Zinc Complexes of Aldehydes and Ketones, 3[+]
Aldehyde Complexes of Zinc Halides

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Aldehyde complexes of the zinc halides were obtained by treating $ZnCl_2$, $ZnBr_2$, and ZnI_2 under anhydrous conditions with large excesses of benzaldehyde and various substituted benzaldehydes. Their constitutions were determined by a total of 12 X-ray structure analyses. Three product types were found: $ZnHal_2(aldehyde)_2$ (**A**), $[ZnHal_2(aldehyde)]_\infty$ (**B**), and $[Zn(aldehyde)_6]$ $[Zn_2Hal_6]$ (**C**). All three dissolve readily in the corresponding aldehyde or in polar nonprotic solvents indicating the presence of solvated zinc species in solution.

In the preceding paper[1] we outlined the motivation for our studies of zinc complexation by aldehydes and ketones. The sharp discrepancy between the importance of metal ion catalysis for reactions of carbonyl-containing compounds and the scant knowledge on the chemical interactions between metal ions and carbonyl functions calls for the gathering of basic information upon which mechanistic insight is to be built. The fact that so little is known about metal complexes (other than organometallic species) of simple carbonyl compounds is a reflection of the low donor strength of these compounds. Thus for their exploration not only are anhydrous reaction conditions essential but also are all reaction media of moderate donor strength to be avoided.

While catalytic zinc in biochemical systems is never bound to halides and in fact halide ions are known to be inhibitors of some zinc enzymes[2], zinc halides are typical activators for reactions of organic carbonyl compounds. Examples in which zinc chloride is employed in higher than stoichiometric amounts are sugar acetylations, the Fischer indole synthesis, Friedel−Crafts acetylations, and various condensations[3]. After studying the coordination of carbonyl compounds to halide-free zinc species[1] we therefore turned to the corresponding studies of the pure zinc halides.

This paper, like the preceding one[1], describes aldehyde complexes. We are aware of only one related publication, i.e. one containing some data on $ZnCl_2$•benzaldehyde[4]. We scanned the coordination abilities of a broad range of aldehydes towards the zinc halides $ZnCl_2$, $ZnBr_2$, and ZnI_2. Again we observed that aliphatic aldehydes undergo condensation or polymerization reactions after addition of the zinc halide. Benzaldehyde and various substituted benzaldehydes, however, were found to be suitable as ligands. A preliminary account of our findings was published in 1994[5].

[+] Part 2: Ref.[1]

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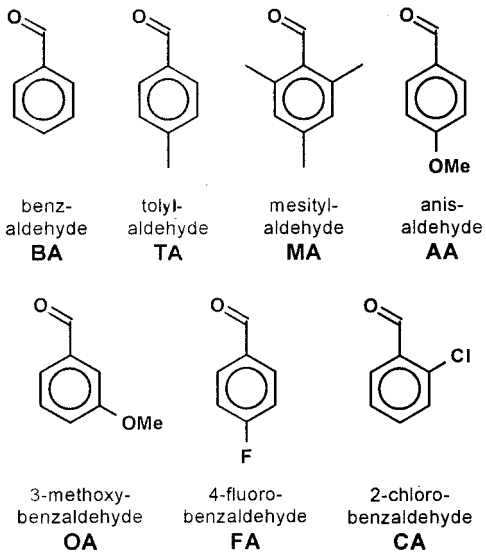
Preparations

In order to obtain the aldehyde complexes as pure, solid materials the aldehyde had to be present in a large excess and in a high concentration. In practice this meant using the aldehyde as the reaction medium which restricted the reaction to only those aldehydes that are low-melting or liquid. Pure and crystalline products were obtained with the following aldehydes:



The water-free zinc halides $ZnCl_2$, $ZnBr_2$, and ZnI_2 were prepared in diethyl ether from zinc and HCl, Br_2, and HI prior to use. They were dissolved in the aldehydes. After complete dissolution an equal volume of dichloromethane was added. The products precipitated on addition of petroleum ether. Crystalline complexes were obtained in lower yields after careful layering with petroleum ether. The resulting zinc complexes belong to one of the three classes **A**, **B**, and **C**.

