Exchange Mechanism on a Zr_{12} Oxo Hydroxo Cluster: Relevance for Reshaping Zr-Carboxylate Coordination Adaptable Networks

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SUPPORTING INFORMATION

1. Experimental Procedures

General. $Zr(OBu)_4$ (80% in 1-butanol, Sigma Aldrich), acetic acid (Carlo Erba), the NMR solvents (Sigma-Aldrich) and all solvents were used without further purification. The $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ compound was synthesized as described in the literature.[1]

NMR measurements. The room temperature ^1H NMR spectra and the variable-temperature ^1H NMR spectra in C_6D_6 (1D and 2D EXSY) were recorded on a Bruker AVANCE 111 400 spectrometer with the following parameters: spectral width 14 ppm, 60° nutation angle, duration 9.5 μs; recycling delay 33 s (3 s acquisition time and 30 s relaxation delay). The variable-temperature ^1H NMR spectra in CD_2Cl_2 (1D and 2D DOSY and EXSY) were recorded on a Bruker Ascend 600 spectrometer. All chemical shifts for ^1H were relative to TMS using the residual ^1H chemical shifts of the solvent as a secondary standard. The following parameters were used to record the low-T spectra in CD_2Cl_2 in the 243−298 K range: spectral width, 10 ppm; 30° nutation angle duration, 8.3 μs; recycling delay, 11.5 s (1.5 s acquisition time and 10 s relaxation delay). The spectra were 2x zero-filled and subjected to an exponential prior for Fourier transformation. The DOSY spectra were acquired with the dstebpgp3s pulse program from Bruker topspin software. All spectra were recorded with 16K time domain data point in the t2 dimension and 16 t1 increments. The gradients strength was linearly incremented in 16 steps from 2% up to 95% of the maximum gradient strength. All measurements were performed with a diffusion delay Δ of 200 ms and a gradient pulse length δ of 3.2. The EXSY spectra were acquired with a mixing time of 50 ms (in CD_2Cl_2) or 100 ms (in C_6D_6), 8 averages for each *t*1 value after 4 dummy scans, a data set of 512 time domain data point in the t2 dimension with 128 *t*1 increments, and the TPPI method for quadrature detection in the *t*1 dimension. The line shape analyses for the low-temperature spectra in CD_2Cl_2 were carried out using

the Dynamic NMR module implemented into the Bruker Topspin 4.1 program, which simulates 1D temperature-dependent NMR spectra of coupled half spin nuclei. The software refines the model parameters to get the best fit of the measured and simulated 1D NMR spectra to obtain the reaction speed parameters of exchange processes. The theory of the calculation of the DNMR module (chemical exchange operators, fitting quality, *etc.*) and detailed procedure are described in the software manual "DNMR Lineshape Analysis" written by Dr. János Rohonczy, 2007. The line shape analyses for the high-temperature spectra in C_6D_6 were carried out by least-squares fitting of the sum of three Lorentzian functions to the experimental spectra using the Solver function of Excel.

X-ray structural analysis. A single crystal was mounted under inert perfluoropolyether at the tip of glass fiber. Data were collected at low temperature (100 K) on a Rigaku XtaLAB Synergy diffractometer, using a PhotonJet-S microfocus X-ray source, with the Cu-Kα radiation (lambda = 1.54184 Å) and equipped with an Oxford Instrument Cooler Device.

The structure was solved by using the integrate space-group and crystal structure determination SHELXT[2] software and refined by least-squares procedures on F^2 using SHELXL-2014.[3] All H atoms attached to carbon atoms were introduced in the calculation at idealised positions and treated with the riding model. The H atoms attached to oxygen atoms were localized on difference Fourier synthesis and their coordinates and U_{iso} were refined using restraints. Some diffused residual electron density was observed around the (0,0,½) position and was difficult to model, therefore the SQUEEZE function of PLATON[4] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. There is one cavity of 877 $Å^3$ per unit cell. PLATON estimated that the cavity contains 222 electrons which may correspond to a mixture of acetic acid and water molecules. The molecular drawings were realised with the help of ORTEP32.[5] Crystal data and refinement parameters are

collected in Table S1 and selected bond distances are listed in Table S2.

