Zirconium(IV) Complexes of Oxydiacetic Acid in Aqueous Solution and in the Solid State as Studied by Multinuclear NMR and X-ray Crystallography

Weiwen Ma, Henk van Koningsveld, Joop A. Peters,* and Thomas Maschmeyer[a]

Abstract: The structures of complexes of Zr^{IV} and oxydiacetate (ODA^{2-}) in aqueous solutions of pH 0–7 were investigated with the use of ^1H, ^{13}C, and ^{17}O NMR spectroscopy. Equilibria of mononuclear $[Zr(oda)]^{2+}$, $[Zr(oda)_2]$, and $[Zr(oda)_3]^{2-}$ complexes have been observed. In all complexes ODA^{2-} is bound in a tridentate fashion through the two carboxylate groups and the ether oxygen. No di- or oligonuclear species containing ODA^{2-} were observed. An excess of free Zr^{IV} remains in solution, probably as a result of weak electrostatic interactions between negatively charged Zr–ODA complexes or free ODA^{2-} and a positively charged cyclic tetranuclear hydroxy zirconium complex. CP-MAS ^{13}C NMR spectra of solid compounds isolated from the samples indicated that the structures of the $[Zr(oda)_2]$ and $[Zr(oda)_3]^{2-}$ complexes in solution are similar to those in the solid state. This is corroborated by the single-crystal X-ray structure of $Na_2[Zr(oda)_3]\cdot 5.5\,H_2O$, which was obtained from a solution containing exclusively the $[Zr(oda)_3]^{2-}$ complex. In this structure Zr^{IV} is nine-coordinate with the three ODA^{2-} ligands bound in a tricapped trigonal prismatic geometry. The negative charge of this $[Zr(oda)_3]^{2-}$ complex is balanced by two Na^+ ions, one of which is on a center of symmetry between Δ and Λ enantiomers of $[Zr(oda)_3]^{2-}$. This Na^+ is octahedrally coordinated to six (non Zr^{IV}-bound) carboxylate oxygen atoms of six different $[Zr(oda)_3]^{2-}$ units.

Keywords: coordination modes · NMR spectroscopy · oxydiacetic acid · structure elucidation · zirconium

Introduction

Zirconium(IV) complexes have found widespread applications in many fields of technology,[1] for example, in the sol–gel process to synthesize glasses, in ceramics and inorganic–organic materials,[2] in metal organic chemical vapor deposition (MOCVD) of ZrO_2 film as a precursor,[3] in the preparation of hydraulic liquids in oil exploration[4] as crosslinker of polysaccharides, and in coatings of paper and textile.[1] In the latter, interactions between Zr^{IV} and polysaccharides and derivatives thereof play an important role. The structures of the Zr^{IV} complexes of organic ligands in aqueous solution, however, are hardly studied. The main reason for this is the well-known tendency of Zr^{IV} complexes to hydrolyze and polymerize even at low pH,[5, 6] which often leads to gelation or precipitation. An X-ray study of $ZrOCl_2\cdot 8\,H_2O$ has shown that, already in the solid state, Zr^{IV} is hydrolyzed into a cyclic tetrameric structure with bridging μ-OH groups (**1**, see Figure 1).[7] A ^1H and ^{17}O NMR study of the aqueous solution of zirconium perchlorate has shown that this tetrameric structure is retained in aqueous solution at low pH.[8] Several solid Zr^{IV} complexes of carboxylic acids have been investigated by infrared and X-ray spectroscopy,[1, 9–14] but the solution structures of only a few complexes have been studied

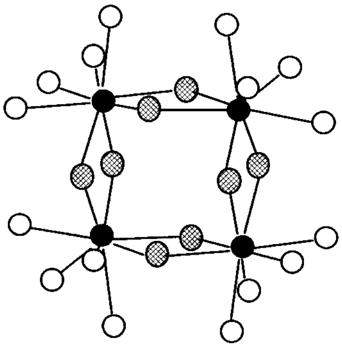

Figure 1. The structure of the $[Zr_4(OH)_8(H_2O)_{16}]$ cation as observed in crystals of $ZrOCl_2\cdot 8\,H_2O$.[7]

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Supporting information for this contribution is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author. It contains listings of atom coordinates (Table S1), bond lengths and angles for group 1 (Table S2), contact distances (Table S3), the least squares plane of the five-membered chelate ring (Table S4), and atomic displacement parameters (Table S5).

by NMR[15] as a result of the hydrolysis and polymerisation described above.

In this paper, we report a study of complexes of Zr^{IV} with oxydiacetate (ODA^{2-}) in aqueous solution and in the solid state under both acidic and neutral conditions using ^1H, ^{13}C, and ^{17}O NMR spectroscopy and X-ray crystallography. So far, two solid Zr^{IV}–ODA complexes have been structurally characterized by single-crystal X-ray diffraction: the organometallic stabilized $[cp_2Zr(oda)]$[16] and $[Zr(oda)_2(H_2O)_2]\cdot 4H_2O$ (**3**).[9] Both of them show mononuclear Zr^{IV} cations, which are coordinated with the ODA^{2-} ligand in a tridentate fashion via the two carboxylate groups and the ether oxygen atom. Solution studies of the latter complex were not performed, because the authors experienced problems with the solubility of these complexes.[9] In the present study, a comparison of the solid state ^{13}C NMR spectra of the single crystals of $[Zr(oda)_2(H_2O)_2]\cdot 4H_2O$ with solution spectra is the starting point for our analysis of Zr^{IV} complexes of ODA^{2-}, both in the solid state and in aqueous solution.

