independent molecules: Zn−O1 2.091(3)/2.118(3), Zn−O2 2.080(3)/2.079(3), Zn−O3 2.105(3)/2.078(3), Zn−O4 2.096(3)/2.086(3), Zn−O5 2.070(4)/2.080(3), Zn−O6 2.017(4)/2.031(4), O1−C1 1.215(6)/1.217(6), O2−C2 1.215(6)/1.213(6), O3−C3 1.211(6) /1.224(6), O4−C4 1.212(6)/1.213(5), O5−C5 1.216(6)/1.231(6), Zn−O1−C1 127.0(3)/129.6(3), Zn−O2−C2 127.4(3)/126.4(3), Zn−O3−C3 132.3(3)/130.3(3), Zn−O4−C4 126.6(3)/128.7(3), Zn−O5−C5 135.1(4)/127.9(3), O1−C−C 123.5(4)/124.3(4), O2−C−C 123.0(5)/123.6(4), O3−C−C 122.6(5)/122.5(5), O4−C−C 124.5(4)/124.5(4), O5−C−C 122.1(5)/123.5(4).

While no hydrated aldehyde complex of zinc nitrate could be obtained in a pure state, this was the case for the water-free complexes. In the reaction with mesitylaldehyde, complex **9** was isolated. The composition of **9** indicated that three coordination positions would be used for the zinc−nitrate interactions, i.e. one nitrate ligand would be monodentate and the other bidentate, a situation observed many times in octahedral zinc complexes. This was borne out by the structure determination (Figure 6). The three

$[Zn(MA)_3(NO_3)_2]$
9

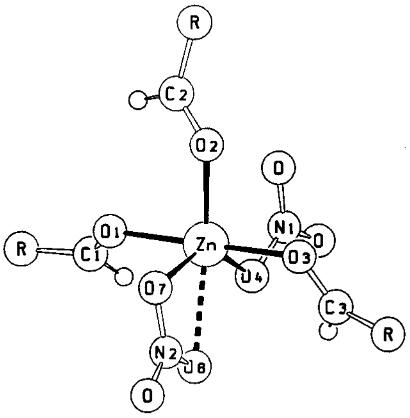


Figure 6. Zinc coordination in $[Zn(MA)_3(NO_3)_2]$ (**9**). Bond lengths [Å] and angles [°]: Zn−O1 2.075(2), Zn−O2 2.032(2), Zn−O3 2.120(2), Zn−O4 2.017(2), Zn−O5 2.098(2), Zn−O6 2.400(2), O1−C1 1.231(3), O2−C2 1.218(2), O3−C3 1.228(3), O1−C−C 125.2(2), O2−C−C 124.7(2), O3−C−C 126.7(2), Zn−O1−C1 127.7(2), Zn−O2−C2 130.7(1), Zn−O3−C3 119.2(1), O2−Zn−O4 125.1(1), O2−Zn−O5 96.3(7), O2−Zn−O6 150.9(1).

aldehyde and the three nitrate oxygen atoms are all arranged meridionally. The unsymmetrically bidentate nature of one nitrate ligand causes a severe distortion of the octahedral ligand arangement (cf. angles involving O2), and the lack of a direct *trans*-ligand makes Zn−O2 an unusually short Zn−O(aldehyde) bond.

Attempts to prepare hexa-aldehyde complexes by way of quantitative dehydration of the zinc salts did not lead to the desired products. Instead tetraaldehyde-bisperchlorate complexes were obtained from $Zn(ClO_4)_2 \bullet 6\ H_2O$. These compounds were isolated in a crystalline form by reaction with benzaldehyde, 4-fluorobenzaldehyde and mesitylaldehyde as **10**, **11**, and **12**. **12** represents another example that contained two equivalents of co-crystallized aldehyde. All three complexes have the four aldehyde ligands in a planar arrangement and the two perchlorate ligands in a *trans*-axial orientation (Figure 7). The presence of two additional aldehyde molecules per formula unit in the crystals of **12** has no influence on bond lengths or angles around zinc. By comparison the Zn−O(aldehyde) bonds are relatively short and the Zn−O(perchlorate) bonds typically long.

$[Zn(A)_4(ClO_4)_2]$
10: A = BA; **11**: A = FA; **12**: A = MA

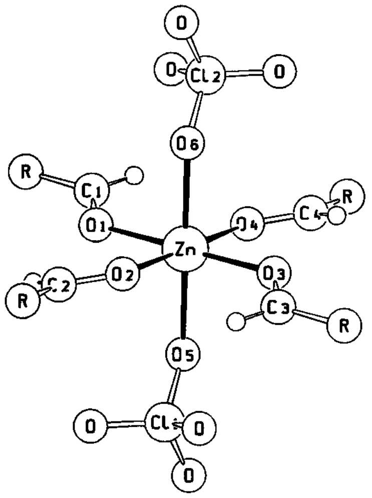


Figure 7. Zinc coordination in **10**, **11**, and **12** (**10** and **11** have zinc on an inversion center). Bond lengths [Å] and angles [°] for **10**/**11**/**12**: Zn−O1 2.063(1)/2.068(1)/2.072(3), Zn−O2 2.057(1)/2.044(1)/2.052(2), Zn−O3 −/−/2.084(3), Zn−O4 −/−/2.043(2), Zn−O5 2.143(1)/2.159(1)/2.134(3), Zn−O6 −/−/2.230(3), O1−C1 1.229(2)/1.227(2)/1.235(4), O2−C2 1.234(2)/1.231(2)/1.233(4), O3−C3 −/−/1.229(4), O4−C4 −/−/1.233(4), Zn−O1−C1 129.0(1)/128.3(1)/121.2(2), Zn−O2−C2 127.0(1)/128.9(1)/123.8(2), Zn−O3−C3 −/−/125.1(2), Zn−O4−C4 −/−/125.2(2), O1−C−C 123.3(2)/123.1(2)/126.9(3), O2−C−C 122.9(2)/122.2(2)/125.4(3), O3−C−C −/−/125.9(3), O4−C−C −/−/125.3(2), Zn−O5−Cl 132.8(3)/133.6(1)/135.0(2), Zn−O6−Cl −/− 142.4(2).