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$[ZnHal_2(aldehyde)_2]$ $[-Hal-ZnHal(aldehyde)-]_\infty$
A **B**
$[Zn(aldehyde)_6][Zn_2Hal_6]$
C

Class **A** type complexes, i.e. monomolecular tetrahedral $ZnHal_2(aldehyde)_2$ species, were obtained from the five aldehydes BA, TA, MA, AA, and OA. Compounds **1b** to **5c** respesent the total of 12 complexes that were isolated analytically pure. They are all extremely hygroscopic, and they should be stored at low temperatures as some of them decompose within a few days at room temperature. Eight of the complexes were subjected to crystal structure determinations; the high structural similarity between them is discussed below.

$[ZnHal_2(aldehyde)_2]$

	1b	**1c**	**2b**	**2c**	**3a**	**3b**	**3c**	**4a**	**4b**	**4c**	**5b**	**5c**
Hal	Br	I	Br	I	Cl	Br	I	Cl	Br	I	Br	I
aldehyde	BA	BA	TA	TA	MA	MA	MA	AA	AA	AA	OA	OA

The alternative class **B** type complexes, i.e. mono-aldehyde−$ZnHal_2$ species, were obtained for almost all cases in which class **A** type complexes did not result. Compounds **6a**−**9c** were isolated. Structure determinations of three of them showed them to be halide-bridged polymers in the solid state (see below). These compounds do not differ in their behaviour (solubility, hygroscopicity, thermal stability) from the monomolecular complexes, which indicates inter alia that they are molecular bis-aldehyde complexes in aldehyde solution. So far we have found no indication for the alternative constitution of the mono-aldehyde complexes as halide-bridged dimeric units.

$[ZnHal_2(aldehyde)]_\infty$

	6a	**7a**	**8a**	**9a**	**9b**	**9c**
Hal	Cl	Cl	Cl	Cl	Br	I
aldehyde	BA	MA	FA	CA	CA	CA

Quite unexpectedly, two compounds of composition $ZnHal_2 \cdot 2$ aldehyde (**10b**, **c**) were found to belong to class **C** rather than class **A**. This was proved for **10b** by structure determination and assumed for **10c** by analogy of composition and spectra. **10b** and **c** share the property of all zinc halide complexes reported here, namely, they contain only covalently bound halide. There is no obvious reason, however, why in this case dismutation into a fully aldehyde-coordinated cation and a fully halide-coordinated anion has occurred. Just like in the cases of benzaldehyde and tolylaldehyde, also in the case of fluorobenzaldehyde reaction with $ZnCl_2$ yields a 1:1 complex (**8a**) whereas reaction with $ZnBr_2$ and ZnI_2 yield 2:1 (aldehyde/zinc) complexes (**10b**, **c**).

$[Zn(FA)_6]\ [Zn_2Hal_6]$
10b: Hal = Br; **10c**: Hal = I

Structures

Eight complexes of class **A** were subjected to structure determinations. Their molecular shapes are remarkably uniform, including the fact that with the exception of **3a** they all have a crystallographic twofold axis. Figure 1 and Table 1 summarize the bonding features. All complexes are distorted tetrahedral with the O−Zn−O angle typically small (94−106°), the Hal−Zn−Hal angle typically large (122−131°), and the O−Zn−Hal angles close to the tetrahedral value (105−111°). The aldehydes are attached to zinc in a strictly anti fashion (dihedral angle Zn−O−C−C average 178°), and the aromatic rings and the CHO groups are coplanar (dihedral angle O−C−C−C average 175°).

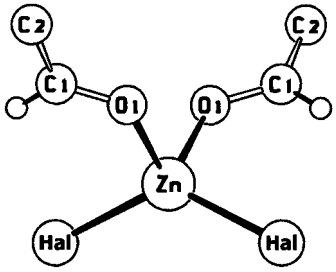

Figure 1. Zinc coordination of class **A** complexes

The zinc halide bond distances are typical and uniform for Zn−Cl, Zn−Br, and Zn−I, cf. Table 1. The Zn−O bond lengths vary only 0.03 Å about their average value of 2.035 Å. Compared to the average value of 2.09 Å for octahedral zinc-aldehyde complexes they are typically shorter. There is only one reference value in the literature for Zn−O(aldehyde) in tetrahedral complexes: in Bochmann's $[Zn(SeR)_2(AA)]_2$ it measures 2.06 Å[6]. The spread of the aldehyde C=O bond lengths is negligible. Relative to the standard value for aromatic aldehydes of 1.22 Å[7] they are only very slightly elongated due to the coordination to the metal.

Three structures of class **B** type complexes were determined. They were found to belong to two different structural types. Compound **6a** has a screw type arrangement of the polymeric backbone made up of Zn and Cl (Figure 2). Compounds **7a** and **9b** crystallize with a linear zig-zag array of zinc and halide (Figure 3). Table 2 compares the structural details of the three complexes.