Results and Discussion

Solid state CP-MAS ^{13}C NMR spectrum of $[Zr(oda)_2(H_2O)_2]\cdot 4H_2O$: Single crystals of $[Zr(oda)_2(H_2O)_2]\cdot 4H_2O$ (**3**) were prepared by addition of H_2ODA to a solution of $ZrOCl_2\cdot 8H_2O$ in water at pH 1.0–1.5. The IR spectrum of the resulting compound was identical to that reported by Baggio et al.[9] The solid state CP-MAS ^{13}C NMR spectrum of this compound (see Figure 2) displays two resonances of equal intensity both for the carboxylate ($\delta = 178.28$ and 177.12) and the methylene carbons ($\delta = 72.30$ and 69.82). The crystal structure shows the complex to be mononuclear with Zr^{IV} coordinated by each of the two ODA^{2-} ligands in a tridentate fashion via the ether oxygen and the two carboxylate groups.[9] Two water molecules complete the inner-coordination sphere of Zr^{IV} (see Figure 3). An inspection of this structure shows that the two carboxymethyl moieties within each ODA^{2-} ligand are chemically non-equivalent, whereas the chemical environments of corresponding ^{13}C nuclei of the two ligands are rather similar. Therefore, the doubling of the carboxylate and methylene ^{13}C NMR resonances can be ascribed to the chemical non-equivalent environment within the ODA^{2-} ligands.

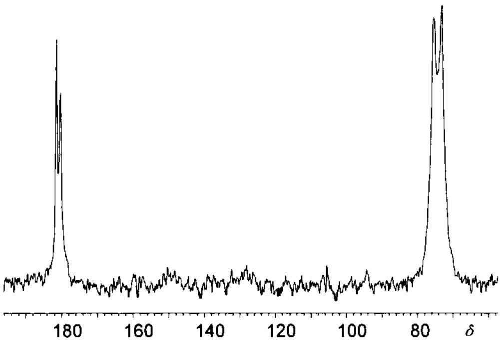


Figure 2. CP-MAS ^{13}C NMR spectrum of $[Zr(oda)_2(H_2O)_2]$.

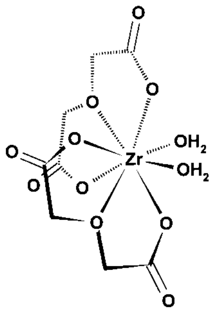


Figure 3. Solid state structure of $[Zr(oda)_2(H_2O)_2]$.[9]

For comparison ^{13}C CP-MAS NMR spectra of amorphous Na_2ODA and H_2ODA were also recorded. These spectra both showed a single set of ^{13}C signals for the ODA nuclei at chemical shifts which are 1–2 ppm lower than the averaged chemical shifts of the Zr^{IV} complex (see Table 1); this also reflects the strong electron-withdrawing character of Zr^{IV}.

Table 1. ^{13}C NMR chemical shifts of Zr–ODA complexes and some related compounds in the solid state and in solution.

Compound	COO	CH_2
solid H_2ODA	178.29	66.62
solid Na_2ODA	176.39	69.83
solid $[Zr(oda)_2(H_2O)_2]$	178.28/177.12	72.30/69.83
solid $Na_2[Zr(oda)_3]$	178.3/176.91	69.77
H_2ODA in D_2O	173.97	67.81
Na_2ODA in D_2O	178.23	69.72
$[Zr(oda)_2]$ in D_2O	176.18	71.88
$[Zr(oda)_3]$ in D_2O	177.28	70.25

NMR of aqueous solutions of H_2ODA and Zr^{IV} at pH 0.6: Upon stepwise addition of $ZrOCl_2$ to a 0.03 M solution of H_2ODA at pH 0.6 and 25 °C, first a new resonance at $\delta = 4.51$ (**3**) was observed next to the signal for free H_2ODA at $\delta = 4.25$ in the ^1H NMR spectrum. The intensity of this signal increased in intensity up to a molar ratio $[Zr^{IV}]_{tot}/[ODA]_{tot}$ (ρ) of 0.5. At $\rho \approx 0.3$, another signal appeared at $\delta = 4.45$ (**2**), which increased in intensity at the expense of the signals at both $\delta = 4.51$ and that of the free ligand. The sample remained homogeneous up to $\rho = 2.2$. The initial slope of a graph of the amounts of ODA^{2-} bound in species **3** (see Figure 4) is 2,

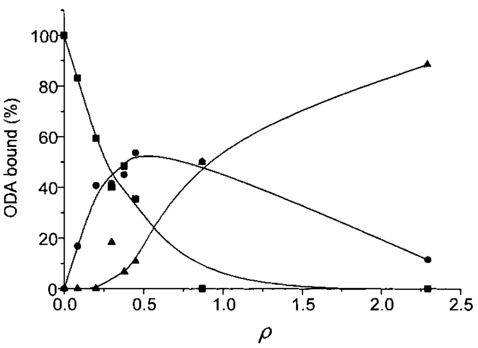


Figure 4. Distribution of species (given as mol% of ODA bound in the concerning species) as a function of ρ at pH 0.6 and 25 °C. Total concentration ODA 0.03 M. ■ free ODA; ● $[Zr(oda)_2]$; ▲ $[Zr(oda)]^{2+}$.

which shows that this complex has a 1:2 Zr^{IV}:ODA stoichiometry. This is consistent with the maximum in the curve at $\rho = 0.5$. Most likely, species **2** has a 1:1 Zr^{IV}:ODA stoichiometry. The exchange between species **2**, **3**, and free ODA^{2-}/H_2ODA is slow on the ^1H NMR time scale, although some broadening due to exchange processes was observed in the signals.

