Synthesis and Crystal Structure of a Novel Hexanuclear Zr(IV) Complex with Hydroxo and Carboxylato Bridging

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A novel hexanuclear eight-coordinate complex, $[Zr_6(OH)_8(OCH_3)_4(Ph_2CHCOO)_{12}]\cdot 2CH_3CN$ (**1**), has been prepared and characterized on the basis of elemental analysis, infrared-spectroscopy measurements, and X-ray crystallography. The crystallographic data for complex **1** are: monoclinic, $P2_1/n$, $a = 18.09(1)$, $b = 21.73(2)$, $c = 20.349(8)$ Å, $\beta = 96.26(4)°$, $V = 7952(8)$ Å^3, $Z = 2$, $R = 0.055$ and $R_w = 0.058$ for 5133 observed reflections $[I > 3\sigma(I)]$. Complex **1** resides on a crystallographic inversion center, thus making only three of the six zirconium unique. The six zirconium ions are arranged in apices of an octahedron. Two axial Zr(IV) metal ions (Zr1, Zr1*) are joined with four equatorial Zr(IV) metal ions (Zr2, Zr2*, Zr3, Zr3*) by eight *syn–syn* bridging carboxylate groups, and both axial Zr(IV) ions have four triangle μ_3-OH bridges through equatorial Zr(IV) metal ions. On the other hand, each equatorial Zr(IV) metal ion is connected with axial Zr(IV) metal ions by two bridging carboxylates and four triangle μ_3-OH bridges. Besides these, each equatorial Zr(IV) metal ion is coordinated by one monodentate carboxylate and one methoxy group.

The carboxylate chemistry of group-4 metals has generated much interest in titanium compounds concerning catalytical and biological activity.[1] In contrast, the chemistry of zirconium and hafnium carboxylates is less developed. In the case of zirconium, some Zirconocene, $(C_5H_5)_2Zr$, complexes of phthalic acids and acetylenedicarboxylic acid have been prepared, and some were characterized with X-ray structure analyses.[2—5] Compared to organometallic carboxylates, few papers have been published on Werner-type zirconium carboxylates of $Zr(O_2CR)_nX_{4-n}$ ($X = Cl$ or $OCHMe_2$, $R = CH_3$, C_2H_5),[6] $Zr_2O(O_2CR)_6$ ($R = C_9H_{19}$, $C_{11}H_{23}$),[7] and polycarboxylate compounds; $Na_4[Zr(C_2O_4)_4]\cdot 3H_2O$,[8] $K_2[Zr\{N(CH_2COO)_3\}_2]\cdot H_2O$,[9] and $[Zr(edta)(H_2O)_2]$.[10] The second type of compound ($Zr_2O(O_2CR)_6$) is expected to have a dinuclear structure; however, no X-ray structure determination has yet been reported. This promted us to prepare zirconium carboxylates and to prove that a μ-carboxylato bridge exists. For this purpose, diphenylacetic acid was used, since we have some knowledge concerning the fexible bridging ability of the ligand through studies on other polynuclear metal complexes.[11,12] Here, we report on the first example of a hexanuclear Zr(IV) complex with two different bridging ligands of OH and Ph_2CHCOO. The orientation of six Zr(IV) ions is characteristically octahedral, and the μ_3-OH bridge in the trigonal surface is also a characteristic of this compound. Precise discussions concerning the structure are made based on single-crystal X-ray crystallography.

Experimental

Reagents and Chemicals. Diphenylacetic acid and zirconium tetrachloride were of Aldrich (analytical reagent) grade. All other chemicals were obtained from Wako, and were used as supplied, except for methanol, which was purified by distillation.

Preparation. $[Zr_6(OH)_8(OCH_3)_4(Ph_2CHCOO)_{12}]\cdot 2CH_3CN$ (1): A mixture of zirconium tetrachloride (1 mmol), a solution of diphenylacetic acid (4 mmol) in acetonitrile (40 ml) including triethylamine (4 mmol), and 2,2′-bipyridine (bpy) (1 mmol) was stirred for 1.5 h at 60 °C. Earlier precipitates were filtered off and the filtrate was allowed to stand for several days after the addition of a few drops of methanol. Colorless crystals were collected, washed with acetonitrile, and air-dried at room temperature. Yield: 33%. Found: C, 61.52; H, 4.69; N, 0.75%. Calcd for $C_{176}H_{158}N_2O_{36}Zr_6$: C, 61.73; H, 4.65; N, 0.82%. IR (Nujol, cm^{-1}) ν_{OH} 3551; $\nu_{C\equiv N}$ 2151; $\nu_{asym(CO)}$ 1593; $\nu_{sym(CO)}$ 1404, 1377.

