Synthesis, Characterization, and X-ray Structure of the Mononuclear Eight-Coordinate Zirconium(IV) 2,2′-Oxydiacetate $[Zr\{(O(CH_2CO_2)_2)\}_2(H_2O)_2]\cdot 4H_2O$

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Introduction

The aqueous solution chemistry of zirconium(IV) has not been highly developed due in large part to the strong tendency of group 4 complexes toward hydrolysis and polymerization reactions even in strong acid solutions.[1,2] The existence of zirconium(IV) carboxylate complexes has been documented,[3] but relatively few have been well characterized. Among these, the crystal structures of the complexes of zirconium(IV) with oxalic acid,[4] nitrilotriacetic acid[5] (NTA), and ethylenediaminetetraacetic acid[6] (EDTA) have been reported. The three complexes are mononuclear eight-coordinate with ZrO_8 and ZrN_2O_6 nuclear cores, respectively. The 2,2′-oxydiacetato ligand (oxydiacetic acid = $[O(CH_2CO_2H)_2]$) is a versatile complexing agent with three oxygen donor atoms and can complex metal ions by forming up to two five-membered chelate rings. This ligand has been extensively used in lanthanide and actinide chemistry, and several structures containing this anion in different environments have been determined.[7]

The only structurally characterized zirconium(IV) oxydiacetato complex to date is the organometallic-stabilized $Cp_2Zr[O(CH_2CO_2)_2]$, a mononuclear five-coordinate species where the oxydiacetato ligand acts as tridentate.[8]

In this note we report the synthesis, characterization, and single-crystal X-ray diffraction study of the novel mononuclear eight-coordinate $[Zr\{O(CH_2CO_2)_2\}_2(H_2O)_2]\cdot 4H_2O$ complex, isolated from the reaction of $ZrOCl_2\cdot 8H_2O$ and 2,2′-oxydiacetic acid in aqueous media.

Experimental Section

All commercially available reagents and chemicals were of analytical or reagent grade purity and were used as received. Water was purified by a Millipore Milli-Q system yielding 18 M Ω cm water. Elemental analyses (C, H) were performed at INQUIMAE (Instituto de Quimica de Materiales, Medio Ambiente y Energia) with a Carlo Erba EA 1108 analyzer. Infrared spectra were recorded as KBr disks or as mulls in Nujol with a Nicolet 510P FT-IR spectrophotometer. Thermogravimetric analyses were recorded on a Mettler TG-50 thermal analyzer in a dynamic atmosphere of pure air at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected using monochromated Cu Kα radiation on a Phillips X'Pert diffractometer.

Table 1. Crystalloraphic Data for **1**

formula	$C_8H_{20}O_{16}Zr$
fw	463.46
crystal system	orthorhombic
space group	*P*212121 (No. 19)
crystal size, mm	0.40 × 0.30 × 0.25
a, Å	7.961(1)
b, Å	9.481(1)
c, Å	23.041(2)
V, Å^3	1739.1(3)
Z	4
d_{calcd}, g cm^{-3}	1.77
F(000)	944
μ, mm^{-1}	0.71
transm factors	0.85, 0.68
data, parameters	1321, 267
goodness-of-fit on F^2	1.094
R1,[a] wR2[b] [$F^2 > 2\sigma(F^2)$]	0.018, 0.047
R1,[a] wR2[b] [all data]	0.024, 0.076
max and min peaks, e Å^{-3}	0.20 and −0.37

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

Preparation of $[Zr\{O(CH_2CO_2)_2\}_2(H_2O)_2]\cdot 4H_2O$. To a solution of $ZrOCl_2\cdot 8H_2O$ (1.6 g, 0.005 mol) in water (70 mL) at pH 1.0−1.5 was added 2,2′-oxydiacetic acid (1.4 g, 0.01 mol) in small portions. After being stirred for 12 h at 80 °C, the solution was filtered and the filtrate allowed to stand at room temperature. After 1 week, colorless crystals of the product were collected and dried under vacuum for 6 h. Yield: 1.85 g, 80%. Anal. Calcd (found) for $C_8H_{20}ZrO_{16}$: C, 20.75 (20.72); H, 4.39 (4.32). IR (KBr disk, cm^{-1}): 3569 (s), 3465 (vs), 2992 (s), 1663 (vs, br), 1454 (m), 1431 (s), 1404 (vs), 1346 (vs), 1316 (s), 1250 (m), 1105 (s), 1042 (s), 1005 (m), 943 (vs), 841 (m), 714 (m), 600 (s), 496 (m), 376 (s), 318 (s), 260 (s). Insolubility of the sample in organic solvents prevented the aquisition of reliable NMR data.