Samples prepared with higher concentrations of H_2ODA showed slow precipitation of crystalline $[Zr(oda)_2(H_2O)_2] \cdot 4H_2O$ (**3**). However, a supersaturated sample of H_2ODA and $ZrOCl_2$ with $\rho = 0.32$, $[H_2ODA] = 0.394$ M at pH 0.55 and room temperature remained homogeneous for long enough to measure both a ^1H and ^{13}C NMR spectrum. The ^1H spectrum was similar to that measured at low concentration and the ^{13}C NMR spectrum displayed resonances for the free ligand at $\delta = 67.81$ and 173.97 in addition to a new set of signals at $\delta = 71.88$ and 176.18. The large downfield shift of the latter signals with respect to the corresponding signals for free H_2ODA indicates that they can be attributed to a Zr^{IV}–ODA complex, in which both the ether oxygen and the carboxylate groups are bound to the metal ion. Therefore, it can be concluded that species **3** is the $[Zr(oda)_2(H_2O)_2]$ complex, which was already observed in the solid state, and which precipitated from the NMR samples upon standing. The presence of only a single CH_2 and a single COO ^{13}C NMR resonance for this complex in the aqueous samples shows that in solution the exchange of the two sets of chemically non-equivalent carboxymethyl nuclei is rapid on the ^{13}C NMR time scale. Most likely, this exchange takes place through decoordination–coordination of the ODA^{2-} ligand, which is consistent with the observation of a single singlet for the CH_2 protons. All CH_2 protons in the $[Zr(oda)_2(H_2O)_2]^{2+}$ complex **3** are chemically non-equivalent. The observation of a single CH_2 ^1H NMR resonance suggests that the exchange of these nuclei is rapid on the ^1H NMR time scale. The most common coordination number of this type of Zr^{IV} complexes is 8, and therefore, the most likely species **2** is $[Zr(oda)(H_2O)_5]^{2+}$.

pH dependence of the NMR spectra: The pH of a sample with $\rho = 0.2$ was increased stepwise from 0.6 to 6.2. At pH 1.76, an AB-system ($\delta = 4.315$ and 4.197, $|J| = 14.4$ Hz) (species **4**) appeared in the ^1H NMR spectrum. The value of the coupling constant is characteristic for a geminal H,H coupling. For example, a value of 14.8 Hz was measured for the coupling between corresponding protons in carboxymethyl oxysuccinate, both in the free ligand and in Ln^{III} complexes.[17] The amount of ODA^{2-} bound in this complex increased until a maximum of about 60 mol% at pH 4 and then decreased under the formation of free ligand upon further increase of the pH. Finally, precipitation occurred at a pH of about 6.2. A similar experiment with a sample with $\rho = 0.87$ resulted in precipitation already at a pH of about 2.

A ^1H NMR 2D exchange spectrum (EXSY)[18] of a sample of Zr^{IV} and ODA in a molar ratio of 0.25 (total ODA concentration 0.03 M, pH 2.3, 25 °C) showed cross peaks between the methylene resonances for $[Zr(oda)_2]$ (**3**), **4**, and free ODA^{2-} (see Figure 5), indicating that exchange processes between all these species are taking place.

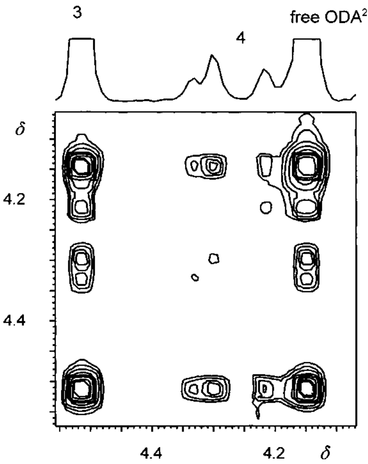


Figure 5. Two-dimensional exchange spectrum of a 0.03 M solution of Na_2ODA upon addition of Zr^{IV}, $\rho = 0.25$, pH 2.3, $T = 25$ °C. In the horizontal projection at the top, the peaks for species A and C are truncated.

The ^{13}C NMR spectrum showed signals for **4** at $\delta = 70.25$ and 177.28. The ^1H and ^{13}C NMR chemical shifts of Zr^{IV} complexes **3** and **4** are independent of the pH, which indicates that the carboxylate groups are deprotonated over the pH range where they are observable. By contrast, the ^1H and ^{13}C NMR titration curves of the free ligand show a jump in chemical shifts between pH 2 and 4.5, which is in agreement with the reported pK_as of this compound (pK_{a1} 3.93, pK_{a2} 2.79).[19]

A possible reaction of $[Zr(oda)_2(H_2O)_2]$ (**3**) upon increase of the pH would be ionization of the bound water molecules followed by self-association to a dimeric complex with μ-OH bridges. A similar dimerization reaction is suggested to be the first step in the hydrolysis of $[Zr(H_2O)_8]^{4+}$ as many di- and oligomeric crystal structures of Zr^{IV} complexes have been reported so far.