The intermediate compound, $[Zr_3Cl_6(Ph_2CHCOO)_6(bpy)_2]$ (**2**), was obtained according to a synthetic procedure similar to that for **1**, except for the use of methanol. Yield: 46%. Found: C, 60.50; H, 4.16; N, 2.63%. Calcd for $C_{104}H_{82}Cl_6N_4O_{12}Zr_3$: C, 60.45; H, 4.00; N, 2.71%. IR (Nujol, cm^{-1}) $\nu_{asym(CO)}$ 1598, 1538; $\nu_{sym(CO)}$ 1407, 1377; ν_{Zr-N} 733, 520.

Physical Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were measured with a Perkin–Elmer 2000 FT-IR spectrophotometer in the region of 4000—450 cm^{-1} on Nujol mulls.

X-Ray Crystal Structure Determination. A colorless crystal (0.30×0.25×0.65 mm) was coated with epoxy glue to prevent efflorescence, and mounted on a Rigaku AFC5S automated four-circle diffractometer. The diffraction intensities were measured using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The unit-cell constants were determined from a least-squares refinement using setting angles of 18 carefully centered reflections in the range of $15 < 2\theta < 30°$. The crystallographic data are listed in Table 1. The data were collected at a temperature of 23±1°C using the ω–2θ scan technique to a maximum 2θ value of 55.0°.

Table 1. Crystallographic Data and Data Collection Details

Formula	$C_{176}H_{158}N_2O_{36}Zr_6$
F. W.	3424.50
Crystal dimensions/mm	0.30 × 0.25 × 0.60
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	18.09(1)
b/Å	21.73(2)
c/Å	20.349(8)
β/°	96.26(4)
V/Å^3	7952(8)
Z	2
D_c/g cm^{-3}	1.430
$F(000)$	3512
μ(Mo $K\alpha$)/cm^{-1}	4.46
No. of measured reflections	10830
No. of observations ($I > 3\sigma(I)$)	5133
No. of variables	961
Final residuals[a)]	
R	0.055
R_w	0.058
Largest peak in final diff. fourier/ e Å^{-3}	0.56

a) Function minimised: $\Sigma w(|F_o|-|F_c|)^2$, where $w=4F_o^2/\sigma^2(F_o^2)$; $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where N_o = number of observations, N_v = number of variables. The final discrepancy factors: $R=\frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$ and $R=\sqrt{(\frac{\Sigma(|F_o|-|F_c|)^2}{\Sigma wF_o^2})}$.

The weak reflections ($I<10\sigma(I)$) were rescanned (maximum 2 rescans), and the counts were accumulated in order to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time was 2 : 1. The intensities of three representative reflections, which were measured after every 150 reflections, slightly declined (ca. 7%). A linear correction factor was applied to the data to account for these phenomena.

An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.67 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[13)] The non-hydrogen atoms were refined anisotropically, except for six carbon atoms of C69, C70, C71, C72, C73, and C74. Refinements were carried out by a full-matrix least-squares method. All of the hydrogen atoms were located at the calculated positions. The final discrepancy factors, (R and R_w), are listed in Table 1.

The neutral-atom scattering factors were taken from Cromer and Waber.[14)] Anomalous dispersion effects were included in F_c; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[14)] All of the calculations were performed using the TEXSAN[15)] crystallographic software package of Molecular Structure Corporation. The final positional and thermal parameters, along with their estimated standard deviations, are given in Table 2. The coordinates and isotropic temperature factors of the hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the F_o-F_c tables have been deposited as Document No. 71001 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis. The reaction mixture of $Ph_2CHCOOH$, 2, 2′-bipyridine, and $ZrCl_4$ in acetonitrile formed the intermediate compound, $[Zr_3Cl_6(Ph_2CHCOO)_6(bpy)_2]$ (**2**), under the presence of triethylamine. The intermediate compound was converted into the hexanuclear Zr(IV) compound, $[Zr_6(OH)_8(OCH_3)_4(Ph_2CHCOO)_{12}]\cdot 2CH_3CN$ (**1**), when methanol was introduced. Since the intermediate compound was micro-crystalline, we have not yet succeed in an X-ray analysis.