Like the complexes of class **A**, those of class **B** are distorted tetrahedral, yet with a different kind of distortion. Their O−Zn−Hal angles are near the tetrahedral value, their Hal1−Zn−Hal2 angles are near 118−120°, and the Hal2−Zn−Hal2′ angles (i.e. those involving both bridging halides) are near 102°. The anti orientation of the zinc-bound aldehydes (dihedral angles 171−179°) and the coplanarity of the arene and CHO groups (dihedral angles 171−176°) are as before. In Table 2 comparison of **6a** and **7a** shows that the backbone structure of the polymers (screw-like or zigzag) is not reflected in the basic bond lengths and angles. The Zn−Hal distances have typical values for the terminal halides, cf. Table 1, but are characteristically elongated for the bridging halides. The Zn−O(al-

Table 1. Structural data [Å, °] of complexes $ZnHal_2$•2 aldehyde

	Hal	Zn−Hal	Zn−O1	O1−C1	Zn−O1−C1	O1−C1−C2
1b	Br	2.334(2)	2.043(3)	1.235(5)	125.5(3)	118.5(3)
1c	I	2.529(1)	2.046(3)	1.229(5)	126.3(3)	123.2(4)
2c	I	2.532(1)	2.046(5)	1.226(7)	127.7(4)	123.3(6)
3a[a]	Cl	2.202(7)	2.046(2)	1.222(8)	123.7(5)	124.9(6)
4a	Cl	2.199(2)	2.016(4)	1.235(7)	127.1(4)	122.0(5)
4b	Br	2.327(1)	2.014(3)	1.228(4)	126.3(3)	124.0(3)
4c	I	2.525(1)	2.024(2)	1.230(3)	126.2(2)	124.0(3)
5c	I	2.524(1)	2.041(2)	1.226(3)	124.8(2)	123.5(2)

[a] Average of two values each.

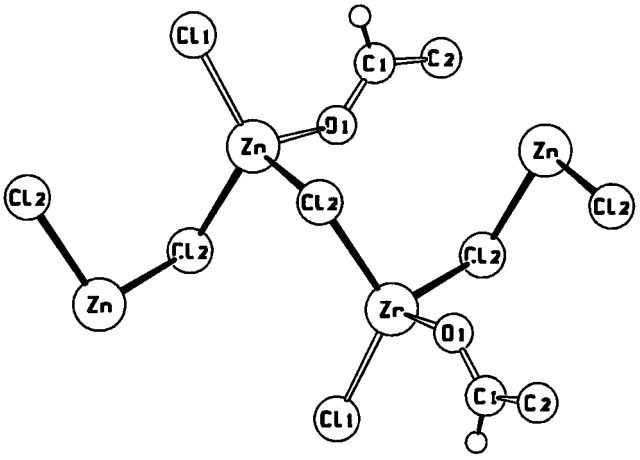

Figure 2. Polymer backbone and zinc coordination of complex **6a**

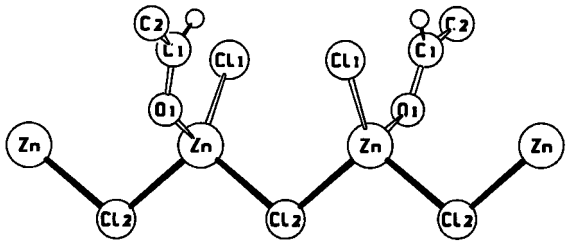

Figure 3. Polymer backbone and zinc coordination of complexes **7a** and **9b**

dehyde) bonds are still a bit shorter than those for class **A**. This must be related to the fact that only one aldehyde ligand per zinc ion is present and that the donor capacity of two of the three halide ligands is reduced because of their bridging nature.

The unexpected class **C** constitution of complexes **10b** and **c** became obvious only after the structure determination of **10b**, cf. Figure 4. The hexaaldehyde−zinc cation of **10b** corresponds to the ones structurally characterized by us for 4-fluorobenzaldehyde and 2-chlorobenzaldehyde with $SbCl_6^-$ counterions[1]. Its structural features, typically its Zn−O bond length of 2.08 Å (av.), are as observed before[1]. The $Zn_2Br_6^{2-}$ anion of **10b** belongs to the well-established class of $Zn_2Hal_6^{2-}$ complexes. While quite a number of these with Hal = Cl have been structurally characterized[8], there is just one structure each for X = Br[9] and X = I[10] in the literature. The structural details of the $Zn_2Br_6^{2-}$ ion in **10b** compare well with the reported ones. Typically both the terminal and bridging Zn−Br bonds are longer than in the neutral complexes like **9b**, and the Zn_2Br_2 rectangle is characterized by rather acute angles both at zinc and bromine.