However, observation of up to 60 mol% bound ODA in species **4** indicates a Zr:ODA stoichiometry of 1:3. Therefore, any di- or oligonuclear structure for **4** is very unlikely. Accordingly, we propose a structure with three ODA^{2-} ligands bound in a tridentate fashion through its ether oxygen atom and the two carboxylate groups for species **4**. The proposed structure has a chiral configuration around Zr^{IV} and, therefore, the geminal methylene protons are diastereotopic. The exchange among the enantiomeric forms is slow on the ^1H NMR time scale, because otherwise a singlet would be expected. It should be noted that Zr^{IV} usually has a maximum coordination number of eight. Therefore, it cannot be excluded that in solution one of the ODA^{2-} ligands is bound in a bidentate fashion via the ether oxygen and only one of the carboxylate groups. Such a structure has low symmetry and as a consequence differences in the chemical shifts of the nuclei of the individual ODA^{2-} ligands may be expected. However, this was not observed; the methylene protons give rise to only a single AB system and in the ^{13}C NMR spectrum only single resonances were present for methylene and carboxylate groups. This might be rationalized by rapid internal substitutions of Zr^{IV}-bound by free carboxylate groups. Previously, we have shown that a similar structure occurs, next to a nine-coordinate species, in aqueous solutions of complexes of ODA^{2-} and the heavier lanthanide(III) ions (Ln = Ho → Lu).[20]

In the solutions of Zr^{IV} and ODA with $\rho = 0.2$ described above the intensity of the signal of species **4** decreased upon increase of the pH above 4, whereas the resonance of the "free ligand" increased in intensity. From the mass balance it can then be deduced that not all Zr^{IV} present in the solution is present in complex **4**. In the absence of ODA, however, precipitation occurred under similar conditions. It must be concluded that the highly charged (8+) cyclic tetrameric hydrolyzed species of Zr^{IV} (**1** or possibly higher oligomers), which are present in a fresh solution of $ZrOCl_2$ in water, are stabilized by interaction with either free ODA^{2-} or $[Zr(oda)_3]^{2-}$ (**4**). The interaction is weak, since the chemical shifts of both species are independent of the composition of the sample. Upon increase of the pH, the distribution of the species was always established before an NMR measurement was performed. However, upon decrease of the pH (starting at pH > 4), it took usually 15 – 30 min before an equilibrium was reached; this indicates that depolymerization of the oligomeric hydrolyzed Zr^{IV} is a relatively slow process, as should be expected. Apart from this phenomenon, the composition of the samples remained unaltered for months.

^{17}O NMR spectra: ^{17}O NMR measurements were performed on aqueous solutions of $ZrOCl_2 \cdot 8H_2O$ and 5% ^{17}O-enriched Na_2ODA with $\rho = 0.19$; $[Na_2ODA] = 0.14$ M, pH 7.62 and 1.76, respectively. In order to reduce the line widths, which are determined by the quadrupolar relaxation, the measurements were performed at elevated temperature (80 °C). Three resonances were observed at $\delta = 292$, 273, and 270. In view of the results of ^{1}H and ^{13}C NMR spectra, the peaks at $\delta = 292$ and 273 were assigned to the carboxylate oxygen nuclei of $[Zr(oda)_2]$ (**3**) and $[Zr(oda)_3]^{2-}$ (**4**), while the other signal at $\delta = 270$ is attributed to the carboxylate oxygens of free ODA^{2-}. After the pH of the sample was lowered by addition of DCl, only two carboxylate resonances were observed at $\delta = 291$ and 254, which are assigned to species **3** and free ODA, respectively. This means that complex **4** is completely converted into **3** upon decrease of the pH, which is in agreement with the conclusions from ^{1}H and ^{13}C NMR spectra.

Longitudinal relaxation times: In order to get further support for the mononuclear character of complex **4**, we measured longitudinal relaxation times of the methylene carbon of this complex in a sample of a 0.3 M solution of Na_2ODA to which $ZrOCl_2 \cdot 8H_2O$ was added ($\rho = 0.6$, pH 6)). The ^{1}H and ^{13}C NMR spectra of this sample showed only resonances for **4** and free ODA^{2-}.

The value of the rotational correlation, τ_R, can be estimated from the intramolecular dipole – dipole relaxation rate ($1/T_{1,DD}$) of a ^{13}C nucleus of the ligand using Equation (1).[21]

$$\frac{1}{T_{1,\mathrm{DD}}} = N\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma^2[^{13}\mathrm{C}]\gamma^2[^{1}\mathrm{H}]}{r_{\mathrm{CH}}^6}\tau_R \qquad (1)$$

Here, N is the number of protons bound to the ^{13}C nucleus under study, $\mu_0/4\pi$ the magnetic permeability of a vacuum, γ a magnetogyric ratio, $\hbar$ is the Dirac constant, and r_{CH} the CH bond length. The dipole – dipole contribution to the observed relaxation rate ($1/T_{1,obs}$) was determined using the nuclear Overhauser enhancement (η_{obs}) and Equation (2).

$$\frac{1}{T_{1,\mathrm{DD}}} = \frac{\eta_{\mathrm{obs}}}{1.986\, T_{1,\mathrm{obs}}} \qquad (2)$$

By assuming that the species can be considered as a sphere, the value of τ_R can be related to the molecular volume with the Debye – Stokes – Einstein Equation (3),[22–24] where η_S is the viscosity of the solvent, a is the effective radius of the complex and k is the Boltzmann constant.

$$\tau_R = \frac{4\pi a^3 \eta_S}{3kT} \qquad (3)$$

In Table 2, the relaxation rates and nuclear Overhauser enhancements measured for complex **4** and free Na_2ODA are given. From these data and Equations (1) – (3), the molecular radii of these species were calculated, which appeared to be in good agreement with radii measured in molecular models of Na_2ODA and $[Zr(oda)_3]$ (see Table 2). An inspection of molecular models shows that any dimeric or oligomeric Zr–ODA species would have a molecular radius of at least 4.3 Å, which would correspond to dipolar relaxation rates that are at 1.7 times higher.