Crystal Structure. Complex **1** crystallizes in the monoclinic $P2_1/n$ space group and possesses a crystallographic inversion center, thus making half of the molecule unique. An ORTEP drawing of the molecule is shown in Fig. 1. Complex **1** consists of a hexanuclear zirconium(IV) core where six zirconium ions are arranged at the apices of an octahedron. The Zr_6 core, however, is slightly compressed in the Zr1–Zr1* direction. Thus, this complex can be taken as a molecule of quasi-D_{4h} symmetry with a C_4 axis passing through the Zr1–Zr1* direction, rather than O_h symmetry when ligand orientation is neglected. The other four zirconium ions are on the equatorial plane (Fig. 2). Three zirconium ions on each trigonal surface of the octahedron are linked by a μ_3-hydroxo bridge. The axial Zr1 is joined to four equatorial zirconium ions with four *syn–syn* bridging carboxylato ligands. An eight-coordination of Zr1 is formed with four hydroxo oxygens and four carboxylato oxygens. On the other hand, the equatorial zirconium ions are not joined to each other by a carboxylato bridge, but are coordinated by monodentate carboxylate and methoxide. Each equatorial zirconium ion also has an eight-coordinate geometry formed with four hydroxo oxygens, two carboxylato (bridging) oxygens, one carboxylato (monodentate) oxygen, and a methoxide oxygen. The hexanuclear core is surrounded by a total of 24 phenyl groups of diphenylacetate ions. Selected bond distances and angles for **1** are listed in Table 3. The axial Zr1···Zr1* distance (4.944(3) Å) is slightly shorter than the equatorial Zr···Zr* distance (5.04 Å, average of Zr2···Zr2* and Zr3···Zr3*), as described above. The three zirconium ions on each trigonal surface of the octahedron form an almost regular triangle with an average Zr···Zr distance of 3.54 Å. This distance is larger than that reported for the trinuclear complex, $[Zr_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}PhCOO)_3(\eta^5\text{-}C_5H_5)_3]^+$ (3.354 Å).[16)] The bond dis-

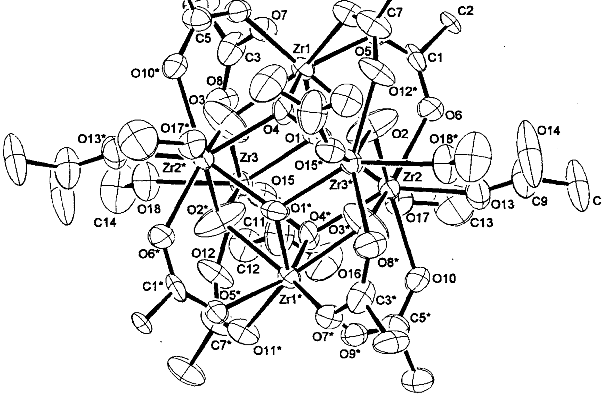


Fig. 1. An ORTEP drawing of complex **1**. Phenyl rings are not shown for clarity.