X-ray Crystallography. Crystallographic data are summarized in Table 1. A colorless crystal of good diffracting power was mounted in a glass fiber on a Siemens R3m diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.710 73 Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections. Intensity data were collected in the range $3° \leq 2\theta \leq 45°$ by the $\omega-2\theta$ scan technique. Within index ranges ($0 \leq h \leq 8$, $0 \leq k \leq 10$, $0 \leq l \leq 24$), 1344 unique reflections were collected, of which 1295 were considered observed, $F_o^2 > 2\sigma(F_o^2)$.

Intensities were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction (ψ scan) was also applied. Two standard reflections, monitored every 98, showed no systematic changes. The structure was solved by a combination of direct methods and difference Fourier syntheses. Refinement of the structure was done by full-matrix least-squares in F^2, with anisotropic thermal parameters for the non-hydrogen atoms.

The four methylene hydrogen atoms were placed at calculated positions (d(C−H) = 0.95 Å) and allowed to ride on the atoms to which they are attached. All the water hydrogen atoms were located in difference Fourier maps and their positions refined in the latest stages with a restrained geometry (d(O−H) = 0.85(3) Å and d(H−H) = 1.37(3) Å). A unique common isotropic thermal parameter fixed at 0.08 Å^2 was applied to all hydrogens. Computer programs used in this study were SHELXLTL/PC and SHELXL 93.[9] The final fractional coordinates for the non-hydrogen atoms are given in Table 2 and bond distances and angles are listed in Table 3.

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(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.

(2) Intorre, B. I.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 358.

(3) Fay, R. C. *Coord. Chem. Rev.* **1986**, *71*, 113.

(4) (a) Glen, G. L.; Silverton, J. V.; Hoard, J. L. *Inorg Chem.* **1963**, *2*, 250. (b) Kojic-Prodic, B.; Ruzic-Toros, Z.; Sljukic, M. *Acta Crystallogr., Sect. B* **1978**, *34*, 2001.

(5) Hoard, J. L.; Silverton, E. W.; Silverton, J. V. *J. Am.Chem. Soc.* **1968**, *90*, 2300.

(6) Pozhidaev, A. I.; Porai-Koshits, M. A.; Polynova, T. N. *J. Struct. Chem. USSR* (*Engl. Transl.*) **1974**, *15*, 548.

(7) (a) Albertsson, J.; Elding, I. *Acta Chem. Scand., Ser. A* **1977**, *31*, 21. (b) Elding, I. *Acta Chem. Scand., Ser. A* **1977**, *31*, 75.

(8) Thewalt, U.; Guthner, T. *J. Organomet. Chem.* **1989**, *379*, 59.

(9) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement. University of Gottingen, Germany, 1993.

0020-1669/95/1334-1961$09.00/0

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for **1**

atom	*x*	*y*	*z*	*U*(eq)^a
Zr1	−0.09400(4)	−0.56595(3)	−0.62047(1)	0.0203(2)
O2	−0.3445(3)	−0.6409(3)	−0.6066(1)	0.0296(7)
C3	−0.4115(5)	−0.7481(4)	−0.6316(2)	0.0336(9)
C4	−0.3127(5)	−0.8137(4)	−0.6797(2)	0.035(1)
O5	−0.1740(3)	−0.7208(3)	−0.6910(1)	0.0276(6)
C6	−0.0540(5)	−0.7738(5)	−0.7316(2)	0.039(1)
C7	0.0964(6)	−0.6789(4)	−0.7281(2)	0.0301(9)
O8	0.0931(4)	−0.5874(3)	−0.6870(1)	0.0311(6)
O9	−0.5479(4)	−0.7980(4)	−0.6179(2)	0.065(1)
O10	0.2111(4)	−0.6901(3)	−0.7633(1)	0.0418(8)
O11	−0.0474(3)	−0.7706(3)	−0.5854(1)	0.0328(7)
C12	0.0672(5)	−0.8066(4)	−0.5494(2)	0.0277(9)
C13	0.1881(5)	−0.6921(4)	−0.5322(2)	0.032(1)
O14	0.1470(3)	−0.5725(3)	−0.5676(1)	0.0312(7)
C15	0.2677(5)	−0.4637(4)	−0.5720(2)	0.033(1)
C16	0.1825(5)	−0.3421(4)	−0.6027(2)	0.032(1)
O17	0.0304(3)	−0.3628(3)	−0.6190(1)	0.0274(6)
O18	0.0790(4)	−0.9257(3)	−0.5290(1)	0.0374(7)
O19	0.2611(4)	−0.2326(3)	−0.6106(2)	0.056(1)
O1w	−0.2502(4)	−0.4242(3)	−0.6714(1)	0.0353(7)
O2w	−0.1681(4)	−0.4881(3)	−0.5365(1)	0.0370(8)
O3w	0.0185(5)	−0.3448(5)	−0.4648(2)	0.066(1)
O4w	0.2584(7)	0.0070(4)	−0.6792(2)	0.070(1)
O5w	−0.1709(5)	−0.1026(4)	−0.5855(2)	0.064(1)
O6w	−0.5137(5)	−0.0405(5)	−0.7662(2)	0.066(1)

