Hexakis(alcohol)zinc Complexes

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Dedicated to Professor Lawrence F. Dahl on the occasion of his 70th birthday

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Hexakis(methanol) and hexakis(ethanol) complexes of zinc were prepared under strictly anhydrous conditions and crystallized as perchlorate or hexafluorosilicate salts in space groups of high symmetry. All their OH functions are engaged in hydrogen-bonded cation–anion networks. Their Zn–O distances correspond to those in $[Zn(H_2O)_6]^{2+}$. Their water sensitivity can be explained by a gain in entropy and by a gain in polar interactions upon replacement of alcohol by water ligands.

Hexaaqua transition-metal cations are commonplace and serve as reference points for the discussion of structures, spectra or ligand-field effects as well as being the natural starting materials in preparative coordination chemistry. In contrast, their simplest organic analogues, the hexakis(alcohol) complexes, are so uncommon that they are normally not mentioned in textbooks or even in comprehensive handbooks.[1] The reason for this is their extremely labile nature which does not allow them to be exposed to even traces of the "better" ligand water.

When it comes to synthetic usefulness this lability becomes favourable. Accordingly, hexakis(methanol) or hexakis(ethanol) complexes have been proposed as starting materials for other complexes with weakly coordinating ligands, and for this purpose a number of them have been prepared as salts of the divalent transition metals.[2][3] They were fully characterized by analyses and spectra. From their UV/Vis spectra it could be concluded that the simple alcohols have about the same position in the spectrochemical series as water. So far, only one hexakis(methanol)vanadium(II) complex[4] and two hexakis(ethanol)cobalt(II) complexes[5] have been subjected to crystal structure determinations.

Our interest in these complexes arose from our attempts at modelling the zinc enzyme alcohol dehydrogenase.[6] These studies required the investigation of zinc−alcohol, zinc−alkoxide, and zinc−aldehyde complexes. It turned out that some of the latter are accessible starting from hexakis(ethanol)zinc salts.[7] This fact, together with the limited knowledge about hexakis(alcohol)zinc complexes,[2][3] prompted us to re-investigate their chemistry and to gather information on their structures.

Preparation and Identification

The extreme sensitivity of the isolated complexes toward water required them to be handled with more than the usual precautions. In contrast, at the beginning of the preparations moisture posed no problems as the zinc reagents were the hexahydrates of the zinc salts. Their dehydration was performed with trimethyl or triethyl orthoformate in the corresponding alcohol, which produces the alcohol itself as the hydrolysis product. This procedure, which was applied by van Leeuwen for compounds **1** and **2**,[2][3] was found to be useful for all three types of hexakis(alcohol)zinc salts prepared here. Thus, from solutions of the hexahydrates of zinc perchlorate, tetrafluoroborate, and hexafluorosilicate in methanol or ethanol, after treatment with a large excess of the corresponding trialkyl orthoformate (10−20 fold), the known perchlorate **1b**, the known tetrafluoroborates **2a**, **b**, and the new hexafluorosilicates **3a**, **b** were obtained {$[(ROH)_6Zn](ClO_4)_2$: **1a**: R = Me; **1b**: R = Et; $[(ROH)_6Zn](BF_4)_2$: **2a**: R = Me; **2b**: R = Et; $[(ROH)_6Zn](SiF_6)$: **3a**: R = Me; **3b**: R = Et}. They are colourless crystalline solids. Their hygroscopicity does not allow them to persist for more than a few seconds in the normal atmosphere.

Unambiguous characterizations of **1b**, **3a** and **3b** were achieved with the structure determinations described below. NMR spectra in deuterioacetone showed that the alcohol ligands stay attached to the zinc ion in this solvent, see Table 1. The observed chemical shifts referred to those of the free alcohols in the same solvent are small, yet significant. Typical dependencies of the chemical shifts upon the nature of the counterions point to cation−anion interactions in solution. The wide spread of the OH NMR resonances indicates the presence of hydrogen bonding. The latter can also be concluded from the IR absorptions in a KBr matrix (see Table 2), which for **1** and **2** roughly resemble those in nujol mulls.[2][3] The $\tilde{\nu}$(OH) bands around

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3500 cm^{-1} are quite broad and of relatively low energy. Other noticeable features in the IR spectra include the OH bending vibrations around 1630 cm^{-1} and the typical intense absorptions of the anions in the 1000−1100 cm^{-1} range for ClO_4^- and BF_4^- and around 750 cm^{-1} for SiF_6^{2-}.

Table 1. ^{1}H-NMR data ([D$_6$]acetone), δ [ppm]

	CH_3[a]	CH_2[a]	OH
1b[2]	1.18	3.72	5.39
2a	3.32		2.97
2b	0.97	3.48	4.72
3a	3.20		2.95
3b	0.98	3.43	3.66

[a] ^3J values for the ethyl groups 6.9−7.0 Hz.