In complexes like **10**−**12** the perchlorate ligands seem to be more difficult to replace than the aldehyde ligands. This became evident when two equivalents of ethanol were added to solutions of the fully dehydrated zinc salts in the neat aldehydes. Complex **13** could be crystallized from its solution in mesitylaldehyde. Figure 8 shows the all-*trans* arrangement of its pairs of aldehyde, alcohol, and perchlorate ligands. The Zn−O(aldehyde) and Zn−O(alcohol) bond lengths are not significantly different in **13**, and all of its Zn−O bond lengths are quite similar to those in **10**−**12**.

$[Zn(MA)_2(EtOH)_2(ClO_4)_2]$
13

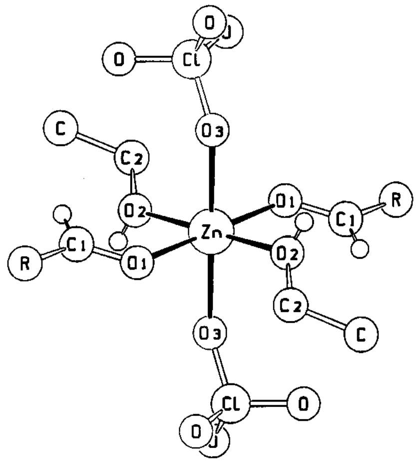


Figure 8. Zinc coordination in **13**. Bond lengths [Å] and angles [°]: Zn−O1 2.069(2), Zn−O2 2.045(3), Zn−O3 2.151(3), O1−C1 1.225(4), O2−C2 1.447(4), Zn−O1−C1 125.6(2), Zn−O2−C2 130.5(2), Zn−O3−Cl 143.1(2), O1−C−C 126.4(3).

It was thus obvious that the aldehydes are not strong enough as donors to occupy all six coordination positions at the zinc ion in the presence of the weakly coordinating anions NO_3^-, BF_4^-, or ClO_4^-. We therefore resorted to solvated zinc hexachloroantimonate as a starting material. By dissolving $[Zn(CH_3CN)_6](SbCl_6)_2$[20] in the aldehydes we found that not more than two of the acetonitrile ligands could be replaced. Complexes **14**−**16** were isolated.

trans-$[Zn(A)_2(MeCN)_4]\ (SbCl_6)_2$
14: A = BA; **15**: A = MA

cis-$[Zn(CA)_2(MeCN)_4]\ (SbCl_6)_2$
16

The structure determinations revealed that **14** and **15** are *trans*-configured (Figure 9). The mediocre quality of the data set for **14** prohibits a detailed comparison, but it is obvious that the Zn−O and Zn−N bond lengths in both complexes are practically identical and that the equatorially arranged acetonitrile ligands show a variable deviation from linearity (157−177°) at their nitrile carbon atoms.

In contrast, complex **16** is *cis*-configured (Figure 10). This time there is a distinction between the Zn−O and Zn−N bond lengths, the latter being shorter, and the acetonitrile ligands are closer to being linear. The structural features do not offer an indication as to why **14** and **15** should be *trans*- and **16** *cis*-configured.

A complete replacement of solvate by aldehyde ligands could be achieved by starting with $[Zn(CH_3NO_2)_6](SbCl_6)_2$[21], as previously reported by Driessen et al.[10][11]. The problem of fast decomposition of the products could

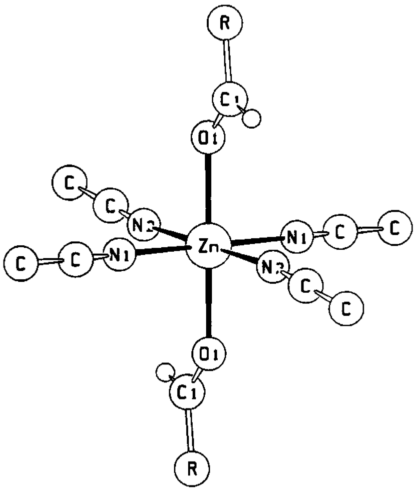


Figure 9. Zinc coordination in **14** and **15**. Bond lengths [Å] and angles [°] in **14**/**15**: Zn−O1 2.116(9)/2.103(3), Zn−N1 2.113(11)/2.137(4), Zn−N2 2.117(12)/2.106(5), O1−C1 1.20(1)/1.23(1), Zn−O1−C1 136(1)/129.2(3), O1−C−C 123(1)/126.4(4), Zn−N1−C 174(1)/157.3(4), Zn−N2−C 172(1)/165.1(4).

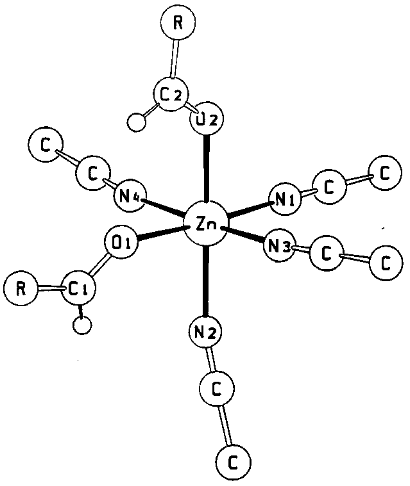


Figure 10. Zinc coordination in **16**. Bond lengths [Å] and angles [°]: Zn−O1 2.168(2), Zn−O2 2.149(2), Zn−N1 2.087(3), Zn−N2 2.165(3), Zn−N3 2.087(3), Zn−N4 2.082(3), O1−C1 1.215(4), O2−C2 1.216(4), Zn−O1−C1 131.0(2), Zn−O2−C2 128.0(2), O1−C−C 123.1(4), O2−C−C 123.8(3), Zn−N1−C 177.4(3), Zn−N2−C 164.3(3), Zn−N3−C 168.4(3), Zn−N4−C 171.5(3).

be overcome for fluoro- and chlorobenzaldehyde, making compounds **17** and **18** accessible in a pure and crystalline form.