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for **1** with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{\mathrm{eq}}/\text{Å}^2$
Zr(1)	0.88356(6)	0.03346(5)	0.04251(5)	2.38(5)
Zr(2)	0.95964(6)	0.05031(5)	−0.10998(5)	2.38(5)
Zr(3)	1.06169(6)	0.09849(5)	0.04131(5)	2.50(5)
O(1)	0.9552(4)	0.0893(4)	−0.0123(4)	5.0(5)
O(2)	0.8954(6)	−0.0081(4)	−0.0549(4)	6.9(6)
O(3)	0.9957(4)	0.0396(4)	0.0951(5)	6.9(5)
O(4)	0.9318(4)	−0.0588(4)	0.0518(4)	6.5(5)
O(5)	0.8024(4)	0.0904(3)	−0.0216(4)	2.8(4)
O(6)	0.8502(4)	0.0988(4)	−0.1181(4)	3.7(4)
O(7)	0.8774(4)	0.1205(3)	0.0950(3)	2.8(4)
O(8)	0.9906(4)	0.1627(4)	0.0968(4)	4.3(4)
O(9)	0.8602(4)	0.0075(3)	0.1429(4)	3.0(4)
O(10)	1.0426(4)	0.0474(3)	−0.1859(3)	3.4(4)
O(11)	0.7839(4)	−0.0233(3)	0.0287(4)	3.2(4)
O(12)	1.1815(4)	0.1091(3)	0.0209(4)	4.2(4)
O(13)	0.9021(4)	0.0210(4)	−0.2013(4)	4.2(4)
O(14)	0.8151(7)	−0.0458(5)	−0.2278(5)	10.1(7)
O(15)	1.0723(4)	0.1890(3)	0.0044(4)	3.2(4)
O(16)	1.1061(5)	0.2010(4)	−0.0962(5)	6.5(6)
O(17)	0.9804(4)	0.1483(3)	−0.1381(4)	3.2(4)
O(18)	1.1263(4)	0.1171(3)	0.1393(4)	4.3(4)
N(1)	0.613(1)	0.125(1)	0.216(1)	14(2)
C(1)	0.8048(6)	0.1126(5)	−0.0779(6)	3.0(6)
C(2)	0.7489(5)	0.1635(5)	−0.1010(5)	3.0(6)
C(3)	0.9261(8)	0.1601(6)	0.1138(6)	4.0(7)
C(4)	0.9020(7)	0.2077(6)	0.1634(7)	4.4(7)
C(5)	0.8917(7)	−0.0289(5)	0.1850(6)	3.3(6)
C(6)	0.8450(6)	−0.0517(6)	0.2383(6)	3.7(6)
C(7)	0.7721(7)	−0.0754(6)	0.0026(6)	3.6(7)
C(8)	0.6921(6)	−0.1000(5)	−0.0023(7)	4.3(7)
C(9)	0.850(1)	0.0013(7)	−0.2396(7)	5.7(9)
C(10)	0.829(1)	0.0400(7)	−0.3033(7)	6.7(9)
C(11)	1.1068(7)	0.2171(6)	−0.0369(8)	4.7(8)
C(12)	1.1504(7)	0.2752(5)	−0.0135(6)	4.2(7)
C(13)	0.9518(8)	0.1755(7)	−0.1993(7)	6.8(9)
C(14)	1.1596(9)	0.1750(6)	0.1568(7)	7(1)
C(15)	0.7901(6)	0.2223(6)	−0.1139(6)	3.6(6)
C(16)	0.8538(7)	0.2398(5)	−0.0734(6)	3.8(6)
C(17)	0.8891(8)	0.2936(7)	−0.0884(8)	6.0(9)
C(18)	0.864(1)	0.3288(7)	−0.141(1)	7(1)
C(19)	0.801(1)	0.3130(8)	−0.1804(9)	8(1)
C(20)	0.7658(8)	0.2602(7)	−0.1658(8)	6.4(9)
C(21)	0.6886(6)	0.1712(6)	−0.0558(6)	3.6(6)
C(22)	0.6244(7)	0.1343(6)	−0.0645(7)	4.7(7)
C(23)	0.5700(8)	0.1411(7)	−0.0255(8)	5.8(9)
C(24)	0.574(1)	0.1845(9)	0.0237(8)	7(1)
C(25)	0.636(1)	0.2217(8)	0.0321(8)	8(1)
C(26)	0.6924(7)	0.2143(7)	−0.0062(7)	5.5(8)
C(27)	0.8804(8)	0.2664(8)	0.1296(8)	5.3(9)
C(28)	0.930(1)	0.3000(8)	0.0972(9)	7(1)
C(29)	0.911(1)	0.356(1)	0.070(1)	10(1)
C(30)	0.843(2)	0.381(1)	0.074(1)	12(2)