Table 2. ^{13}C NMR longitudinal relaxation data for the methylene carbon nuclei of a 0.3 M solution of Na_2ODA and of $[Zr(oda)_3]$ in D_2O at pH 6,[a] 25 °C and 75 MHz.

	Na_2ODA	$[Zr(oda)_3]$
T_{1obs} (s)	1.82	0.44
η_{obs}	1.38	1.65
τ_R [ps]	8.9	43.4
a [Å], estimated from T_1[b]	2.1	3.6
a [Å], estimated from molecular model	2.0	3.6

[a] Measured in a solution of 0.3 M Na_2ODA after addition of $ZrOCl_2 \cdot 8H_2O$ ($\rho = 0.6$); [b] calculated from T_{1obs} values using Eqautions (1) – (3). For the viscosity, the value for water was taken.

Solid $Na_2[Zr(oda)_3]$: Pure **4** could be prepared by evaporation of the solvent from a sample obtained upon mixing of aqueous solutions of $ZrOCl_2$ and $Na_2(ODA)$ with a molar ratio of Zr^{IV}:ODA of 0.33, followed by crystallization from water. A CP-MAS solid state NMR spectrum showed a carboxylate resonance at $\delta = 176.9$ accompanied with a shoulder at somewhat higher chemical shift (see Figure 6), which is consistent with the proposed structure.

Single-crystal X-ray structure of $Na_2[Zr(oda)_3] \cdot 5.5H_2O$: Upon slow evaporation of water from an aqueous solution of **4**, colorless crystals were obtained that were suitable for X-ray analysis, yielding $Na_2[Zr(oda)_3] \cdot 5.5H_2O$ (**4**). Its structure is illustrated in Figure 7; the fractional coordinates are given in Table 3 and selected bond lengths and angles in Table 4. The Zr^{IV} ion is nine-coordinate comprising three ODA^{2-} ligands each bound in a tridentate fashion through the ether oxygen atom (O2) and two monodentate carboxylate

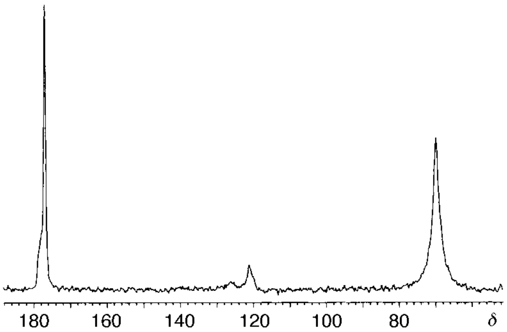


Figure 6. CP-MAS ^{13}C NMR spectrum of $Na_2[Zr(oda)_3]$. The peak at about $\delta = 120$ is a spinning side band of the carboxylate resonance.

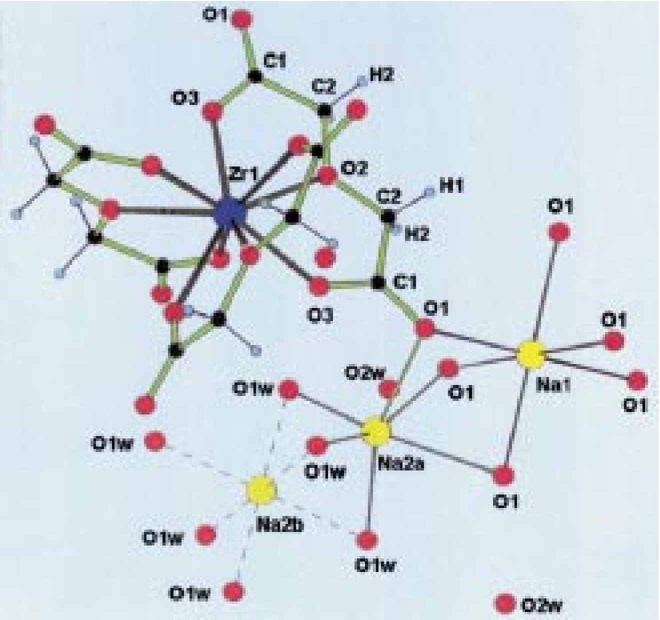


Figure 7. Structure of **4** with atom labels. No thermal ellipsoids are drawn, because of clarity ($R = 0.049$).