Table 2. IR data (KBr), [cm^{-1}]

	ṽ(OH)	δ(OH)	ṽ(anion)
1b[2]	3460m	1620m	1088s
2a	3530s	1629m	1054s
2b	3510s	1636m	1031s
3a	3520s	1635m	765s
3b	3510s	1600m	738s

Solid-State Structures

Crystals of **1b**, **3a** and **3b** were found suitable for an X-ray data collection at ca. −100°C. All three compounds crystallize in rhombohedral or hexagonal space groups with the zinc ions located on threefold axes in positions with sixfold point symmetry. Thus, there is only one alcohol ligand each in the asymmetric unit, and one Zn−O bond length and two O−Zn−O angles define the coordination sphere. In the case of **3b** a disorder problem of both the coordinated and a co-crystallized ethanol molecule affects the precision of the molecular details which therefore are not discussed here. The general features of the complex cation of **3b**, however, are the same as those of **1b**.

Figures 1 and 2 are combined views of the complex cations, showing both the ball-and-stick and the space-filling displays. The symmetry of the complexes is close to ideally octahedral. The Zn−O bond lengths (average 2.08 Å) are virtually identical to those in the $Zn(H_2O)_6^{2+}$ cation (average 2.09 Å).[8] Hence, there is no lengthening due to steric crowding of the six alcohol molecules, and the lability of the zinc−alcohol complexes cannot be explained by a weakness of the Zn−O bonds.

While the ball-and-stick models in Figures 1 and 2 emphasize the symmetry of the complexes and their similarity to the aqua complexes, their peculiarities can better be visualized by space-filling models. Figure 1 shows that the methanol complex has an ellipsoid-like shape. The separation of hydrophilic and hydrophobic parts therein is noticeable from the orientations of the O−H bonds which cause the O−H hydrogen atoms to occur in two groups of three on opposite sides of the ellipsoid, cf. the top center of Figure 1. Figure 2 shows that in both ethanol complexes the C−C bonds of the ethyl groups are oriented similarly and roughly parallel to the threefold crystallographic axis, arranging the ethanol ligands in two groups of three. The van der Waals contacts of the ethanol ligands are maximized in this arrangement, forming two hydrophobic islands separated from the polar center of the complex comprised of the Zn−O and O−H bonds. The resulting and characteristic barrel shape of the ethanol complex cations is also verified for the hexakis(ethanol)cobalt(II) complex.[5] It is reminiscent of the layered arrangement of the two *cis*-1,3,5-cyclohexanetriol ligands in their ZnL_2 complex.[9]

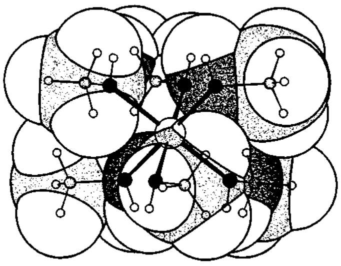

Figure 1. Cation of the methanol complex **3a**; code: Zn and H white, C light grey, O dark grey; bond lengths [Å] and angles [°]: Zn−O 2.086(1), O−C 1.430(2); O−Zn−O 180.0, 87.26(3), and 92.74(3), Zn−O−C 125.5(1)

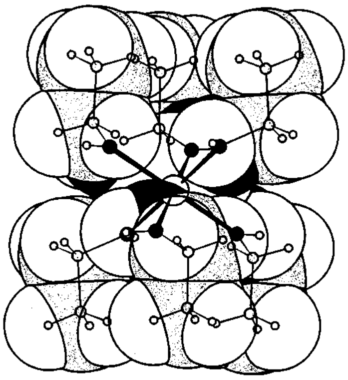

Figure 2. Cation of the ethanol complex **1b** (and similarly **3b**); code: Zn and H white, C light grey, O dark grey; bond lengths [Å] and angles [°] for **1b**: Zn−O 2.078(2), O−H 0.82(6), O−C 1.445(4), C−C 1.483(7); O−Zn−O 180.0, 86.9(1) and 93.1(1), Zn−O−C 130.2(2), O−C−C 110.9(4)

The separation of the hydrophilic and hydrophobic regions in the complexes also has the consequence that the alcoholic O−H bonds are exposed to the exterior of the cations. For instance in Figure 2 the white ball to the top right of the zinc ion represents an OH hydrogen atom. This in turn means that these quite acidic hydrogen atoms are within contact distance of the anions in the lattice, facilitating hydrogen bonding between cations and anions. It turns out that this is the case in all three compounds. Each OH group is engaged in a reasonably strong (< 2.8 Å) hydrogen bond. For **1b** this means that three oxygen atoms of each perchlorate anion are hydrogen-bonded. For **3a** and **3b** the number of fluorine atoms matches that of the OH