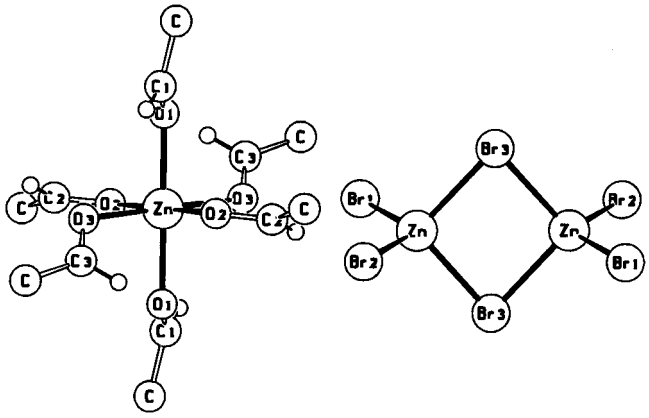

Figure 4. Coordination of zinc in the cation and anion of complex **10b**
Bond lengths [Å] and angles [°] for the cation: Zn−O1 2.073(4), Zn−O2 2.081(4), Zn−O3 2.080(4), O1−C1 1.224(8), O2−C2 1.222(7), O3−C3 1.229(7), Zn−O1−C1 124.1(4), Zn−O2−C2 129.5(4), Zn−O3−C3 119.4(4), O1−C1−C 123.6(6), O2−C2−C 124.0(6), O3−C3−C 125.3(6); for the anion: Zn−Br1 2.335(1), Zn−Br2 2.336(1), Zn−Br3 2.474(1), Zn−Br3′ 2.497(1), Br3−Zn−Br3′ 97.33(4), Zn−Br3−Zn′ 82.67(4).

Table 2. Structural data [Å, °] for complexes $[ZnHal_2$•aldehyde$]_\infty$

	Hal	Zn−Hal1	Zn−Hal2	Zn′−Hal2	Zn−O1	O1−C1	Zn−O1−C1	O1−C1−C2	Zn−Hal−Zn
6a	Cl	2.172(2)	2.293(2)	2.300(2)	2.009(5)	1.225(8)	127.8(5)	122.8(6)	107.92(7)
7a	Cl	2.177(1)	2.304(2)	2.275(2)	2.015(2)	1.230(4)	122.0(2)	122.7(3)	102.77(3)
9b	Br	2.305(2)	2.409(2)	2.408(2)	2.021(6)	1.223(9)	125.8(6)	120.5(8)	99.51(5)

Spectra

The characteristic IR bands of the complexes, i.e. the aldehyde ν(CO) bands, are listed in Table 3. A significant shift to lower wavenumbers occurs upon coordination to zinc. There is no correlation between this shift and the bonding type (i.e. classes **A**, **B**, and **C**). Instead it seems to be correlated with the electron density of the aldehydes: for electron-rich aldehydes (BA, AA), the shift is small, and for electron-poor aldehydes (FA, CA) it is large. The same observations were made for zinc-aldehyde complexes with weakly coordinating anions[1].

Table 3. ν(CO) IR bands (KBr, cm^{-1}) and their relative shifts

	ν(CO)	Δν		ν(CO)	Δν
1b	1651	−50	**5b**	1645	−57
1c	1638	−63	**5c**	1645	−57
2b	1646	−58	**6a**	1638	−63
2c	1643	−61	**7a**	1645	−59
3a	1637	−53	**8a**	1638	−62
3b	1632	−58	**9a**	1628	−70
3c	1629	−61	**9b**	1627	−71
4a	1638	−52	**9c**	1624	−74
4b	1640	−50	**10b**	1635	−65
4c	1638	−52	**10c**	1636	−64

The characteristic ^{1}H- and ^{13}C-NMR resonances result from the aldehyde CHO functions. In the complexes these resonances are shifted by small, yet significant, amounts. The ^{1}H signals are moved upfield and downfield in an irregular fashion, the ^{13}C signals are all shifted downfield, as expected due to deshielding resulting from coordination. While for the zinc−aldehyde complexes with noncoordinating anions[1] the ^{1}H-NMR shifts were so small that the possibility of aldehyde substitution by [D_6]acetone upon dissolution could not be ruled out, this is not the case here. Obviously the molecular nature and the lower coordination number of the zinc-halide complexes reported here result in a tighter binding between the cation and the aldehyde ligands.