Table 3. Atomic positional, isotropic displacement [Å^2] and site occupation parameters for **4**.

	x/*a*	*y*/*b*	*z*/*c*	*U*/*U*(eq)[a]	*PP*
Zr1	1/4	1/4	1/4	0.0311(1)[a]	
Na1	0	1/4	1/4	0.0421(5)[a]	
Na2a	0.0722(3)	$-X+1/4$	$-X+1/4$	0.114(3)[a]	0.406(7)
Na2b	1/8	1/8	1/8	0.18(1)[a]	0.38(3)
C1	0.1299(1)	0.2595(1)	0.2443(2)	0.042(2)[a]	
C2	0.1339(2)	0.2552(2)	0.3014(2)	0.065(2)[a]	
O1	0.0879(1)	0.2637(1)	0.2241(1)	0.056(1)[a]	
O2	0.18574(9)	1/4	$-X+1/2$	0.045(1)[a]	
O3	0.1726(1)	0.2595(1)	0.2201(1)	0.043(1)[a]	
O1w	1/8	0.2125(3)	1/8	0.184(5)[a]	
O2w	1/8	0.3247(6)	1/8	0.239(9)[a]	0.86(2)
H1	0.120(1)	0.2850(6)	0.3169(2)	0.070	
H2	0.116(1)	0.2258(7)	0.3127(2)	0.070	

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

oxygen atoms (O3). Nine-coordination is exceptional for Zr^{4+} complexes which is also proven by the fact that no complexes with a ZrO_9 inner coordination sphere could be found in the Cambridge Structural Database.

Table 4. Some relevant bond lengths [Å] and angles [°] for **4**.

Zr1–O2	2.372(2)	C2–H1	0.95(2)
Zr1–O3	2.179(3)	C2–H2	0.95(2)
C1–C2	1.498(6)	Na1–O1	2.418(3)
C1–O1	1.221(5)	Na2a–O1	2.578(8)
C1–O3	1.279(5)	Na2a–O1w	2.148(8)
C2–O2	1.399(5)	Na2b–O1w	2.283(9)
O2-Zr1-O2[a]	120.00(5)	O1-Na2a-O1w[i]	157.6(4)
O2-Zr1-O3	66.31(9)	O1w-Na2a-O1w[b]	97.4(4)
O2-Zr1-O3[a]	137.44(9)	O1w-Na2b-O1w[j]	180.0(0)
O2-Zr1-O3[b]	70.52(8)	O1w-Na2b-O1w[a]	90.0(0)
O3-Zr1-O3[a]	79.3(1)	C2-C1-O1	120.0(4)
O3-Zr1-O3[c]	85.2(1)	C2-C1-O3	115.4(4)
O3-Zr1-O3[d]	132.5(1)	O1-C1-O3	124.6(4)
O3-Zr1-O3[e]	141.0(1)	C1-C2-O2	108.3(2)
O1-Na1-O1[f]	85.2(1)	C1-C2-H1	109.4(8)
O1-Na1-O1[g]	94.8(1)	C1-C2-H2	109.5(8)
O1-Na1-O1[h]	180.0(0)	O2-C2-H1	111(2)
O1-Na2a-O1[f]	78.8(2)	O2-C2-H2	109(2)
O1-Na2a-O1w	80.3(3)	H1-C2-H2	109(2)
O1-Na2a-O1w[b]	104.9(3)	C2-O2-C2^d	118.3(3)

[a] Symmetry codes: a) *y*, *z*, *x*; b) *z*, *x*, *y*; c) $0.5-y$, $0.5-x$, $0.5-z$; d) $0.5-z$, $0.5-y$, $0.5-x$; e) $0.5-x$, $0.5-z$, $0.5-y$; f) $0.25-z$, $0.25-x$, y; g) $-0.25+y$, $0.5-z$, $0.25+x$; h) $-x$, $0.5-y$, $0.5-z$; i) $0.25-y$, $0.25-z$, x; j) x, $0.25-y$, $0.25-z$.

The crystal structure has a threefold axis through Zr^{IV} perpendicular to the plane formed by the O2 atoms. Furthermore, the structure is defined by twofold axes of symmetry along the Zr–O2 bonds. Two pairs of three O3 atoms form two planes, which are perpendicular to a threefold axis. The coordination polyhedron of Zr^{IV} can be best described as a tricapped trigonal prism. The chelate rings Zr-O3-C1-C2-O2 are almost perfectly planar (maximum deviation from planarity: 0.027 Å (C1)). The Zr–O2 bond coincides with the twofold axis and, consequently, the two five-membered chelate rings of the Zr^{IV} bound ODA^{2-} ligands are coplanar.

Two types of Zr–O bond lengths are observed. The Zr–O3 bond lengths are 2.179(3) Å, which are similar to those observed in the crystal structure of $[Zr(oda)_2(H_2O)_2]$ (**3**) (2.134–2.166 Å).[9] However, the Zr–O2 bond lengths are 2.372(2) Å, which appears to be significantly longer than the corresponding bond lengths in **3** (2.282 and 2.273 Å). This may be ascribed to a minimization of the repulsion energy in the tricapped trigonal prismatic coordination polyhedron by stretching of the bonds to the capping atoms.[25]

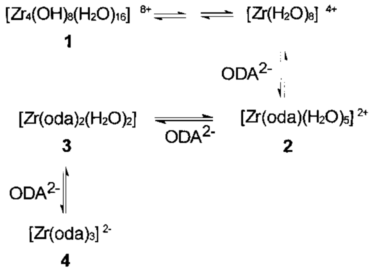
The negative charge of the $[Zr(oda)_3]^{2-}$ core is balanced by two Na^+ cations. Each of the carboxylate oxygens not bound to Zr^{IV} (O1) coordinates a Na^+ cation (Na1). One of the six carboxylate O1 atoms in each $[Zr(oda)_3]^{2-}$ unit is also coordinated to another Na^+ ion (Na2a) with a partial occupation of 0.406. Consequently, the carboxylate functions are locally different, which is in agreement with the shoulder observed on the carboxylate ^{13}C resonance in the CP-MAS ^{13}C NMR spectrum. The Na1 ions are bridging the $[Zr(oda)_3]^{2-}$ moieties; each Na1 is coordinated, in an octahedral arrangement, by six O1 atoms of six different $[Zr(oda)_3]^{2-}$ units. A threefold axis is passing through Zr and Na1.