$[Zn(FA)_6](SbCl_6)_2$ $[Zn(CA)_6](SbCl_6)_2 \bullet 4\ CA$
17 **18**

Structurally **17** and **18** are symmetrical octahedral complexes (Figure 11). Specifically, **18** shows very uniform bond lengths and angles for the aldehyde ligands and a very narrow spread of 88−92° for the angles at zinc. The lower data quality for **17** seems to have caused a wider spread of bond lengths and angles, the averages of which, however, agree well with those for **18**. The two complexes define the structural standards for homoleptic zinc-aldehyde complexes with bond lengths of ca. 2.08 Å for Zn−O and ca. 1.23 Å for C−O.

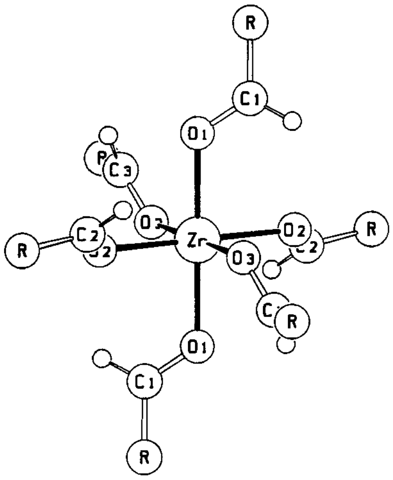


Figure 11. Zinc coordination in **17** and **18** (**18** has zinc on an inversion center). Bond lengths [Å] and angles [°] for **17**/**18**: Zn−O1 2.07(1)/2.073(2), Zn−O2 2.05(1)/2.078(2), Zn−O3 2.15(1)/2.075(2), Zn−O4 2.11(1)/−, Zn−O5 2.09(1)/−, Zn−O6 2.08(1)/−, O1−C1 1.26(2)/1.219(4), O2−C2 1.24(2)/1.219(4), O3−C3 1.21(2)/1.222(4), O4−C4 1.25(2)/−, O5−C5 1.19(2)/−, O6−C6 1.28(2)/−, Zn−O1−C1 122(1)/124.6(2), Zn−O2−C2 130(1)/124.5(2), Zn−O3−C3 119(1)/127.3(2), Zn−O4−C4 125(1)/−, Zn−O5−C5 130(1)/−, Zn−O6−C6 130 (1)/−.

Discussion of the Structures

All these aldehyde complexes are octahedral to a very good approximation. In most cases the valence angles at zinc deviate by not more than ±3° from 90° or ±5° from 180°, with the extremes being ±6° and ±8°, respectively. The aldehyde ligands are attached to zinc in a strict anti fashion, as expressed by the dihedral angles Zn−O−C−R, which range from 158° to 180° with an average over all structures of 174°. Furthermore, and despite some steric hindrance, the aromatic rings of the aldehydes are always coplanar with the RCHO functions, again expressed by dihedral angles ranging from 166° to 179° with an average of 176°.

Details of the Zn−O bond lengths and some internal comparisons were mentioned above for the complex types. Table 1 gives the data for a general comparison. The most interesting question is whether the bonding strength of the aldehydes can be deduced from their Zn−O distances. An inspection of Table 1 reveals that for a given complex type there is no distinction between Zn−O bond lengths according to the type of aldehyde. Instead the coligands seem to have the major influence on the strength of the zinc-aldehyde interaction. When two or more water (**1**−**6**) or acetonitrile ligands (**14**−**16**) are present the Zn−O(aldehyde) bonds are long. In turn, when only aldehyde ligands are present (**17**, **18**) or when only perchlorate is the coligand (**10**−**12**), the Zn−O(aldehyde) bonds are short. This is another demonstration of the fact that the aldehydes are very weak ligands.

Table 1. Bonding features (average values of bond lengths [Å] and angles [°]) for the zinc–aldehyde interactions

	aldehyde			coligands	
	Zn–O	O–C	Zn–O–C	X	Zn–X
1	2.13	1.23	135	$O(H_2O)$	2.06
2	2.13	1.23	136	$O(H_2O)$	2.06
3	2.10	1.23	132	$O(H_2O)$	2.06
4	2.12	1.23	126	$O(H_2O)$	2.04
5	2.08	1.23	130	$O(H_2O)$	2.08
				O(EtOH)	2.08
6	2.10	1.23	135	$O(H_2O)$	2.01
				O(EtOH)	2.06
7	2.08	1.21	128	$O(H_2O)$	2.03
				$O(ClO_4)$	2.19
8	2.09	1.22	129	$O(H_2O)$	2.02
9	2.08	1.23	126	$O(NO_3)$	2.02
				$O(NO_3)$	2.10, 2.40
10	2.06	1.23	128	$O(ClO_4)$	2.14
11	2.06	1.23	129	$O(ClO_4)$	2.16
12	2.06	1.23	124	$O(ClO_4)$	2.18
13	2.07	1.23	126	O(EtOH)	2.05
				$O(ClO_4)$	2.15
14	2.12	1.20	136	N(MeCN)	2.12
15	2.10	1.23	129	N(MeCN)	2.12
16	2.16	1.22	130	N(MeCN)	2.11
17	2.09	1.24	126	–	–
18	2.08	1.22	126	–	–

The spread of the Zn–O distances finds no reflection in the other structural features of the aldehydes. The details of the aldehyde orientation (cf. dihedral angles, see above) show no systematic relation with the Zn–O(aldehyde) bond lengths. The range of the aldehyde C=O bond lengths is too small to warrant a discussion. There is just a barely noticeable proportionality between the Zn–O–C angles and the Zn–O(aldehyde) bond lengths. When compared to the three other reported structures of zinc-aldehyde complexes[13][17][18] the structural features listed in Table 1 span the range observed there.