Computational details. The calculations made use of the Gaussian09 suite of programs.[6] Geometry optimizations were carried out without any symmetry constraint using the B3LYP functional, the 6-31G(d,p) basis functions for all light atoms (H, C, O) and the SDD basis set augmented by an f polarisation function ($\alpha = 0.875$) for the Zr atom.[7] The effects of dispersion forces and of solvation effects were considered by using a polarizable continuum (SMD[8] in CH_2Cl_2) and Grimme's D3 empirical method[9] during the optimization process. The thermal corrections leading to the Gibbs energy (zero-point vibrational energy or ZPVE, PV, and TS) were obtained from the solution of the nuclear equation using the standard ideal gas and harmonic approximations at T = 298.15 K (25 °C), which also verified the nature of all optimized geometries as local minima or first-order saddle points. A correction of 1.95 kcal/mol was applied to all G values to change the standard state from the gas phase (1 atm) to solution (1 M).[10]

2. X-ray diffraction results

Table S1. Crystal data and refinement parameters for compound $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$.

CCDC deposition number	2253409
Empirical formula	$[C_{48}H_{80}O_{64}Zr_{12}]$ $(C_8H_{16}O_8)(H_4O_2)$
Formula weight	3052.00
Temperature, K	100(2)
Wavelength, Å	1.54184
Crystal system	Triclinic
Space group	P -1
a, Å	12.5024(1)
b, Å	16.6275(2)
c, Å	17.2067(2)
α,°	100.567(1)
β,°	109.891(1)
γ,°	104.994(1)
Volume	3100.64(6)
Z	1
Density (calculated)	1.634
Absorption coefficient	8.746
F(000)	1508
Crystal size	0.100 x 0.050 x 0.050
Theta range for data collection	2.862 to 77.005
Reflections collected	57874
Indpt reflections (R_{int})	12418 (0.0371)
Absorption correction	Multi-scan
Max. / min. transmission	1.0 / 0.68732
Refinement method	F^2
Data /restraints/parameters	12418 / 7 / 662
Goodness-of-fit on F^2	1.081
R1, wR2 [I>2σ(I)]	0.0370, 0.1077
R1, wR2 (all data)	0.0395, 0.1097
Residual density, e.Å^{-3}	1.499 / -1.339

Table S2. Comparison of the most relevant bond distances (Å) for the two different structures of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$.