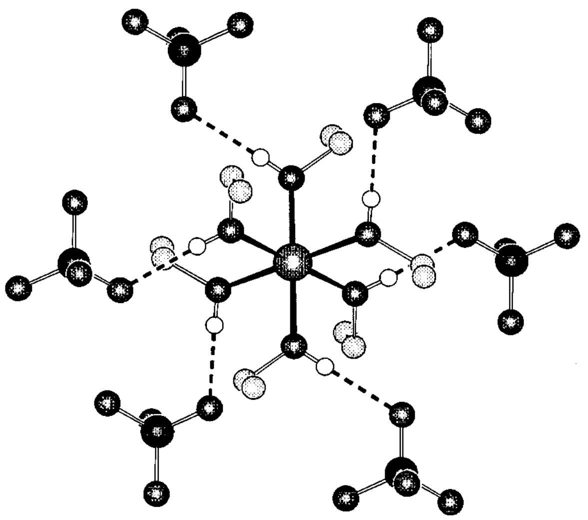

Figure 3. Hydrogen-bonded cation−anion contacts of one Zn-$(EtOH)_6$ unit in **1b** (O···O = 2.79 Å)

groups implying that there are also six hydrogen-bonding interactions per SiF_6^{2-} anion. The resulting networks are different in all three cases, see Figures 3−5. Complex **3a** displays a one-dimensional array of hydrogen-bonded cations and anions with triple junctions, complex **3b** a single-layered two-dimensional array with double junctions, and complex **1b** a double-layered two-dimensional array with single junctions.

Discussion

In an alcoholic or water-free environment the hexakis(alcohol) complexes of zinc are stable as salts with noncoordinating anions. Even traces of water, however, lead to their hydrolysis. The alcohols are weaker ligands for zinc than acetone, as can be seen from the persistence of the complexes in acetone solution. They compete with aromatic al-

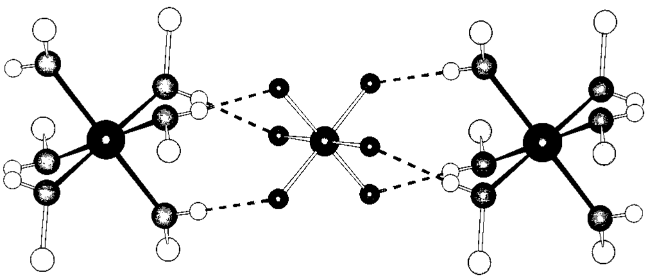

Figure 4. Hydrogen-bonded cation−anion contacts of one SiF_6 unit in **3a** (O···F = 2.66 Å)

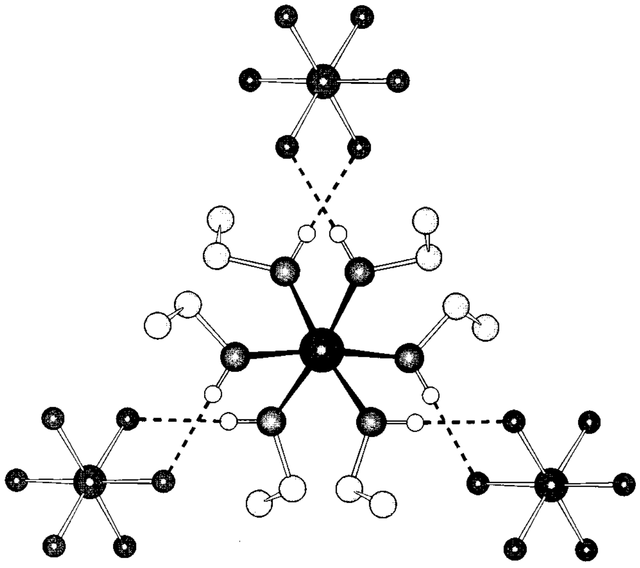

Figure 5. Hydrogen-bonded cation−anion contacts of one Zn-$(EtOH)_6$ unit in **3b** (O···F = 2.75 Å)