C(31)	0.795(1)	0.349(1)	0.106(2)	13(2)
C(32)	0.811(1)	0.292(1)	0.134(1)	9(1)
C(33)	0.9573(8)	0.2156(8)	0.2250(7)	5.1(8)
C(34)	0.997(1)	0.1675(9)	0.2512(9)	10(1)
C(35)	1.045(1)	0.172(1)	0.311(1)	10(1)
C(36)	1.052(1)	0.226(1)	0.340(1)	8(1)
C(37)	1.013(1)	0.273(1)	0.316(1)	12(2)
C(38)	0.965(1)	0.2700(8)	0.257(1)	9(1)
C(39)	0.8756(8)	−0.1095(7)	0.2725(7)	4.8(8)
C(40)	0.855(1)	−0.1659(8)	0.2433(8)	8(1)
C(41)	0.882(2)	−0.219(1)	0.271(1)	13(2)
C(42)	0.934(2)	−0.219(1)	0.324(1)	13(2)
C(43)	0.953(1)	−0.165(1)	0.356(1)	11(2)
C(44)	0.926(1)	−0.1078(8)	0.3273(9)	8(1)
C(45)	0.8323(8)	−0.0003(7)	0.2881(7)	4.9(8)
C(46)	0.883(1)	0.042(1)	0.307(1)	12(2)
C(47)	0.869(2)	0.083(1)	0.355(1)	16(2)
C(48)	0.809(2)	0.084(1)	0.385(1)	15(2)
C(49)	0.755(1)	0.043(1)	0.365(1)	10(1)
C(50)	0.7653(9)	−0.0001(8)	0.3151(8)	7(1)
C(51)	0.6480(7)	−0.0744(6)	0.0516(7)	4.2(7)
C(52)	0.5978(7)	−0.0269(7)	0.0453(7)	5.4(8)
C(53)	0.5600(8)	−0.0087(7)	0.098(1)	7(1)
C(54)	0.572(1)	−0.036(1)	0.159(1)	7(1)
C(55)	0.622(1)	−0.0825(8)	0.1670(8)	7(1)
C(56)	0.6590(8)	−0.1015(7)	0.1135(9)	6(1)
C(57)	0.6566(6)	−0.0874(6)	−0.0721(7)	4.1(7)
C(58)	0.6678(8)	−0.0341(7)	−0.1045(8)	7(1)
C(59)	0.636(1)	−0.0241(8)	−0.168(1)	8(1)
C(60)	0.593(1)	−0.068(1)	−0.1981(8)	7(1)
C(61)	0.579(1)	−0.121(1)	−0.168(1)	8(1)
C(62)	0.6095(8)	−0.1299(7)	−0.104(1)	7(1)
C(63)	0.748(1)	0.057(1)	−0.308(1)	8(1)
C(64)	0.736(2)	0.112(2)	−0.290(1)	17(2)
C(65)	0.673(2)	0.141(2)	−0.293(2)	17(3)
C(66)	0.614(2)	0.109(2)	−0.308(2)	17(3)
C(67)	0.614(1)	0.049(2)	−0.331(1)	15(2)
C(68)	0.689(1)	0.022(1)	−0.330(1)	13(2)
C(69)	0.850(1)	0.003(1)	−0.365(1)	10.3(6)
C(70)	0.823(2)	−0.057(2)	−0.377(2)	17(1)
C(71)	0.842(2)	−0.092(2)	−0.447(2)	23(2)
C(72)	0.889(2)	−0.046(2)	−0.476(2)	19(1)
C(73)	0.895(2)	0.002(2)	−0.457(2)	25(2)
C(74)	0.877(3)	0.032(2)	−0.406(3)	30(2)
C(75)	1.2317(9)	0.2729(6)	−0.022(1)	6(1)
C(76)	1.257(1)	0.2613(8)	−0.080(1)	8(1)
C(77)	1.333(1)	0.261(1)	−0.087(2)	12(2)
C(78)	1.382(2)	0.275(2)	−0.033(3)	18(4)
C(79)	1.356(2)	0.286(2)	0.025(2)	17(3)
C(80)	1.283(1)	0.2846(8)	0.032(1)	11(1)
C(81)	1.1149(8)	0.3342(6)	−0.040(1)	5.4(8)
C(82)	1.0890(9)	0.3420(8)	−0.104(1)	8(1)
C(83)	1.061(1)	0.397(1)	−0.128(1)	12(2)
C(84)	1.059(1)	0.444(1)	−0.088(2)	12(2)
C(85)	1.083(2)	0.439(1)	−0.018(2)	13(2)
C(86)	1.111(1)	0.3834(8)	0.003(1)	9(1)
C(87)	0.711(1)	0.0907(9)	0.145(1)	11(1)
C(88)	0.664(2)	0.113(1)	0.186(1)	14(2)