Table 4. ^{1}H- and ^{13}C-NMR data for the aldehyde CHO functions (in [D_6]acetone, δ)

	δ(H)	Δδ	δ(C)	Δδ
1b	9.96	−0.10	192.8	+0.1
1c	9.96	−0.10	192.6	−0.1
2b	9.94	−0.04	192.3	+0.2
2c	9.95	−0.03	192.3	+0.2
3a	10.45	−0.03	193.8	+1.2
3b	10.49	+0.01	193.5	+0.9
3c	10.49	+0.01	193.6	+1.0
4a	9.83	−0.06	191.7	+0.7
4b	9.79	−0.10	192.3	+1.3
4c	9.83	−0.06	191.9	+0.9
5b	9.97	+0.01	192.6	+0.2
5c	9.99	+0.03	192.6	+0.2
6a	9.90	−0.16	193.0	+0.3
7a	9.94	−0.04	192.5	+0.4
8a	10.00	+0.05	191.5	+0.5
9a	10.37	+0.01	189.7	+0.3
9b	10.31	−0.05	189.4	±0
9c	10.23	−0.13	188.9	−0.5
10b	9.94	−0.01	191.2	+0.4
10c	9.96	+0.01	191.1	+0.3

Discussion

The strict maintenance of anhydrous conditions has made it possible to isolate zinc halide complexes of seven different aromatic aldehydes. In all compounds obtained the halides are attached covalently to zinc. Two compositions have been observed, represented by the formulae $ZnHal_2$•aldehyde and $ZnHal_2$•2 aldehyde. They appear in three structural types, monomolecular $ZnHal_2$•2 aldehyde (**A**), polymeric and halide-bridged $ZnHal_2$•aldehyde (**B**), and ionic $[Zn(aldehyde)_6][Zn_2Hal_6]$ (**C**). Notably the dimeric halide-bridged structural type $[ZnHal_2$•aldehyde$]_2$ is missing.

The NMR spectra prove the compositions of the products, and the solid-state IR data prove the aldehyde coordination by large Δν values for the aldehyde CO bands. They give no indication of the complex structures which could only be obtained by crystal structure determinations. Typically complex **10b** of type **C** does not differ spectroscopically from other $ZnBr_2$ complexes like **3b** or **5b**. Altogether the uniformity within groups of spectra or structures does not allow conclusions on structure and bonding to be drawn.

There seems to be a relation between the composition of the complexes and the electron-donor properties of the ligands. Both electron-rich aldehydes (MA, AA) and low-electronegativity halides (Br, I) favour the $ZnHal_2$•2 aldehyde composition. Conversely zinc chloride yields only polymeric 1:1 complexes with the "normal" aldehydes BA and TA, and the most electron-poor aldehyde CA appears only in the polymeric 1:1 complexes. The formation of the 1:1 complexes even in the neat aldehydes is a demonstration of the low donor strength of the aldehydes, which cannot compete with bridging halide for the coordination to zinc. The formation of complexes **10** is an unusual result of this competition in that both aldehyde and halide get their own zinc ions.

With the exception of the cation of **10** all complexes described here are tetrahedral. This can be related to the soft character of the halide ligands, while the homoleptic aldehyde complexes in **10** and the other complexes with hard coligands (water, alcohol, oxoanion) are octahedral[1]. The tetrahedral complexes are of relevance for zinc-catalyzed reactions of organic carbonyl compounds, as in organic synthesis the catalyst is most often $ZnCl_2$[3] and in the enzyme alcohol dehydrogenase the catalytic zinc has a tetrahedral $ZnNS_2O$ environment[2].