^{a}*U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Bond Lengths (Å) and Angles (deg) for **1**

Zr1-O11	2.134(3)	Zr1-O2	2.141(2)
Zr1−O8	2.147(3)	Zr1−O2w	2.154(3)
Zr1−O17	2.166(2)	Zr1−O1w	2.175(3)
Zr1−O14	2.273(3)	Zr1−O5	2.282(2)
O2−C3	1.284(5)	C3−O9	1.227(5)
C3−C4	1.494(6)	C4−O5	1.436(5)
O5−C6	1.428(5)	C6−C7	1.500(6)
C7−O10	1.227(5)	C7−O8	1.284(5)
O11−C12	1.279(5)	C12−O18	1.226(5)
C12−C13	1.504(6)	C13−O14	1.435(5)
O14−C15	1.413(5)	C15−C16	1.513(6)
C16−O19	1.226(5)	C16−O17	1.283(5)
O11−Zr1−O2	78.70(10)	O11−Zr1−O8	93.64(11)
O2−Zr1−O8	136.15(10)	O11−Zr1−O2w	91.09(12)
O2−Zr1−O2w	74.01(10	O8−Zr1−O2w	149.79(10)
O11−Zr1−O17	136.27(10)	O2−Zr1−O17	135.94(10)
O8−Zr1−O17	77.20(10)	O2w−Zr1−O17	78.83(11)
O11−Zr1−O1w	149.94(11)	O2−Zr1−O1w	75.70(11)
O8−Zr1−O1w	94.00(11)	O2w−Zr1−O1w	96.70(12)
O17−Zr1−O1w	73.78(10)	O11−Zr1−O14	68.01(10)
O2−Zr1−O14	134.19(10)	O8−Zr1−O14	78.16(11)
O2w−Zr1−O14	76.05(11)	O17−Zr1−O14	68.27(10)
O1w−Zr1−O14	142.05(11)	O11−Zr1−O5	74.54(10)
O2−Zr1−O5	68.46(9)	O8−Zr1−O5	67.89(9)
O2w−Zr1−O5	141.68(10)	O17−Zr1−O5	135.33(10)
O1w−Zr1−O5	81.56(11)	O14−Zr1−O5	126.87(10)
C3−O2−Zr1	125.6(3)	O9−C3−O2	123.9(4)
O9−C3−C4	119.8(4)	O2−C3−C4	116.3(4)
O5−C4−C3	106.5(3)	C6−O5−C4	114.7(3)
C6−O5−Zr1	120.4(2)	C4−O5−Zr1	118.6(2)
O5−C6−C7	106.7(3)	O10−C7−O8	124.2(4)
O10−C7−C6	120.4(3)	O8−C7−C6	115.4(4)
C7−O8−Zr1	127.2(3)	C12−O11−Zr1	127.8(2)
O18−C12−O11	123.3(4)	O18−C12−C13	121.0(4)
O11−C12−C13	115.7(3)	O14−C13−C12	106.0(3)
C15−O14−C13	117.6(3)	C15−O14−Zr1	121.0(2)
C13−O14−Zr1	121.2(2)	O14−C15−C16	106.6(3)
O19−C16−O17	124.6(4)	O19−C16−C15	119.1(4)
O17−C16−C15	116.3(3)	C16−O17−Zr1	124.9(3)

Results and Discussion

Addition of 2,2′-oxydiacetic acid to an aqueous solution of $ZrOCl_8$·$8H_2O$ produces the mononuclear $[Zr\{O(CH_2CO_2)_2\}_2(H_2O)_2]$·$4H_2O$ (**1**) complex in high yield. The complex is a stable colorless crystalline solid and can be stored in a dry atmosphere for extended periods of time. TGA measurements show that the compound is thermally stable up to 60 °C, at which temperature loss of water commences.