Table 3. Selected Bond Distances (Å) and Angles (°) for **1**

Zr1–O1	2.171(8)	Zr1–O2	2.211(8)	Zr1–O3	2.192(8)
Zr1–O4	2.19(1)	Zr1–O5	2.229(7)	Zr1–O7	2.181(7)
Zr1–O9	2.204(7)	Zr1–O11	2.177(7)	Zr2–O1	2.170(7)
Zr2–O2	2.122(8)	Zr2–O3*	2.123(8)	Zr2–O4*	2.188(8)
Zr2–O6	2.233(8)	Zr2–O10	2.269(7)	Zr2–O13	2.126(8)
Zr2–O17	2.248(7)	Zr3–O1	2.117(7)	Zr3–O2*	2.118(9)
Zr3–O3	2.132(9)	Zr3–O4*	2.098(7)	Zr3–O8	2.279(8)
Zr3–O12	2.264(8)	Zr3–O15	2.122(8)	Zr3–O18	2.235(8)
Zr1–Zr3	3.521(3)	Zr1–Zr2	3.548(2)	Zr2–Zr3	3.570(2)
Zr1–Zr3*	3.533(2)	Zr1–Zr2*	3.521(2)	Zr2–Zr3*	3.560(3)
Zr1–Zr1*	4.944(3)	Zr2–Zr2*	5.052(3)	Zr3–Zr3*	5.03(3)
Zr3–O1–Zr2	112.8(3)	Zr3–O1–Zr1	110.4(4)	Zr2–O1–Zr1	109.7(4)
Zr3*–O2–Zr2	114.2(4)	Zr3*–O2–Zr1	109.4(4)	Zr2–O2–Zr1	109.9(4)
Zr2*–O3–Zr3	113.6(4)	Zr2*–O3–Zr1	109.3(4)	Zr3–O3–Zr1	109.0(4)
Zr3*–O4–Zr1	111.1(4)	Zr3*–O4–Zr2*	112.8(3)	Zr1–O4–Zr2*	107.2(4)
O1–Zr1–O2	69.3(3)	O1–Zr1–O3	69.1(3)	O1–Zr1–O4	107.6(3)
O1–Zr1–O5	77.4(3)	O1–Zr1–O7	80.3(3)	O1–Zr1–O9	143.6(3)
O1–Zr1–O11	141.5(3)	O2–Zr1–O3	106.7(3)	O2–Zr1–O4	68.0(3)
O2–Zr1–O5	79.9(3)	O2–Zr1–O7	144.0(3)	O2–Zr1–O9	140.7(3)
O2–Zr1–O11	79.2(3)	O3–Zr1–O4	71.0(3)	O3–Zr1–O5	140.1(3)
O3–Zr1–O7	78.6(3)	O3–Zr1–O9	79.9(3)	O3–Zr1–O11	143.8(3)
O4–Zr1–O5	142.3(3)	O4–Zr1–O7	142.5(3)	O4–Zr1–O9	78.5(3)
O4–Zr1–O11	78.9(3)	O5–Zr1–O7	74.9(3)	O5–Zr1–O9	120.2(3)
O5–Zr1–O11	75.9(3)	O7–Zr1–O9	75.1(3)	O7–Zr1–O11	118.0(3)
O9–Zr1–O11	74.6(3)	O1–Zr2–O2	70.9(3)	O1–Zr2–O3	106.2(3)
O1–Zr2–O4	65.9(3)	O1–Zr2–O6	76.3(3)	O1–Zr2–O10	136.6(3)
O1–Zr2–O13	148.7(3)	O1–Zr2–O17	83.5(3)	O2–Zr2–O3	66.2(3)
O2–Zr2–O4	106.0(4)	O2–Zr2–O6	77.8(3)	O2–Zr2–O10	141.6(3)
O2–Zr2–O13	92.1(3)	O2–Zr2–O17	144.9(3)	O3–Zr2–O4	72.2(3)
O3–Zr2–O6	139.9(3)	O3–Zr2–O10	78.6(3)	O3–Zr2–O13	89.5(3)
O3–Zr2–O17	146.8(3)	O4–Zr2–O6	137.5(3)	O4–Zr2–O10	75.4(3)
O4–Zr2–O13	145.4(3)	O4–Zr2–O17	83.8(3)	O6–Zr2–O10	127.6(3)
O6–Zr2–O13	74.4(3)	O6–Zr2–O17	72.9(3)	O10–Zr2–O13	72.2(3)
O10–Zr2–O17	73.2(3)	O13–Zr2–O17	98.1(3)	O1–Zr3–O2	106.2(4)
O1–Zr3–O3	71.3(3)	O1–Zr3–O4	68.5(3)	O1–Zr3–O8	77.4(3)
O1–Zr3–O12	138.7(3)	O1–Zr3–O15	91.0(3)	O1–Zr3–O18	146.6(3)
O2–Zr3–O3	66.1(3)	O2–Zr3–O4	71.4(3)	O2–Zr3–O8	136.2(3)
O2–Zr3–O12	76.9(3)	O2–Zr3–O15	149.3(3)	O2–Zr3–O18	84.4(3)
O3–Zr3–O4	107.9(4)	O3–Zr3–O8	74.7(3)	O3–Zr3–O12	139.2(3)
O3–Zr3–O15	144.6(3)	O3–Zr3–O18	85.3(3)	O4–Zr3–O8	142.2(3)
O4–Zr3–O12	74.1(3)	O4–Zr3–O15	92.6(4)	O4–Zr3–O18	143.6(3)
O8–Zr3–O12	129.2(3)	O8–Zr3–O15	71.6(3)	O8–Zr3–O18	73.5(3)
O12–Zr3–O15	73.4(3)	O12–Zr3–O18	74.1(3)	O15–Zr3–O18	95.1(3)

Symmetry code: $2-x$, $-y$, $-z$.

tances between the three zirconium ions and the μ_3-hydroxo oxygen (Zr–O_{OH}) are in the range of 2.098(7)—2.211(8) Å (average, 2.15 Å). The average bond distance is comparable to those reported for Zr(IV) complexes with analogous bridging distances (2.10—2.14 Å).[17—19] The distances from O1, O2, O3, and O4 to the corresponding trigonal surfaces are 0.662, 0.657, 0.672 and 0.688 Å, respectively. The bridging angles around μ_3-O_{OH} are nearly 109°, indicating the sp^3 linkage of μ_3-bridging hydroxide oxygens. The sp^3 linkage is similar to those in a trinuclear compounds, $[Zr_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}PhCOO)_3(\eta^5\text{-}C_5H_5)_3]PhCOO$[16] and $[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CN\mathit{i}Pr_2)_6]$,[20] which have Zr–$\mu_3$-O–Zr angles of about 108°.