The coligands in complexes **1**–**16** bind to zinc in a fashion that is known to occur in such complexes[22]. Specifically the bonding alternatives for the nitrate ligand between strictly monodentate and symmetrically bidentate and the weak and variable zinc–perchlorate interactions are well known. Similarly the Zn–N(acetonitrile) bond lengths in **14**–**16** are in the reported range, as are the deviations of the Zn–N–C units from linearity found here (157–177°) in comparison to the reported range (156–178°)[22].

Complexes **17** and **18** are of general significance as they define the standard of ZnO_6 coordination by aldehydes. Their Zn–O distances of 2.08–2.09 Å compare very well with the average values for Zn–O in $Zn(H_2O)_6^{2+}$ (2.09 Å)[23] and in $Zn(alcohol)_6^{2+}$ (2.08 Å)[24]. Other reported complexes with a homoleptic ZnO_6 coordination belong to the types $Zn(pyridine\ oxide)_6^{2+}$[25], $Zn(urea)_6^{2+}$[26], and $Zn(DMSO)_6^{2+}$[27] with average Zn–O bond lengths of 2.10, 2.10, and 2.11 Å, respectively. The Zn–O bond length for the aldehyde complexes is at the lower end of all these ZnO_6 species, indicating again that donor strength and bond distances are not clearly correlated for such compounds. Instead the very narrow spread of all these Zn–O bond lengths (2.08–2.11 Å) indicates that the packing of six oxygen atoms around one zinc ion does not allow shorter contacts irrespective of the variation of the attractive forces.

Spectroscopy

The most important indication for the formation of the aldehyde complexes was the observation of the aldehyde ν(CO) IR bands at their typical locations. As shown in Table 2, the bands for coordinated aldehydes are shifted by ca. 50–80 cm^{-1} to lower wavenumbers, which is in agreement with previous observations on zinc-hexaaldehyde complexes[10][11]. In contrast, those complexes that contain cocrystallized uncoordinated aldehyde display additional ν(CO) bands that are practically unshifted.

Contrary to expectation, the ν(CO) band shifts are neither proportional to the donor strength (i.e. electron richness of the aromatic system) of the aldehydes nor inversely proportional to the donor power of the coligands (i.e. water stronger than perchlorate). Indeed complex **10**, containing benzaldehyde as one of the better aldehyde donors together with only the very weak donor perchlorate, shows the smallest Δν, and complex **6**, containing electron-poor 2-chlorobenzaldehyde together with two water and two ethanol ligands, shows the largest Δν. There seem to be, however, rather uniform Δν values for each aldehyde, e.g. −50 cm^{-1} for BA, −55 cm^{-1} for MA, −65 cm^{-1} for FA, and −80 cm^{-1} for CA. This trend should be of diagnostic value.

The IR data of the coligands and anions also yield some information (Table 2). While the water and ethanol ligands

Table 2. IR data (KBr, cm^{-1}) of the complexes

	aldehyde	$-\Delta\bar{\nu}$	coligand	anion
1	1685 s, 1635 s	5, 55	3517 m, br	1149 s, 1110 s, 1088 s, 940 m
2	1684 s, 1634 s	6, 56	3565 m, br	1148 s, 1034 s
3	1685 s, 1636 s	5, 54	3456 m	1148 s, 1110 s, 1089 s, 940 m
4	1638 s	52	3448 m	1043 s, br
5	1635 s	55	3442 m, br	1149 s, 1108 s, 1085 s, 940 w
6	1616 s	50	3526 m	1146 s, 1107 s, 1087 s, 940 w
7	1619 s	79	3446 m, br	1109 s, 1088 s
8	1651 s	50	3450 m, br	1034 s, br
9	1640 s	50	–	1465 s, br, 1390 s, 1290 s, br
10	1654 s	47	–	1149 s, 1108 s, 1086 s
11	1638 s	62	–	1150 s, 1095 s, br
12	1689 s, 1635 s	1, 55	–	1149 s, 1104, 1088 s
13	1634 s	56	3415 m	1150 s, 1091 s
14	1650 s	51	2316 m, 2290 m	–
15	1639 s	51	2317 m, 2287 m	–
16	1643 s	55	2316 m, 2296 m	–
17	1635 s	65	–	–
18	1698 s, 1627 s	0, 71	–	–

display a broad and unspecific absorption between 3400 and 3550 cm^{-1}, the ν(CN) bands of the acetonitrile ligands are characteristically shifted by 25−40 cm^{-1} to higher wavenumers[28] as compared to those of free CH_3CN. The ν(NO) bands of the nitrate ligands, as is usual[29], give no clear indication of their bonding mode (uni- or bidentate). The BF_4^- and ClO_4^- ions show their strong absorptions near 1100 cm^{-1}. For perchlorate, a medium-intensity band near 940 cm^{-1}, assignable to a fully symmetrical stretch[19], is observed only in complexes **1**, **3**, **5**, and **6**, in accord with the structural data showing that these complexes contain uncoordinated ClO_4^-.

The suitability of NMR spectroscopy for bonding discussions of the aldehyde complexes is hampered by the fact that, other than in the neat aldehydes, they dissolve only in polar organic solvents that may be stronger donors for zinc than the aldehydes. Accordingly, only small shift effects were observed when recording the spectra in [D$_6$]acetone. Table 3 lists the data.