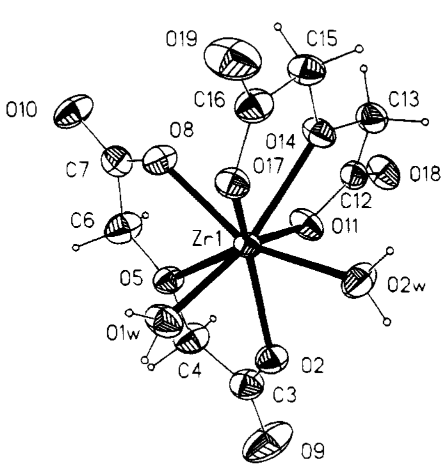

Figure 1. Structure of **1** with atom labels (50% thermal ellipsoids). The four crystallization water molecules have been omitted for clarity.

Crystal Structure. The schematic drawing of $[Zr\{O(CH_2CO_2)_2\}_2(H_2O)_2]$·$4H_2O$ (**1**) given in Figure 1 shows that the oxydiacetato ligands are coordinating in a tridentate fashion involving two monodentate carboxylate oxygens and the ether oxygen of each ligand. The ligands are completely deprotonated, so that the resulting complex is neutral.

The zirconium is eight-coordinate, the coordination sphere being completed by two oxygen water molecules forming a mononuclear unit. The ZrO_8 inner coordination sphere is defined by two interpenetrating trapezoids (O11, O14, O17, O1w and O8, O5, O2, O2w) including the Zr atom which exhibit only minor departures from planarity (0.003 and 0.073 Å, respectively) and are nearly perpendicular (89.9(1)°). Analysis of the ZrO_8 polyhedron by the procedure described by Kepert[10] indicates that the geometry at the zirconium atom is best described as a D_1 dodecahedron ($\Phi_A = 35°$, $\Phi_B = 106°$ and $\Theta_A - \Theta_B = 6(2)°$).

Three sets of Zr−O distances are observed for three kinds of Zr−O bonds in **1**. One set consists of Zr−O bond lengths of the negatively charged carboxylate oxygens O2, O8, O11, and O17. These distances have a range and an average value of 2.134(3)−2.166(2) and 2.147[12] Å, respectively. Three Zr−O bonds are similar within experimental error (mean 2.141[4] Å) whereas the Zr−O17 bond is 0.025 Å longer. This lengthening may be associated with the engagement of O17 in hydrogen bonding with the water molecules (vide infra).

A second set includes the Zr−O bonds of the neutral ether oxygens O5 and O14, 2.282(2) and 2.273(3) Å, respectively. These bonds are significantly longer than the former with an average value of 2.278[4] Å and demonstrate the comparative weakness of the less polar Zr−O(ether) bonds. Interestingly, the corresponding values in the five-coordinate $Cp_2Zr[O(CH_2CO_2)_2]$ are very similar (2.156(2) and 2.271(2) Å, respectively), suggesting that the oxydiacetato ligands strongly complex zirconium(IV) in **1**.

The donor−acceptor $Zr-OH_2$ bond lengths in **1** (2.175(3) and 2.154(3) Å (average 2.165[10] Å)) are comparable to the above mentioned ionic bonds and somewhat shorter than the average $Zr-OH_2$ of 2.26[5] Å in tetrameric $ZrOCl_2$·$8H_2O$.[11]

The average (all bonds) Zr−O distance (2.18[5] Å) is comparable to the values in other related complexes containing

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(10) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.
(11) Mak, T. C. V. *Can. J. Chem.* **1968**, *46*, 3491.
(12) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.
(13) Powers, D. A.; Gray, H. B. *Inorg. Chem.* **1973**, *12*, 2721.