The challenge to improve this relevance faces two problems. One of them is the mostly unpredictable composition and structure of the zinc halide/aldehyde complexes. This means that reaction intermediates and catalytic pathways of zinc halide catalyzed carbonyl reactions are equally unpredictable as yet. The other is the weak attachment of the

Table 5. Reaction details

Compl.		$ZnHal_2$			aldehyde			yield	m.p.
		g	mmol		mL	g	mmol	g	%	°C
1b	$ZnBr_2$	1.11	4.93	BA	5	5.22	49.19	2.01	93	115
1c	ZnI_2	1.01	3.16	BA	5	5.22	49.19	1.57	93	94
2b	$ZnBr_2$	1.69	7.50	TA	10	10.19	84.81	3.28	94	124
2c	ZnI_2	1.02	3.20	TA	5	5.10	42.41	1.72	96	122
3a	$ZnCl_2$	0.48	3.52	MA	10	10.05	67.81	1.13	74	120
3b	$ZnBr_2$	1.57	6.97	MA	10	10.05	67.81	3.40	94	92
3c	ZnI_2	0.74	2.32	MA	5	5.03	33.91	1.28	90	136
4a	$ZnCl_2$	0.72	5.28	AA	10	11.19	82.19	2.08	96	91
4b	$ZnBr_2$	1.13	5.02	AA	6	6.71	49.31	2.23	89	117
4c	ZnI_2	0.92	2.88	AA	5	5.60	41.09	1.66	97	116
5b	$ZnBr_2$	1.11	4.93	OA	8	8.95	65.75	1.67	68	92
5c	ZnI_2	0.79	2.48	OA	5	5.60	41.09	1.24	85	86
6a	$ZnCl_2$	0.71	5.21	BA	10.5	10.96	103.30	0.96	76	117
7a	$ZnCl_2$	0.46	3.38	TA	5	5.10	42.41	0.76	88	116
8a	$ZnCl_2$	0.44	3.23	FA	5	5.79	46.61	0.81	96	125
9a	$ZnCl_2$	0.77	5.65	CA	5	6.24	44.39	1.16	74	132
9b	$ZnBr_2$	1.51	6.71	CA	7.5	9.36	66.59	2.10	86	153
9c	ZnI_2	0.93	2.91	CA	5	6.24	44.39	1.21	90	132
10b	$ZnBr_2$	1.41	6.26	FA	7.5	8.68	69.91	2.86	97	65
10c	ZnI_2	1.06	3.32	FA	5	5.79	46.61	1.70	90	71

aldehydes, which should render $ZnNX_2O$ complexes (i.e. structural models of alcohol dehydrogenase) unstable when N represents a good nitrogen donor. We have been working to overcome the latter problem, and the succeeding paper presents one possible solution[11].

Experimental Section

All preparations required strictly anhydrous conditions. The general working and measuring conditions were as in ref.[12], and the specific ones as in ref.[1]. The aldehydes were obtained commercially and distilled prior to use. The anhydrous zinc halides were prepared from zinc and HHal or Hal_2 in diethyl ether[13][14]. The new complexes were prepared following the general procedure below, details for which are given in Table 5. When they were too hygroscopic for ordinary C/H/N analysis, they were also characterized by zinc and halide analyses. Table 6 gives the analytical characterizations.

Preparation of the Complexes: The zinc halide was dissolved in a 10−20 fold excess of the aldehyde with stirring and heating. After cooling to room temp. 10 mL of dichloromethane was added. By adding 50 mL of petroleum ether (b.p. 60−70°C) a colourless precipitate was obtained, which was filtered off, washed with the petroleum ether, and dried in vacuo.

Structure Determinations[15]: Crystals were obtained by careful layering of the reaction solutions with petroleum ether (b.p. 70−90°C). They 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 with direct methods and refined anisotropically with the SHELX program suite[16]. The aldehyde C-H hydrogen atoms were located and refined freely. All other hydrogen atoms were in-