Table 3. ^{1}H- and ^{13}C-NMR data for the aldehyde CHO functions (in [D$_6$]acetone, δ)

	δ(H)	Δδ	δ(C)	Δδ
1	10.49	+0.01	193.9	+1.3
2	10.46	−0.02	194.1	+1.5
3	10.50	+0.02	193.8	+1.2
4	10.49	+0.01	193.8	+1.2
5	10.48	±0	194.4	+1.8
6	10.31	−0.05	190.2	+0.8
7	10.39	+0.03	190.0	+0.6
8	10.12	+0.06	193.4	+0.7
9	10.45	−0.03	195.3	+2.7
10	9.96	−0.10	194.6	+1.9
11	10.00	+0.05	191.7	+0.9
12	10.46	−0.02	194.8	+2.2
13	10.48	±0	194.6	+2.0
14	10.01	−0.05	193.0	+0.3
15	10.50	+0.02	193.5	+0.9
16	10.39	+0.03	189.8	+0.4
17	9.96	+0.01	191.3	+0.5
18	10.39	+0.03	189.7	+0.3

Metal coordination of the aldehyde function should lead to deshielding of both the H and C of RCHO. Such a deshielding is actually observed with Δδ values of 1−2 ppm for the ^{13}C resonances while the ^{1}H resonances are so close to those of the free aldehydes that they cannot be discussed. The extent of deshielding decreases in the order MA > BA > FA > CA, which can be correlated with the donor strengths. The NMR spectra, however, do not show a distinction between coordinated and uncoordinated aldehydes in complexes **1**−**3**, **12**, and **18**.

The coligands ethanol and acetonitrile seem to stay coordinated to zinc in acetone solutions. Their ^{1}H-NMR resonances are shifted by 0.5−1 ppm to lower field in comparison to those of the free ligands. Likewise the ^{13}C-NMR signals are shifted downfield by up to 2.5 ppm for ethanol-CH_2, but show almost no shift for the acetonitrile resonances.

Conclusions

This work has shown that two to six aldehyde molecules can be coordinated to zinc under carefully controlled conditions. The complexes described here are those that were isolated in an analytically pure form. Many more have been prepared in a less pure form, and it is to be assumed that the various structural types can be realized by most of the aldehydes. The aldehydes are completely expelled from the ligand sphere of zinc when excess water is present. In the presence of strongly coordinating anions like the halides, completely different structural types are observed[8].

All isolated complexes were found to be octahedral. Normally they contain one to four coligands together with the aldehyde ligands. In addition to water, ethanol and acetonitrile can also not be completely replaced by the aldehydes. Under anhydrous conditions the nitrate and perchlorate anions are preferred over the aldehydes as ligands. Hexaaldehyde complexes could only be obtained by replacement of the very weak donor nitromethane and by applying an anion ($SbCl_6^-$) of extremely low donor strength.

X-ray structure determination was found to be the only method of unambiguous product identification. It has provided the structural features of zinc−aldehyde bonding. It has delivered examples of the basic ZnL_6 structure for L = aldehyde, which need to be complemented for other L, e.g. alcohol, acetone, ethers, nitromethane, acetonitrile, etc. It has been shown that slight variations in the reaction conditions can lead to quite different compositions of the complexes. Together with the low donor strength of the aldehydes this means that there exists a high degree of uncertainty when mechanistic conclusions are drawn from such structures or even from the composition of reaction solutions.

With respect to modelling the zinc enzyme alcohol dehydrogenase, this work has provided some elementary information. On the one hand it was shown that aldehydes can be bound to zinc in the presence of water, i.e. zinc can be involved in the process of aldehyde reduction. On the other hand it has become very clear that excess water replaces zinc-bound aldehydes very easily, e.g. the last step of alcohol oxidation is facile. Furthermore, the possible coexistence of alcohol and aldehyde ligands in the same complex was demonstrated. With respect to the chemical reactions happening in the enzyme, the findings of this work are of little relevance as neither the low coordination number of zinc nor the presence of a redox reagent were reproduced. It was partly for this reason that we extended our studies of zinc−aldehyde coordination to further types of ligands and coligands[8][9].

Experimental Section

The general working and measuring techniques were as described previously[30]. All experiments were carried out using carefully dried atmospheres (nitrogen or argon) and solvents. As some of the products were too moisture-sensitive for ordinary C/H/N analyses, all compounds were also characterized by zinc and anion analyses