Table 4. Hydrogen-Bonding Contacts in **1**[a]

O–H···O	O–H (Å)	H···O (Å)	O–H···O (deg)	O···O (Å)
$(O1w{-}H1w)\cdots O6w^{a}$	0.86(3)	1.76(3)	170.9(4)	2.61(1)
$(O1w{-}H1w')\cdots O10^{b}$	0.85(3)	1.85(3)	171.5(4)	2.70(1)
$(O2w{-}H2w)\cdots O3w$	0.85(3)	1.75(3)	177.6(4)	2.60(1)
$(O2w{-}H2w')\cdots O18^{c}$	0.85(3)	1.80(3)	172.2(4)	2.65(1)
$(O3w{-}H3w)\cdots O19^{g}$	0.83(3)	1.98(3)	163.0(4)	2.78(1)
$(O3w{-}H3w')\cdots O5w^{f}$	0.83(3)	2.05(3)	144.7(4)	2.78(1)
$(O4w{-}H4w)^{d}\cdots O9^{h}$	0.82(3)	1.96(3)	175.9(4)	2.79(1)
$(O4w{-}H4w')^{d}\cdots O19^{d}$	0.82(3)	1.95(3)	167.3(4)	2.77(1)
$(O5w{-}H5w)^{f}\cdots O18^{i}$	0.83(3)	2.08(3)	173.3(4)	2.91(1)
$(O5w{-}H5w')^{f}\cdots O17^{f}$	0.82(3)	2.22(3)	172.6(4)	3.04(1)
$(O6w{-}H6w)^{a}\cdots O10^{e}$	0.82(3)	2.05(3)	174.3(4)	2.88(1)
$(O6w{-}H6w')^{a}\cdots O4w^{d}$	0.82(3)	1.95(3)	160.7(4)	2.74(1)

[a] Symmetry codes: (a) $-1 - x, -0.5 + y, -1.5 - z$; (b) $-x, 0.5 + y, -1.5 - z$; (c) $-0.5 + x, -1.5 - y, -1 - z$; (d) $-x, -0.5 + y, -1.5 - z$; (e) $-1 + x, y, z$; (f) $0.5 + x, -0.5 - y, -1 - z$; (g) $-0.5 + x, -0.5 - y, -1 - z$; (h) $-1 - x, 0.5 + y, -1.5 - z$; (i) $0.5 + x, -1.5 - y, -1 - z$.

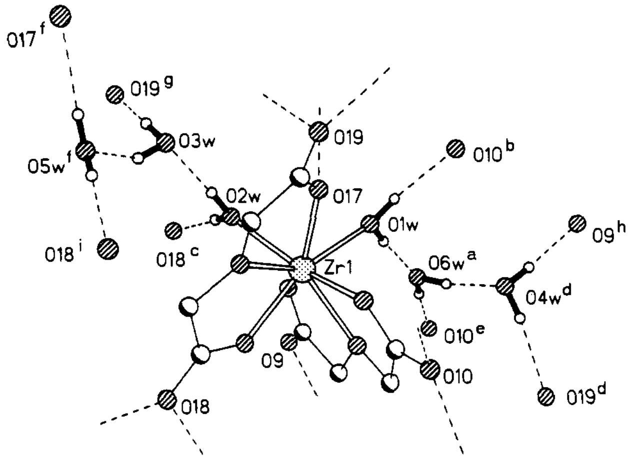

Figure 2. Schematic representation of the hydrogen-bonding system in the crystal structure of **1**. Atom labels and symmetry codes are as in Table 4.

the ZrO_8 coordination polyhedron.[4a] The two five-membered chelate rings with a common Zr–O bond for each ligand, Zr,O14,C15,C16,O17 and Zr,O11,C12,C13,O14 and Zr,O5,C6,C7,O8 and Zr,O2,C3,C4,O5, are planar and the angles between them are 8.5 and 2°, respectively. Other distances and angles within the ligand molecules are consistent with the values for other metal oxydiacetato compounds.[7]

The crystal structure of **1** is a complex three-dimensional network of dodecahedra connected by hydrogen bonds involving all coordinated and noncoordinated water molecules and the carboxylate oxygen atoms O9, O10, O18, O19, and O17. A summary of bond distances and angles involving hydrogen bonding contacts is given in Table 4. An interesting feature in this structure is the existence of three different types of hydrogen-bonding links by water molecules connecting the symmetry-related units. These links involve one, two, and three water molecules and are illustrated in Figure 2.