The bond distances around the axial zirconium are as follows. The distances to the μ_3-bridging hydroxide oxygens (Zr1–O_{OH}) are in the range of 2.171(8)—2.211(8) Å, and the distances to the carboxylato oxygens (Zr1–O_{COO}) are in the range of 2.177(7)—2.229(7) Å (average, 2.20 Å). This average Zr1–O_{COO} distance (2.20 Å) is equal to the average Zr–O distance (2.20 Å) reported for the mononuclear Zr(IV) complex with oxalato chelates, $Na_4Zr(C_2O_4)_43H_2O$.[8] It is interesting to note that chelating dibasic carboxylato and the *syn–syn* bridging monobasic carboxylato Zr–O distances are almost identical. The same Zr–O bond distances were also observed in the other Zr(IV) complexes with eight-coordination.[21—24] The O–Zr1–O angles in the $Zr1O_8$ coordination sphere are classified into three types: (i) the angles around the Zr1 ion with oxygen atoms of

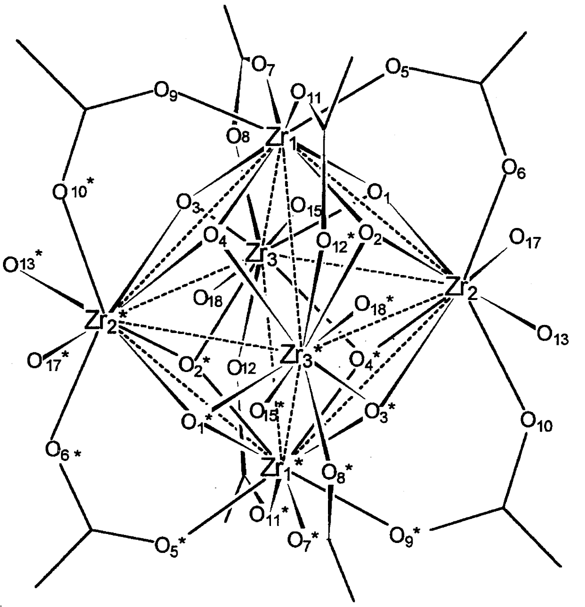
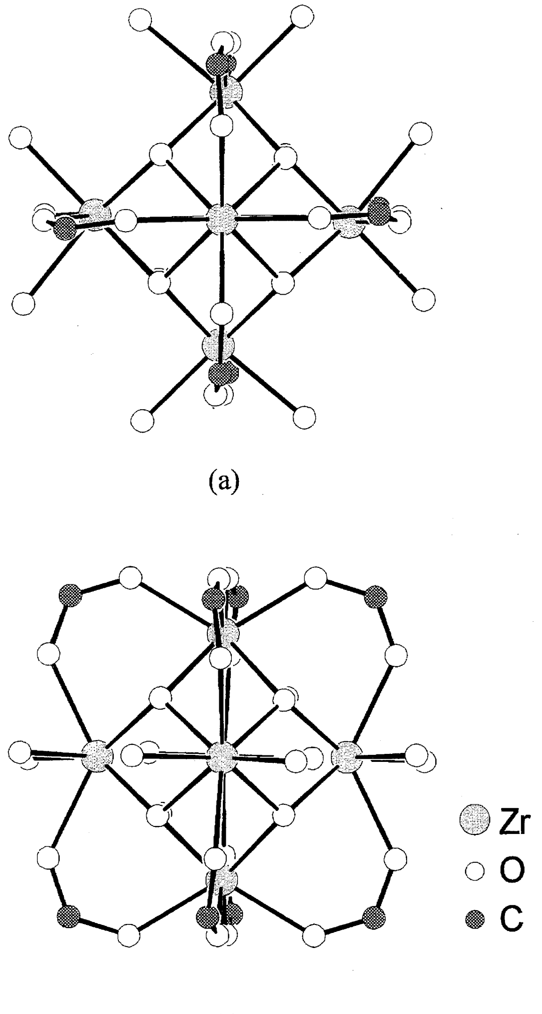


Fig. 2. Schematic drawing of complex **1** including view of Zr_6 arrangement, $[Zr_6(OH)_8]$ system and also zirconium ions with bridging carboxylates, monodentate carboxylates, and methoxy groups.

bridging hydroxides, O_{OH}–Zr1–O_{OH}; (ii) the angles around the Zr1 ion with oxygen atoms of bridging carboxylates, O_{COO}–Zr1–O_{COO}; and (iii) the bond angles of the Zr1 ion between the bridging hydroxide and the bridging carboxylate oxygens, O_{OH}–Zr1–O_{COO}; and two kinds of angles (narrow angles and wide angles) are included in each group. These angles fall in the range of 68.0(3)—71.0(3)° and 106.7(4)—107.6(3)° for O_{OH}–Zr1–O_{OH}; 74.6(3)—75.9(3)° and 118.0(3)—120.2(3)° for O_{COO}–Zr1–O_{COO}; 77.4(3)—78.3(3)° and 140.7(3)—144.0(3)° for O_{OH}–Zr1–O_{COO}, respectively. In the case of an eight-coordinate system with the ideal square-antiprismatic geometry, the angles around a central atom to the surrounding atoms are at 74.89° and 141.59°.[25)] The former narrow angle is formed with neighboring directions, and the later one is formed by more remote directions. Thus, the coordination environment of the axial eight-coordinate Zr(IV) ion is best described as a slightly distorted square antiprism defined by two square faces consisting of four hydroxide oxygens (O1, O2, O3, and O4) and four carboxylate oxygens (O5, O7, O9, and O11).