The mode of wrapping of the ODA^{2-} ligands around the Zr^{IV} makes this metal ion chiral. Both the Δ and the Λ enantiomers of $[Zr(oda)_3]^{2-}$ occur in the unit cell, which are bridged by a Na1 ion at a center of symmetry.

Conclusion

Coordination of oxydiacetic acid by Zr^{IV} results in a large increase of its acidity. Already at a pH value as low as 0, ODA with Zr^{IV} bound to fully deprotonated carboxylates can be observed. This reflects the high acidity of Zr^{IV}. This high acidity frequently results in oligomeric Zr^{IV} species. However, in the solutions with ODA, exclusively mononuclear complexes with 1:1, 1:2, and 1:3 metal:ligand stoichiometries are formed. In these complexes ODA^{2-} is bound in a tridentate fashion via the two carboxylate groups and the ether oxygen. It cannot be excluded that in solutions of $[Zr(oda)_3]^{2-}$ one of the carboxylate groups is not bound to Zr^{IV}. In that case, an internal substitution of bound and free carboxylate groups takes place, which is rapid on the NMR time scale. The structure of solid $[Zr(oda)_2]$ is similar to that in aqueous solution. Solid $[Zr(oda)_3]^{2-}$ has a nine-coordinate Zr^{IV} with three tridentately bound ODA^{2-} ligands.

In solution the stabilities of the complexes, obviously, decrease upon increasing ligation and, consequently, the $[Zr(oda)_3]^{2-}$ complex is only observed at pH values larger than 1.7, where the concentration of the dissociated free dicarboxylate starts to increase substantially. Some excess of Zr^{IV} is kept in solution due to weak interactions between oligomeric hydrolyzed Zr^{IV} species and the free Zr–ODA complexes or free ODA^{2-}. At high pH, OH^- competes with ODA^{2-} for coordination of Zr^{IV}, which results in precipitation. The pH value at which precipitation starts depends on the total concentrations of Zr^{IV} and ODA. The equilibria involved are summarized in Scheme 1.



Scheme 1.

Experimental Section

Materials: Oxydiacetic acid (H_2ODA) and $ZrOCl_2 \cdot 8H_2O$ were obtained from Aldrich and Fluka, respectively. Both were used without further purification. Na_2ODA was prepared by neutralization of an aqueous solution of H_2ODA with NaOH, followed by precipitation with ethanol. ^{17}O-enriched (5% labeling) oxydiacetate was synthesized as described previously.[20] Single crystals of $[Zr(oda)_2(H_2O)_2] \cdot 4H_2O$ were prepared according to the procedure described by Baggio et al.[9]

Preparation of $Na_2[Zr(oda)_3]$: A 0.1 M aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (30 mL) was added dropwise to a stirred 0.1 M solution of Na_2ODA (90 mL) at room temperature. After stirring overnight, a small amount of white precipitate formed was removed by centrifugation. The resulting solution was evaporated until dryness to yield a white powder. Colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of water from an aqueous solution of the powder.

NMR measurements: ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 S spectrometer, at 399.952 and 100.577 MHz, respectively. Chemical shifts are reported with respect to 1,4-dioxane as internal standard ($\delta = 3.6$ and 66.8 for ^1H and ^{13}C NMR, respectively). ^{17}O NMR spectra were obtained on a Varian Inova-300 spectrometer, at 40.696 MHz and 80 °C using a 10 mm sample tube. The signal of D_2O was used as internal reference at $\delta = 0$ for ^{17}O chemical shift. The ^{13}C MAS NMR spectrum was measured on the Varian VXR-400 S spectrometer with a broadband Doty probe (5 mm diameter). Chemical shifts are reported with respect to $SiMe_4$ in $CDCl_3$ as external standard at $\delta = 0$. All ^1H and ^{13}C NMR measurements were carried out at 25 °C, except if stated otherwise. Line widths and chemical shifts were determined by fitting the NMR signals with Lorentzian line functions. When necessary, deconvolution was applied. Spin-lattice relaxation rates (T_1) were measured using the inversion recovery method.[26] Two-dimensional exchange spectra were performed in the phase sensitive mode using the States–Haberkorn–Ruben method,[27] a mixing time varying between 0.01 and 0.2 s, and an acquisition delay of 2.5 s. An array of 64 spectra of 320 data points was collected. Samples for measurement of T_1 data and two-dimensional exchange spectra were deoxygenated by bubbling through nitrogen for 15 min.

All pH measurements were made at room temperature using a Corning 125 pH meter and a calibrated micro combination electrode purchased from Aldrich Chemical Co. The pH was adjusted with diluted D_2O solution of DCl and Na_2OD (all supplied by Merck). No correction was made for the deuterium isotope effect.

X-ray crystallography: Crystallographic data are summarized in Table 5. A colorless crystal of **4** was mounted in a glass fiber on a Nonius CAD4 diffractometer equipped with a graphite monochromator and $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections with $10° \leq \theta \leq 15°$. Intensity data were collected to $\theta_{max} = 30°$ by the $\omega/2\theta$ scan technique. For $(h,k,l) \leq 36$, 5086 reflections were collected and merged ($R_{merge} = 0.035$) to 1082 independent reflections, of which 488 were considered observed ($F_0^2 > 2.0\sigma(F_0^2)$).