Infrared Spectra. As a result of complex formation, the strong absorption of 2,2′-oxydiacetic acid at 1734 cm^{-1} indicative of the acid carbonyl groups disappears and is replaced by a very strong and broad band centered at ca. 1663 cm^{-1} and two strong and well-defined bands at 1404 and 1346 cm^{-1}. The former corresponds to the asymmetric vibrations of the RCO_2- groups and overlaps with the coordinated and lattice water deformation modes usually assigned at 1640 and 1625 cm^{-1}, respectively. The bands at 1404 and 1346 cm^{-1} may be assigned to the symmetric vibrations of the RCO_2- groups. The Δ values [$\Delta = \nu(CO_2-)_{asym} - \nu(CO_2-)_{sym}$] above 200 cm^{-1} suggest that the coordinate carboxylate groups are probably unidentate.[14] The strong absorption at 943 cm^{-1} has been associated with modes of coordinated water in $ZrOCl_2{\cdot}8H_2O$ and the bands in the 600–300 cm^{-1} range are usually assigned to Zr–O modes by comparison with the spectrum of ZrO2 (baddeleyite)[13,14].

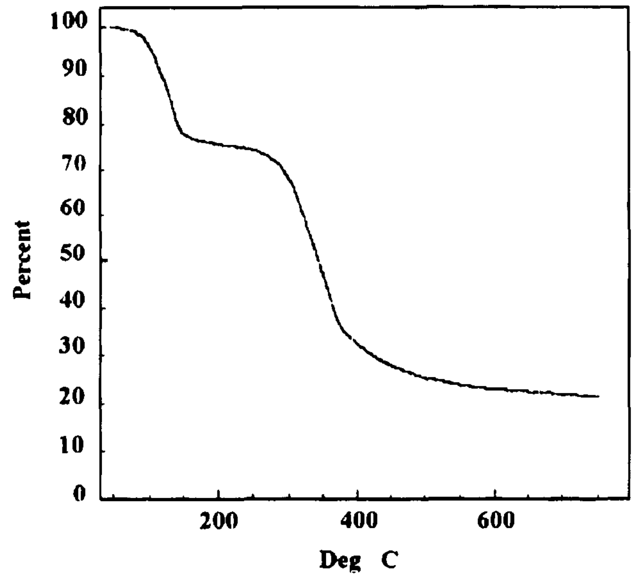

Figure 3. Thermogravimetric analysis of **1** under an atmosphere of pure air. Theoretical values for weight changes: 77%, **1**-6(H_2O); 27%, ZrO_2/**1**.

Thermolysis. Thermal decomposition of **1** was followed by TGA, and the composition of the final pyrolysate was determined by XRD. No attempt was made to identify the intermediate products formed during this thermolysis. The first step in the thermogram in Figure 3 corresponds to the distinct loss of the six water molecules.[15] The final weight loss corresponds to complete decomposition of the complex to crystalline ZrO_2 (baddeleyite and zirconia) as shown by the X-ray powder diffraction pattern.[16]

In summary, 2,2′-oxydiacetate has proven to be a useful coordinating ligand for the isolation of Zr(IV) in aqueous media at high acidity. The present structure suggests that complexation may occur by displacement of the hydroxyl groups in the tetranuclear $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ species present in the Zr(IV) aqueous solution.[17] The crystallization of **1** from a solution likely to contain a multiplicity of species depends, we believe, upon relative solubility factors in the solution. The very low solubility of **1** at high acidity precludes further hydrolytic polymerization reactions, a reactivity characteristic of zirconium(IV) complexes in aqueous media.[18]

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Supplementary Material Available: Tables giving relevant relevant least-squares planes, anisotropic thermal parameters, and hydrogen positional parameters (4 pages). Ordering information is given on any current masthead page.

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(14) Perec, M. *Inorg. Chim. Acta* **1985**, *103*, 163.

(15) Isothermal dehydrations of $[Zr\{(O(CH_2CO_2)_2)\}_2(H_2O)_2]{\cdot}4H_2O$ in stagnant atmosphere show that 2, 4, and 6 equiv of water are lost at 60, 75 and 95 °C, respectively.

(16) JCPDS International Center for Diffraction Data, 1989: Powder Diffraction File No. 37-1484 (baddeleyite) and No. 17-0923 (zirconia).

(17) Toth, L. M.; Lin, J. S.; Felker, L. K. *J. Phys. Chem.* **1991**, *95*, 3106.

(18) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley and Sons: New York, 1976.