Table 4. Reaction details

Compl.	zinc salt			HC(OEt)$_3$			aldehyde/EtOH				yield		m.p.
		g	mmol	mL	g	mmol		mL	g	mmol	g	%	°C
1	$Zn(H_2O)_6(ClO_4)_2$	1.58	4.25	2.12	1.89	12.75	MA	10	10.05	67.81	3.71	94	91
2	$Zn(H_2O)_6(BF_4)_2$	1.09	3.14	1.57	1.40	9.42	MA	7	7.04	47.50	2.64	93	99
3	$Zn(H_2O)_6(ClO_4)_2$	0.92	2.47	2.05	1.83	12.35	MA	5	5.03	33.94	2.08	71	87
4	$Zn(H_2O)_6(BF_4)_2$	0.56	1.61	1.35	1.20	8.07	MA	5	5.03	33.94	0.59	42	93
5	$Zn(H_2O)_6(ClO_4)_2$	1.03	2.77	2.30	2.05	13.83	MA	5	5.03	33.94	0.95	50	70
							EtOH	0.323	0.25	5.43			
6	$Zn(H_2O)_6(ClO_4)_2$	1.03	2.77	2.29	2.04	13.79	CA	5	6.24	44.39	1.25	67	80
							EtOH	0.323	0.25	5.43			
7	$Zn(H_2O)_6(ClO_4)_2$	1.01	2.71	2.71	2.41	16.27	CA	5	6.24	44.39	0.52	23	131
8	$Zn(H_2O)_6(BF_4)_2$	0.81	2.33	2.34	2.08	14.00	BA	5	5.22	49.19	1.06	58	87
9	$Zn(H_2O)_6(NO_3)_2$	0.48	1.61	2.14	1.91	12.91	MA	10	10.05	67.81	0.72	70	79
10	$Zn(H_2O)_6(ClO_4)_2$	1.19	3.20	4.25	3.79	25.57	BA	9	9.40	88.54	1.60	73	122
11	$Zn(H_2O)_6(ClO_4)_2$	1.10	2.95	3.93	3.50	23.63	FA	5	5.79	46.65	0.52	23	135 (dec.)
12	$Zn(H_2O)_6(ClO_4)_2$	0.87	2.34	3.11	2.77	18.69	MA	5	5.03	33.94	1.88	70	81
13	$Zn(H_2O)_6(ClO_4)_2$	1.04	2.79	3.72	3.31	22.34	MA	5	5.03	33.94	0.51	28	117
							EtOH	0.325	0.26	5.64			
14	$Zn(MeCN)_6(SbCl_6)_2$	1.09	1.11	–	–	–	BA	5	5.22	49.19	1.07	87	117 (dec.)
15	$Zn(MeCN)_6(SbCl_6)_2$	1.45	1.48	–	–	–	MA	5	5.03	33.94	1.28	72	93 (dec.)
16	$Zn(MeCN)_6(SbCl_6)_2$	1.23	1.25	–	–	–	CA	5	6.24	44.39	1.27	86	86
17	$Zn(MeNO_2)_6(SbCl_6)_2$	1.65	1.50	–	–	–	FA	5	5.79	46.65	2.10	95	105
18	$Zn(MeNO_2)_6(SbCl_6)_2$	1.51	1.37	–	–	–	CA	5	6.24	44.39	2.66	91	80

(Table 5). All starting compounds were obtained commercially, recrystallized or distilled prior to use, and stored under anhydrous conditions. The acetonitrile[20] and nitromethane[21] complexes of zinc were prepared as described. Although none of the perchlorate-containing materials were found to be explosive, all of them were handled in small quantities and with the appropriate safety precautions. The new complexes were prepared following two procedures that are outlined below and the details for which are given in Table 4. Table 5 gives data of the analytical characterizations.

Preparation of Complexes 1−13: The hydrated zinc salt was dissolved in the appropriate amount of triethoxymethane (n + 1 equivalents for removal of n equivalents of water). The solution was heated to reflux using a hot air blower for a few seconds. After cooling to room temperature, all volatiles were removed in vacuo and the residue dried in vacuo at 40−50°C for 2 h. An approximately 10-fold excess of the aldehyde was then added and the mixture stirred with warming until all reactants had dissolved. After cooling the solution to room temperature the aldehyde solution was layered carefully with 30 mL of petroleum ether (b.p. 60−70°C). Within one to two days the colourless product complex had precipitated. In those cases where the product was crystalline it was also found to be pure. The complex was filtered off, washed with a small amount of petroleum ether (b.p. 60−70°C) and dried in vacuo.

Preparation of Complexes 14−18: The solvated zinc salt was suspended in 5 mL of dichloromethane. 5 mL of the aldehyde was added with stirring upon which a clear solution was formed. This solution was layered carefully with 40 mL of petroleum ether (b.p. 60−70°C). Within a few days the product complex had precipitated as colourless crystals, which were filterd off, washed with a few mL of petroleum ether (b.p. 60−70°C) and dried for a short time in vacuo.

Structure Determinations[31]: Crystals were obtained from the reaction solutions. The crystals were then immersed in perfluorinated polyether oil for protection and attachment to the goniometer head and immediately subjected to the nitrogen flow from the diffractometer's cooling system. Diffraction data were recorded at low temperatures with the $\omega/2\theta$ technique on a Nonius CAD4 dif-

Table 5. Analytical characterization

	formula	Analyses calcd./found				
	mol. wt.	C	H	Zn	X	
1	$C_{20}H_{32}Cl_2O_{14}Zn \bullet$ $2\ C_{10}H_{12}O$ 632.8 + 296.4	51.71/ 52.05	6.08/ 6.07	7.04/ 7.01	ClO_4	21.41/ 21.50
2	$C_{20}H_{32}B_2F_8O_6Zn \bullet$ $2\ C_{10}H_{12}O$ 607.5 + 296.4	– –	– –	7.23/ 7.17	BF_4	25.45/ 25.34
3	$C_{40}H_{52}Cl_2O_{14}Zn \bullet$ $2\ C_{10}H_{12}O$ 893.2 + 296.4	– –	– –	5.50/ 5.56	ClO_4	16.72/ 16.84
4	$C_{40}H_{52}B_2F_8O_6Zn$ 867.9	55.36/ 56.86	6.04/ 6.11	7.54/ 7.62	BF_4	20.01/ 19.96
5	$C_{24}H_{40}Cl_2O_{14}Zn$ 688.9	41.85/ 41.64	5.85/ 5.82	9.49/ 9.62	ClO_4	28.87/ 28.95
6	$C_{18}H_{26}Cl_4O_{14}Zn$ 673.6	32.10/ 32.56	3.89/ 3.38	9.71/ 9.84	ClO_4	29.53/ 29.76
7	$C_{28}H_{22}Cl_6O_{13}Zn$ 844.6	39.82/ 39.46	2.63/ 2.76	7.74/ 7.80	ClO_4	23.55/ 23.41
8	$C_{35}H_{32}B_2F_8O_6Zn$ 787.6	53.37/ 54.78	4.10/ 3.33	8.30/ 8.36	BF_4	22.04/ 21.83
9	$C_{30}H_{36}N_2O_9Zn$ 634.0	– –	– –	10.31/ 10.24	NO_3	19.56/ 19.62
10	$C_{28}H_{24}Cl_2O_{12}Zn$ 688.8	– –	– –	9.49/ 9.61	ClO_4	28.88/ 28.64
11	$C_{28}H_{20}Cl_2F_4O_{12}Zn$ 760.8	44.21/ 44.10	2.65/ 2.57	8.60/ 8.58	ClO_4	26.15/ 26.23
12	$C_{40}H_{48}Cl_2O_{12}Zn \bullet$ $2\ C_{10}H_{12}O$ 857.1 + 296.4	– –	– –	5.67/ 5.69	ClO_4	17.24/ 17.21
13	$C_{24}H_{36}Cl_2O_{12}Zn$ 652.8	– –	– –	10.02/ 9.98	ClO_4	30.47/ 30.38
14	$C_{22}H_{24}Cl_{12}N_4O_2Sb_2Zn$ 1110.8	– –	– –	5.89/ 5.74	Cl	38.30/ 38.42
15	$C_{28}H_{36}Cl_{12}N_4O_2Sb_2Zn$ 1194.9	– –	– –	5.47/ 5.52	Cl	35.60/ 35.68
16	$C_{22}H_{22}Cl_{14}N_4O_2Sb_2Zn$ 1179.7	22.40/ 22.37	1.88/ 1.67	5.54/ 5.50	Cl	42.07/ 42.18
17	$C_{42}H_{30}Cl_{12}F_6O_6Sb_2Zn$ 1479.0	34.11/ 34.31	2.05/ 2.26	4.42/ 4.39	Cl	28.77/ 28.86
18	$C_{42}H_{30}Cl_{18}O_6Sb_2Zn \bullet$ $4\ C_7H_5ClO$ 1577.7 + 562.3	39.29/ 38.72	2.36/ 2.62	3.06/ 3.14	Cl	36.45/ 36.73