Table 6. Analytical characterization

	formula mol. wt.	Analyses calcd./found C	H	Zn	Hal
1b	$C_{14}H_{12}Br_2O_2Zn$	−	−	14.95/	36.53/
	437.5	−	−	14.82	36.61
1c	$C_{14}H_{12}I_2O_2Zn$	−	−	12.30/	47.76/
	531.5	−	−	12.27	47.85
2b	$C_{16}H_{16}Br_2O_2Zn$	41.28/	3.47/	14.05/	34.33/
	465.5	42.00	3.11	14.01	34.21
2c	$C_{16}H_{16}I_2O_2Zn$	34.35/	2.88/	11.69/	45.36/
	559.5	33.52	2.77	11.75	45.20
3a	$C_{20}H_{24}Cl_2O_2Zn$	−	−	15.11/	16.39/
	432.7	−	−	15.17	16.44
3b	$C_{20}H_{24}Br_2O_2Zn$	46.05/	4.64/	12.54/	30.64/
	521.6	45.90	4.56	12.60	30.52
3c	$C_{20}H_{24}I_2O_2Zn$	39.02/	3.93/	10.62/	41.23/
	615.6	38.30	3.83	10.67	41.33
4a	$C_{16}H_{16}Cl_2O_4Zn$	47.03/	3.95/	16.00/	17.35/
	408.6	46.86	3.91	15.81	17.45
4b	$C_{16}H_{16}Br_2O_4Zn$	38.63/	3.24/	13.14/	32.12/
	497.5	37.89	3.17	13.21	32.00
4c	$C_{16}H_{16}I_2O_4Zn$	32.49/	2.73/	11.06/	42.91/
	591.5	32.20	2.62	11.14	42.88
5b	$C_{16}H_{16}Br_2O_4Zn$	38.63/	3.24/	13.14/	32.12/
	497.5	36.76	3.17	13.23	31.98
5c	$C_{16}H_{16}I_2O_4Zn$	32.49/	2.73/	11.06/	42.91/
	591.5	33.14	2.67	11.18	43.03
6a	$C_7H_6Cl_2OZn$	34.68/	2.50/	26.97/	29.25/
	652.8	34.88	2.55	27.02	29.05
7a	$C_8H_8Cl_2OZn$	37.47/	3.14/	25.50/	27.65/
	256.5	37.74	3.29	25.38	27.51
8a	$C_7H_5Cl_2FOZn$	−	−	25.11/	27.23/
	260.4	−	−	25.22	27.10
9a	$C_7H_5Cl_3OZn$	30.37/	1.82/	23.62/	38.42/
	276.9	29.89	2.24	23.84	38.30
9b	$C_7H_5Br_2ClOZn$	22.99/	1.38/	17.88/	−
	365.8	22.03	1.49	17.76	−
9c	$C_7H_5ClI_2OZn$	18.29/	1.10/	14.22/	−
	459.8	16.04	1.17	14.34	−
10b	$C_{42}H_{30}Br_6F_6O_6Zn_3$	35.52/	2.13/	13.81/	33.76/
	1420.3	35.03	2.09	13.91	33.83
10c	$C_{42}H_{30}F_6I_6O_6Zn_3$	29.63/	1.78/	11.52/	44.73/
	1702.3	29.59	2.10	11.61	44.64

Table 7, part 1. Crystallographic details

	1b	**1c**	**2c**	**3a**	**4a**	**4b**
formula	$C_{14}H_{12}Br_2O_2Zn$	$C_{14}H_{12}I_2O_2Zn$	$C_{16}H_{16}I_2O_2Zn$	$C_{20}H_{24}Cl_2O_2Zn$	$C_{16}H_{16}Cl_2O_4Zn$	$C_{16}H_{16}Br_2O_4Zn$
mol. mass	437.43	531.41	559.46	432.66	408.56	497.48
crystal size [mm]	0.6 × 0.2 × 0.1	1.0 × 0.6 × 0.5	0.4 × 0.05 × 0.03	0.8 × 0.1 × 0.1	0.5 × 0.5 × 0.5	1.2 × 0.5 × 0.3
space group	*C*2/*c*	*C*2/*c*	*Fdd*2	*Pca*2$_1$	*P*2$_1$2$_1$2	*C*2/*c*
Z	4	4	8	4	2	4
a [Å]	18.816(2)	19.407(2)	19.883(2)	24.848(2)	8.964(4)	20.361(3)
b [Å]	4.832(1)	5.0240(4)	35.747(5)	4.712(2)	19.918(1)	5.634(2)
c [A]	17.030(3)	16.878(1)	5.0360(5)	17.279(2)	4.776(3)	16.859(4)
α [°]	90	90	90	90	90	90
β [°]	104.51(11)	105.20(1)	90	90	90	110.79(2)
γ [°]	90	90	90	90	90	90
V [A^3]	1499.0(5)	1588.0(2)	3579.4(7)	2023.1(1)	852.7(8)	1808.0(7)
d(calc.) [g·cm^{-3}]	1.94	2.22	2.08	1.42	1.59	1.83
d(obs.) [g·cm^{-3}]	–	–	–	–	1.53	1.81
temp. [K]	183(2)	183(2)	183(2)	183(2)	183(2)	183(2)
μ(Mo*K*a) [mm^{-1}]	6.96	5.43	4.82	1.49	1.77	5.79
hkl range	*h*: 0 to 23 *k*: −6 to 0 *l*: −21 to 20	*h*: 0 to 26 *k*: 0 to 7 *l*: −23 to 22	*h*: −24 to 0 *k*: −44 to 0 *l*: 0 to 6	*h*: 0 to 30 *k*: −5 to 0 *l*: 0 to 21	*h*: −11 to 0 *k*: −1 to 25 *l*: −6 to 6	*h*: −23 to 25 *k*: 0 to 7 *l*: −20 to 0
refl. measd.	1550	2359	983	2051	2007	1889
indep. refl.	1504	2298	983	2049	1846	1821
obs. refl. [$I>2\sigma(I)$]	1261	2190	905	1633	1688	1575
parameters	87	88	97	226	105	105
refl. refined	1504	2298	983	2048	1846	1821
R_1 (obs. refl.)	0.031	0.032	0.021	0.036	0.053	0.036
wR_2 (all refl.)	0.083	0.099	0.053	0.104	0.163	0.098
residual el. density [e/A^{-3}]	+0.7 −0.8	+1.6 −1.1	+0.6 −0.5	+1.0 −0.5	+1.1 −0.7	+1.1 −0.8