Table 5. Crystallographic data for **4**.

formula	$C_{12}H_{23}O_{22.5}ZrNa_2$
M_w	640.50
crystal system	cubic
space group	$Fd\bar{3}c$ (No. 228)
crystal size [mm]	$0.30 \times 0.30 \times 0.20$
a [Å]	26.084(8)
V [Å^3]	17747(4)
Z	32
ρ_{calcd} [g cm^{-3}]	1.89
$F(000)$	10272
μ [mm^{-1}]	0.64
transm. factors	0.84, 0.90
data, parameters	488, 68
goodness-of-fit on F^2	2.22
R, $R(w)$ [$F^2 > 2\sigma(F^2)$][a]	0.049, 0.057
R, $R(w)$ [all data][a]	0.146, 0.066
max and min peaks [e Å^{-3}]	−1.51, 1.92

[a] $R(w) = [\Sigma[(w)(F_0^2 - F_c^2)^2]/\Sigma[((w)F_0^2)^2]]^{0.5}$.

Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Three standard reflections were measured every 2 h of X-ray measuring time. The observed decay of 2% in the intensities was applied to the measured intensities. The structure was solved by difference Fourier syntheses. Refinement of the structure was done by full-matrix least-squares on F_0^2 with anisotropic parameters for the non-hydrogen atoms.

The positions of the Zr and Na atoms are constrained by the space group symmetry to the positions with point symmetry 32 (¼,¼,¼) and $\bar{3}$ (0,¼,¼), respectively, with $Z = 32$.

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The two independent methylene hydrogen atoms were placed at calculated tetrahedral positions (d(C–H) = 0.95 Å) and allowed to ride on the atoms to which they are attached. Water hydrogen atoms were not located.

All calculations were performed on a SUN-IPX workstation using programs of the Xtal 3.2 system.[28] The final fractional coordinates and some selected (bond) lengths and angles are listed in Tables 3 and 4, respectively.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142151. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] A. L. Hock, *Chem. Ind.* **1974**, 864.

[2] D. Hoebbel, T. Reinert, H. Schmidt, E. Arpac, *J. Sol-Gel Sci. Technol.* **1997**, *10*, 115.

[3] K. A. Fleeting, P. O'Brien, D. J. Otway, A. J. P. White, D. J. Williams, A. C. Jones, *Inorg. Chem.* **1999**, *38*, 1432.

[4] J. W. Ely, *Stimulation Engineering Handbook*, Penn Well Books, Tulsa, Oklahoma, USA, **1994**.

[5] C. F. Baes, Jr., R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, **1976**, p. 152.

[6] F. A. Cotton, G. Wilkinsen, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, **1988**.

[7] T. C. W. Mak, *Can. J. Chem.* **1968**, *46*, 3491.

[8] M. Åberg, J. Glaser, *Inorg. Chim. Acta* **1993**, *206*, 53.

[9] R. Baggio, M. T. Garland, M. Perec, D. Vega, *Inorg. Chem.* **1995**, *34*, 1961.

[10] R. Baggio, M. T. Garland, M. Perec, *Inorg. Chem.* **1997**, *36*, 737.

[11] E. M. Larsen, E. H. Homeier, *Inorg. Chem.* **1972**, *11*, 2687.

[12] G. L. Glen, E. W. Silverton, J. L. Hoard, *Inorg. Chem.* **1963**, *2*, 250.

[13] J. L. Hoard, E. W. Silverton, J. V. Silverton, *J. Am. Chem. Soc.* **1968**, *90*, 2300.

[14] R. Baggio, M. T. Garland, M. Perec, *Inorg. Chem.* **1997**, *36*, 3918.

[15] A. H. Van de Zijden, C. Mattheis, R. Fröhlich, F. Zippel, *Inorg. Chem.* **1997**, *36*, 4444.

[16] U. Thewalt, T. Guthner, *J. Organomet. Chem.* **1989**, *339*, 59.

[17] C. A. M. Vijverberg, J. A. Peters, W. M. M. J. Bovée, H. Vroon, A. P. G. Kieboom, H. van Bekkum, *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 255.

[18] C. L. Perrin, T. J. Dwyer, *Chem. Rev.* **1990**, *90*, 935.

[19] A. E. Martell, R. M. Smith, *Critical Stability Constants*, *Vol. 3*, Plenum Press, New York, **1977**, p. 133.

[20] J. A. Peters, *J. Chem. Soc. Dalton Trans.* **1988**, 961.

[21] I. Solomon, *Phys. Rev.* **1995**, *99*, 559.

[22] S. Stokes, *Trans. Cambridge Philos. Soc.* **1956**, *9*, 5.

[23] A. Einstein, *Investigations on the Theory of Brownian Movement*, Dover, New York, **1956**.

[24] P. Debye, *Polar Molecules*, Dover, New York, **1929**.

[25] M. C. Favas, D. L. Kepert, *Prog. Inorg. Chem.* **1981**, *28*, 309.

[26] R. V. Vold, J. S. Waugh, M. P. Klein, D. E. Phelps, *J. Chem. Phys.* **1968**, *48*, 3831.

[27] D. J. States, R. A. Haberkorn, D. J. Ruben, *J. Magn. Reson.* **1982**, *48*, 286.

[28] *Xtal 3.2 Reference Manual* (Eds.: S. R. Hall, H. D. Flack, J. M. Stewart), Universities of Western Australia, Geneva, Maryland, **1992**.

Received: April 7, 2000 [F2408]

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