fractometer 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[32]. The aldehyde C−H and water and alcohol O−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*

Table 6, part 1. Crystallographic details

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{20}H_{32}Cl_2O_{14}Zn$ • 2 $C_{10}H_{12}O$	$C_{20}H_{32}B_2F_8O_6Zn$ • 2 $C_{10}H_{12}O$	$C_{40}H_{52}Cl_2O_{14}Zn$ • 2 $C_{10}H_{12}O$	$C_{40}H_{52}B_2F_8O_6Zn$	$C_{24}H_{40}Cl_2O_{14}Zn$	$C_{18}H_{26}Cl_4O_{14}Zn$
mol. mass	929.12	903.84	1189.48	867.81	688.83	673.56
crystal size [mm]	0.9 × 0.6 × 0.5	0.9 × 0.7 × 0.5	1.2 × 0.8 × 0.7	0.8 × 0.7 × 0.6	0.6 × 0.5 × 0.4	0.6 × 0.5 × 0.5
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P1$
Z	1	1	1	2	1	1
a [Å]	8.560(2)	8.500(6)	8.008(2)	8.172(2)	7.734(1)	7.604(1)
b [Å]	11.565(2)	11.505(3)	14.046(7)	15.484(2)	8.828(1)	7.616(1)
c [Å]	11.587(4)	11.547(3)	14.721(3)	17.248(3)	12.507(2)	12.640(1)
α [°]	71.94(2)	72.48(2)	109.89(4)	90	79.14(1)	86.68(1)
β [°]	87.29(2)	87.16(4)	91.30(2)	101.980(15)	89.46(1)	75.69(1)
γ [°]	84.56(2)	85.20(4)	98.50(3)	90	65.60(1)	71.54(1)
V [Å^3]	1085.5(5)	1072.7(9)	1535.2(9)	2134.9(6)	761.5(2)	672.6(2)
d(calc.) [g•cm^{-3}]	1.42	1.340	1.29	1.35	1.502	1.66
d(obs.) [g•cm^{-3}]	1.41	1.39	1.27	1.33	−	1.61
temp. [K]	183(2)	183(2)	293(2)	183(2)	183(2)	183(2)
μ(Mo-$K\alpha$) [mm^{-1}]	0.76	0.66	0.55	0.65	1.05	1.38
hkl range	h: −10 to 10 k: −14 to 13 l: −14 to 0	h: −10 to 0 k: −14 to 14 l: −14 to 14	h: −9 to 9 k: −17 to 0 l: −17 to 18	h: −10 to 9 k: 0 to 19 l: 0 to 21	h: −9 to 9 k: −10 to 10 l: −14 to 0	h: 0 to 9 k: −8 to 9 l: −15 to 15
refl. measd.	4498	4508	6256	4318	2662	2849
indep. refl.	4276	4208	6000	4176	2531	2641
obs. refl. [I>2σ(I)]	4116	4068	5047	3777	1752	2502
parameters	284	285	366	267	191	175
refl. refined	4276	4208	6000	4176	2531	2641
R_1 (obs. refl.)	0.026	0.062	0.055	0.031	0.058	0.055
wR_2 (all refl.)	0.076	0.204	0.183	0.087	0.175	0.132
residual el. density [e/Å^{-3}]	+0.3 −0.5	+1.3 −2.1	+0.9 −0.5	+0.4 −0.4	+0.6 −1.0	+1.4 −1.0