Table 7, part 2. Crystallographic details

	4c	**5c**	**6a**	**7a**	**9b**	**10b**
formula	$C_{16}H_{16}I_2O_4Zn$	$C_{16}H_{16}I_2O_4Zn$	$C_7H_6Cl_2OZn$	$C_8H_8Cl_2OZn$	$C_7H_5Br_2ClOZn$	$C_{42}H_{30}Br_6F_6O_6Zn_3 \cdot 2\ C_7H_5FO$
mol. mass	591.46	591.46	242.39	256.41	365.75	1668.45
crystal size [mm]	0.6 × 0.4 × 0.2	0.6 × 0.2 × 0.1	0.7 × 0.03 × 0.03	0.7 × 0.3 × 0.3	0.4 × 0.2 × 0.1	0.9 × 0.8 × 0.3
space group	*C*2/*c*	*C*2/*c*	P2$_1$/*n*	*Pca*2$_1$	*Pbca*	*Pbca*
Z	4	4	4	4	8	4
a [Å]	21.303(5)	22.975(1)	12.060(3)	22.047(2)	7.352(1)	18.490(4)
b [Å]	5.673(1)	5.345(3)	4.914(1)	6.256(1)	14.026(5)	15.788(7)
c [Å]	17.182(5)	19.026(6)	14.560(5)	7.155(1)	20.262(7)	20.707(5)
α [°]	90	90	90	90	90	90
β [°]	111.25(2)	126.54(3)	94.96(3)	90	90	90
γ [°]	90	90	90	90	90	90
V [A^3]	1935.4(8)	1877.2(2)	859.6(4)	986.9(2)	2089.4(11)	6045(3)
d(calc.) [g·cm^{-3}]	2.03	2.09	1.87	1.73	2.33	1.83
d(obs.) [g·cm^{-3}]	1.98	–	–	–	2.29	1.82
temp. [K]	183(2)	183(2)	183(2)	183(2)	183(2)	183(2)
μ(Mo*K*a) [mm^{-1}]	4.47	4.61	3.41	2.98	10.21	5.22
hkl range	*h*: −28 to 0 *k*: 0 to 7 *l*: −21 to 22	*h*: −28 to 22 *k*: 0 to 6 *l*: 0 to 23	*h*: −14 to 14 *k*: −5 to 0 *l*: −17 to 0	*h*: −27 to 0 *k*: −7 to 0 *l*: −8 to 0	*h*: −9 to 9 *k*: −17 to 0 *l*: −24 to 24	*h*: −22 to 9 *k*: −7 to 19 *l*: 0 to 25
refl. measd.	2396	1911	1678	1051	7706	5914
indep. refl.	2336	1849	1615	1051	2045	5905
obs. refl. [$I>2\sigma(I)$]	2231	1751	1096	993	1093	3991
parameters	105	105	100	109	109	367
refl. refined	2336	1849	1615	1051	2045	5905
R_1 (obs. refl.)	0.023	0.019	0.049	0.023	0.050	0.044
wR_2 (all refl.)	0.071	0.054	0.151	0.075	0.145	0.130
residual el. density [e/A^{-3}]	+0.5 −1.1	+0.8 −0.6	+1.1 −1.0	+0.4 −0.5	+1.3 −1.6	+0.7 −1.2

cluded 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 w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL[17]. Table 7 lists the crystallographic data.

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