The bond distances from the equatorial zirconium to the μ_3-bridging oxygens are in the range of 2.122(8)—2.188(8) Å and 2.098(7)—2.188(7) Å for Zr2 and Zr3, respectively. The bond distances from that to the bridging carboxylato oxygens are in the range of 2.233(8)—2.279(8) Å (average, 2.25 Å). The average bond distance from the equatorial zirconiums to the monodentate carboxylato oxygens is 2.12 Å, and that from the equatorial zirconiums to methoxide oxygens is 2.24 Å. The bond angles around the equatorial Zr2 and Zr3 ions are in the range of 65.9(3)—72.2(3)° and 106.0—106.2° for O_{OH}–Zr(2 or 3)–O_{OH}; 74.7(3)—83.8(3)° and 136.2(4)—144.9(3)° for O_{OH}–Zr(2 or 3)–$O_{COO(bridging)}$; 89.5(3)—92.6(4)° and 144.6(3)—149.3(3)° for O_{OH}–Zr(2 or 3)–$O_{COO(monodentate)}$; 83.5(3)—85.3(3)° and 143.6(3)—146.8(3)° for O_{OH}–Zr(2 or 3)–$O_{methoxo}$, respectively. Beside these, the angles of $O_{COO(monodentate)}$–Zr(2 or 3)–$O_{COO(bridging)}$, $O_{COO(bridging)}$–Zr-(2 or 3)–$O_{COO(bridging)}$, $O_{methoxo}$–Zr(2 or 3)–$O_{COO(bridging)}$, and $O_{methoxo}$–Zr(2 or 3)–$O_{COO(monodentate)}$ are in the range of 71.6(3)—74.4(3)°, 127.6(3)—129.2(3)°, 72.9(3)—74.1(3)°, and 95.1(3)—98.1(3)°, respectively. Thus, the coordination environment around each equatorial zirconium ion is a distorted square antiprism with one square face consisting of four μ_3-hydroxo bridging oxygens (O1, O2, O3*, O4* for Zr2 and O1, O2*, O3, O4* for Zr3), and the other square face consisting of two bridging carboxylato, one methoxo and one monodentate carboxylato oxygens (O6, O10, O13, O17 for Zr2 and O8, O12, O15, O18 for Zr3) (Fig. 2).

Two sets of the Zr–O bond distances are grouped for the axial zirconium ions, one set for Zr1–O_{OH} and another for Zr1–O_{COO}. The Zr1–O bond distances are in the range of 2.171(8)—2.211(8) Å (average, 2.19 Å) for Zr1–O_{OH} and 2.177(7)—2.229(7) Å (average, 2.20 Å) for Zr1–O_{COO}, re-



(a)

(b)

Fig. 3. Perspective view through the axis of Zr1–Zr1* (a) and Zr2–Zr2* (b).

spectively. The average Zr1–O_{OH} bond distance (2.19 Å) is larger than the average equatorial Zr–O_{OH} bond distance (2.13 Å). The average bond distance (2.25 Å) of the equatorial zirconium ions for the bridging Zr–O_{COO} is longer than the average bond distance (2.20 Å) of axial zirconium ions for the bridging Zr–O_{COO}. The average Zr–O distances for all of the bonds around Zr2 (2.18 Å) and Zr3 (2.17 Å) are almost identical, but slightly shorter than the average Zr–O bond distance around Zr1 (2.19 Å). Around the equatorial zirconium ions, the O_{OH}–Zr(2 or 3)–O_{OH} angles are equal to those observed for the axial Zr1 ion. The remote methoxo and monodentate carboxylato oxygen angles, $O_{methoxo}$–Zr(2 or 3)–$O_{COO(monodentate)}$, are 95.1(3)—98.1(3)° (Fig. 3b), and are much smaller than the corresponding remote angles (O_{COO}–Zr1–O_{COO}, 118.0(3)—120.2(3)°) (Fig. 3a). On the other hand, another remote angle of $O_{COO(bridging)}$–Zr(2 or 3)–$O_{COO(bridging)}$ (127.6(3)—129.2(3)°) is larger than the later angles. However, the other O–Zr(2 or 3)–O angles have a wide distribution around 80° and 140°. Therefore, these results indicate that the coordination around each equatorial zirconium ion is assignable to a distorted square-antiprism, and that the extent of its distortion is larger than that of the axial zirconium ion (Fig. 3).

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