Table 6, part 2. Crystallographic details

	7	**8**	**9**	**10**	**11**	**12**
formula	$C_{28}H_{22}Cl_6O_{13}Zn$	$C_{35}H_{32}B_2F_8O_6Zn$	$C_{30}H_{36}N_2O_9Zn$	$C_{28}H_{24}Cl_2O_{12}Zn$	$C_{28}H_{20}Cl_2F_4O_{12}Zn$	$C_{40}H_{48}Cl_2O_{12}Zn$ • 2 $C_{10}H_{12}O$
mol. mass	844.53	787.60	633.98	688.74	760.71	1153.45
crystal size [mm]	1.2 × 1.0 × 0.5	1.1 × 1.0 × 1.0	1.2 × 1.0 × 0.9	0.6 × 0.5 × 0.4	1.2 × 1.2 × 0.3	0.8 × 0.7 × 0.6
space group	$C2/c$	$P2_1$	$Pbca$	$P1$	$P1$	$P2_1$
Z	8	4	8	1	1	2
a [Å]	34.263(6)	10.250(1)	15.65(4)	8.637(3)	8.366(1)	13.967(1)
b [Å]	14.709(3)	20.549(3)	17.40(3)	9.472(1)	9.776(1)	14.059(2)
c [Å]	13.677(3)	17.602(3)	22.24(4)	10.350(3)	10.533(1)	14.493(1)
α [°]	90	90	90	68.55(2)	68.62(1)	90
β [°]	94.640(16)	90.220(12)	90	68.88(2)	68.71(1)	90.820(9)
γ [°]	90	90	90	69.99(2)	70.56(1)	90
V [Å^3]	6870(2)	3707.4(9)	6058(2)	713.2(3)	727.2(1)	2845.6(5)
d(calc.) [g•cm^{-3}]	1.633	1.411	1.390	1.60	1.74	1.346
d(obs.) [g•cm^{-3}]	1.610	1.384	1.384	1.59	−	1.322
temp. [K]	293(2)	183(2)	183(2)	183(2)	183(2)	183(2)
μ(Mo-$K\alpha$) [mm^{-1}]	1.24	0.75	0.87	1.11	1.12	0.59
hkl range	h: −41 to 41 k: 0 to 18 l: 0 to 16	h: −12 to 12 k: −25 to 0 l: 0 to 22	h: −18 to 0 k: 0 to 20 l: 0 to 26	h: −10 to 9 k: −11 to 10 l: −12 to 0	h: −10 to 9 k: −12 to 0 l: −12 to 12	h: −17 to 17 k: 0 to 17 l: −18 to 0
refl. measd.	4376	7940	5259	2960	3016	6456
indep. refl.	4376	7692	5258	2798	2840	6210
obs. refl. [I>2σ(I)]	4376	7213	4553	2701	2765	5576
parameters	441	945	379	196	214	694
refl. refined	4376	7692	5258	2798	2840	6210
R_1 (obs. refl.)	0.057	0.041	0.032	0.027	0.034	0.037
wR_2 (all refl.)	0.171	0.124	0.093	0.079	0.094	0.108
residual el. density [e/Å^{-3}]	+1.0 −0.6	+0.5 −0.4	+0.5 −0.6	+0.4 −0.5	+0.7 −0.9	+0.5 −0.5

Table 6, part 3. Crystallographic details

	13	14	15	16	17	18
formula	$C_{24}H_{36}Cl_2O_{12}Zn$	$C_{22}H_{24}Cl_{12}N_4$-O_2Sb_2Zn	$C_{28}H_{36}Cl_{12}N_4$-O_2Sb_2Zn	$C_{22}H_{22}Cl_{14}N_4$-O_2Sb_2Zn	$C_{42}H_{30}Cl_{12}F_6O_6$ Sb_2Zn • C_7H_5FO	$C_{42}H_{30}Cl_{18}O_6$ Sb_2Zn • 4 C_7H_5ClO
mol. mass	652.80	1110.72	1194.88	1179.61	1603.04	2139.87
crystal size [mm]	0.6 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.7 × 0.5 × 0.4	0.7 × 0.5 × 0.5
space group	$P2_1/c$	$Pbca$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$
Z	2	4	2	8	1	1
a [Å]	12.077(2)	19.63(2)	13.237(5)	28.648(3)	11.450(1)	12.386(1)
b [Å]	15.989(2)	10.12(2)	12.906(7)	11.432(1)	11.851(1)	13.803(1)
c [Å]	7.390(2)	20.25(2)	13.637(7)	25.909(2)	14.604(2)	15.211(2)
α [°]	90	90	90	90	66.25(1)	114.05(1)
β [°]	96.31(2)	90	102.26(4)	100.64(1)	67.06(1)	93.58(1)
γ [°]	90	90	90	90	74.78(1)	112.57(1)
V [Å^3]	1418.4(5)	4023(8)	2276.6(2)	8339.4(1)	1657.4(3)	2117.8(3)
d(calc.) [g•cm^{-3}]	1.53	1.83	1.74	1.88	1.61	1.68
d(obs.) [g•cm^{-3}]	1.50	−	−	−	−	−
temp. [K]	183(2)	183(2)	183(2)	183(2)	183(2)	183(2)
μ(Mo-$K\alpha$) [mm^{-1}]	1.12	2.749	2.436	2.78	1.71	1.66
hkl range	h: −14 to 14 k: 0 to 19 l: −9 to 0	h: 0 to 23 k: −11 to 0 l: 0 to 23	h: −15 to 15 k: 0 to 14 l: 0 to 15	h: −39 to 13 k: −14 to 13 l: −31 to 31	h: −13 to 13 k: 0 to 14 l: −16 to 17	h: −15 to 15 k: −15 to 17 l: −18 to 0
refl. measd.	3007	3419	3204	14166	6220	8629
indep. refl.	2782	3416	3204	8594	6216	8295
obs. refl. [$I>2\sigma(I)$]	2027	2298	3204	6723	5716	7371
parameters	182	191	223	408	703	503
refl. refined	2782	3416	3204	8594	6216	8295
R_1 (obs. refl.)	0.039	0.081	0.028	0.028	0.056	0.034
wR_2 (all refl.)	0.104	0.233	0.090	0.077	0.192	0.098
residual el. density [e/Å^{-3}]	+0.6 −0.4	+2.4 −1.9	+0.5 −0.6	+1.3 −0.9	+3.0 −0.8	+1.1 −1.0

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[33]. Table 6 lists the crystallographic data.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft.

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Received August 3, 1998
[I98256]