Table 3. Crystallographic details

	1b	**3a**	**3b**
Empirical formula	$C_{12}H_{36}Cl_2O_{14}Zn$	$C_6H_{24}F_6O_6SiZn$	$C_{12}H_{36}F_6O_6SiZn\cdot C_2H_5OH$
Molecular mass	540.7	399.7	529.9
Crystal size [mm]	0.2 × 0.2 × 0.1	1.2 × 1.0 × 0.9	0.6 × 0.4 × 0.4
Space group	$P-3$	$R-3$	$P-31c$
Z	1	3	2
a [Å]	8.720(3)	11.850(3)	8.650(1)
b [Å]	8.720(3)	11.850(3)	8.650(1)
c [Å]	9.359(1)	9.383(2)	17.450(3)
V [Å^3]	616.3(2)	1141.1(5)	1130.7(3)
$d_{calcd.}$ [g cm^{-3}]	1.46	1.75	1.56
μ(Mo-K_α) [mm^{-1}]	1.27	1.78	1.22
hkl range	h: −9 to 0	h: −10 to 15	h: 0 to 11
	k: −9 to 0	k: −17 to 6	k: −9 to 0
	l: −12 to 12	l: −13 to 12	l: −23 to 23
Measured reflections	1185	1452	2059
Independent reflections	995	878	915
Observed reflections [$I > 2\sigma(I)$]	913	871	555
Parameters	49	32	67
Refined reflections	995	878	915
R_1 (obs. refl.)	0.059	0.022	0.093
wR_2 (all refl.)	0.163	0.061	0.286
Residual electron density	+1.0	+0.3	+0.9
[e/Å^3]	−1.5	−0.6	−1.4

dehydes, as evident from the synthesis of mixed alcohol/aldehyde complexes of zinc.[7] Thus, the alcohol complexes should be valuable as starting materials for other complexes of zinc with weakly coordinating ligands.

The solid-state structures of the alcohol complexes reveal a contrast between the polar environment of the zinc ion as well as the O−H bonds and the hydrophobic nature of the alkyl groups. The former results in hydrogen-bonded cation−anion networks in which all OH functions are engaged. The latter gives rise to a typical barrel shape of the hexakis(ethanol)zinc cations.

The Zn−O bonds in the complexes are as long as the Zn−O bonds in the $Zn(H_2O)_6^{2+}$ ion which indicates that they are equally strong. Hence, the lability toward hydrolysis cannot be explained by bond-strength arguments. However, the structures of the hexakis(ethanol) complexes offer two arguments for the water sensitivity. One of them is a gain of entropy upon release of the alcohol ligands which experience a high degree of order in the complexes. The other is a gain of polar and hydrogen-bonded interactions upon replacement of alcohol by water ligands, both between cations and anions in the solid state and between complex cations or the released alcohols and the solvent molecules in aqueous solution

Experimental Section

General: General working and measuring procedures, see ref.[10]. The zinc salts were obtained commercially. The alcohols were obtained water-free and further dried with magnesium. [D_6]Acetone and petroleum ether (b.p. 50−70°C) were distilled from and kept over 4-Å molecular sieves. Nitrogen (99.999%) as inert gas was dried with BTS catalyst. Reaction vessels, gas pipes etc. were heated in vacuum before use. − Complexes **1b**, **2a**, and **2b** were prepared according to the published procedures.[2][3] The hygroscopicity of the complexes did not allow for C/H determinations.

Hexakis(methanol)zinc Hexafluorosilicate (3a): 6.00 g (19.02 mmol) of $Zn(H_2O)_6(SiF_6)$ in 25 mL of methanol was treated with 40 mL (38.8 g, 366 mmol) of trimethyl orthoformate which caused heating of the mixture and complete dissolution. After stirring for 24 h at room temp. and filtration, all volatiles were removed in vacuo. The residue was taken up in methanol and layered with petroleum ether to yield 5.80 g (76%) of **3a** which was freed from solvent by a syringe and dried in vacuo. − $C_6H_{24}F_6O_6SiZn$ (399.7): calcd. Zn 16.36; found Zn 16.23.

Hexakis(ethanol)zinc Hexafluorosilicate (3b): Like **3a** from 6.00 g (19.02 mmol) of $Zn(H_2O)_6(SiF_6)$ and 40 mL (35.6 g, 240 mmol) of triethyl orthoformate in 25 mL of ethanol with 48 h of stirring. Yield 4.20 g (46%) of **3b**. − $C_{12}H_{36}F_6O_6SiZn$ (483.9): calcd. Zn 13.51; found Zn 13.75.

Structure Determinations:[11] The crystals were obtained directly from the reaction solutions and used without drying in vacuo. They were immersed in fluorinated polyether oil and immediately placed in the nitrogen stream of the diffractometer's cooling system. Diffraction data were recorded at ca. −100°C with the $\omega/2\theta$ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, $\lambda = 0.7107$ Å) and a graphite monochromator. Empirical absorption corrections based on ψ scans were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.[12] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 times those of their attached atoms. The OH hydrogen atom of **1b** was located and refined freely. 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.[13] Table 3 lists the crystallographic data.

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[11] The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115889 (for **1b**), -115887 (for **3a**), and -115888 (for **3b**). Copies of these data are available free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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