Parameter[a]			This work	Reference 1
Zr-Zr	Inner face	Zr(1)-Zr(2)	3.5925(3)	3.5835(7)
		Zr(1)-Zr(5)	3.5767(4)	3.5883(7)
		Zr(2)-Zr(5)	3.5108(3)	3.5079(7)
		Average	***3.56(3)***	***3.56(4)***
	Belt	Zr(1)-Zr(4)	3.4537(4)	3.4619(7)
		Zr(1)-Zr(6)	3.4647(3)	3.4482(7)
		Zr(2)-Zr(3)	3.4929(3)	3.4934(7)
		Zr(2)-Zr(6)	3.4981(3)	3.4967(7)
		Zr(5)-Zr(3)	3.5108(3)	3.4881(7)
		Zr(5)-Zr(4)	3.4950(3)	3.4947(7)
		Average	***3.49(2)***	***3.48(2)***
	Outer face	Zr(3)-Zr(4)	3.5049(3)	3.5074(8)
		Zr(3)-Zr(6)	3.5295(4)	3.5088[b]
		Zr(4)-Zr(6)	3.5221(4)	3.5242[b]
		Average	***3.519(9)***	***3.513(7)***
$Zr(\mu_3\text{-OH})$		Zr(1)-O(135)	2.306(2)	2.293(3)
		Zr(2)-O(135)	2.301(2)	2.302(4)
		Zr(5)-O(135)	2.281(2)	2.291(3)
		Zr(1)-O(146)	2.308(2)	2.211(4)
		Zr(4)-O(146)	2.201(2)	2.396(3)
		Zr(6)-O(146)	2.214(2)	2.197(4)
		Zr(2)-O(256)	2.373(2)	2.217(4)
		Zr(3)-O(256)	2.226(2)	2.198(4)
		Zr(6)-O(256)	2.193(2)	2.382(3)
		Zr(3)-O(356)	2.211(2)	2.308(3)
		Zr(4)-O(356)	2.191(2)	2.210(4)
		Zr(5)-O(356)	2.382(2)	2.216(4)
		Average	***2.27(6)***	***2.27(6)***
$Zr(\mu_3\text{-O})$		Zr(1)-O(136)	2.0619(19)	2.095(4)
		Zr(2)-O(136)	2.085(2)	2.102(4)
		Zr(6)-O(136)	2.061(2)	2.092(4)
		Zr(1)-O(145)	2.067(2)	2.033(3)
		Zr(4)-O(145)	2.059(2)	2.046(3)
		Zr(5)-O(145)	2.079(2)	2.045(4)
		Zr(2)-O(235)	2.047(2)	2.066(4)
		Zr(3)-O(235)	2.037(2)	2.081(4)
		Zr(5)-O(235)	2.045(2)	2.056(3)
		Zr(3)-O(346)	2.095(2)	2.070(3)
		Zr(4)-O(346)	2.092(2)	2.046(3)
		Zr(6)-O(346)	2.113(2)	2.086(3)
		Average	***2.07(2)***	***2.07(2)***

[a] Atoms numbers are as shown in Figure S1. The parameters in the reference 1 column are topologically related to those of the present structure, although they are numbered differently in reference 1. [b] Absent in the CIF of this compound (CCDC-604528); distances measured from the xyz coordinates.

Table S2 (contd).

Zr-OCOMe	chelating	Zr(3)-O(33)	2.282(2)	2.288(4)
		Zr(3)-O(34)	2.277(2)	2.253(4)
		Zr(4)-O(43)	2.258(2)	2.299(4)
		Zr(4)-O(44)	2.304(2)	2.260(4)
		Zr(6)-O(63)	2.274(2)	2.259(4)
		Zr(6)-O(64)	2.265(2)	2.296(4)
		Average	***2.277(11)***	***2.28(2)***
	outer-belt	Zr(3)-O(31)	2.223(2)	2.220(4)
		Zr(3)-O(32)	2.211(2)	2.198(4)
		Zr(4)-O(41)	2.247(2)	2.200(4)
		Zr(4)-O(42)	2.229(2)	2.230(4)
		Zr(6)-O(61)	2.236(2)	2.217(4)
		Zr(6)-O(62)	2.202(2)	2.229(4)
	inner-belt	Zr(1)-O(11)	2.192(2)	2.202(4)
		Zr(1)-O(12)	2.209(2)	2.210(4)
		Zr(2)-O(21)	2.192(2)	2.193(4)
		Zr(2)-O(22)	2.214(2)	2.222(4)
		Zr(5)-O(53)	2.170(2)	2.220(4)
		Zr(5)-O(54)	2.217(2)	2.229(4)
	inner-face-bridging	Zr(2)-O(25)	2.219(2)	2.216(4)
		Zr(5)-O(51)	2.253(2)	2.196(4)
	intercluster-bridging	Zr(1)-O(14)	2.217(2)	2.215(4)
		Zr(1)-O(15)	2.202(2)	2.200(3)
		Zr(2)-O(55)	2.191(2)	2.176(4)
		Zr(5)-O(52)	2.185(2)	2.199(4)
		Average	***2.21(2)***	***2.210(12)***

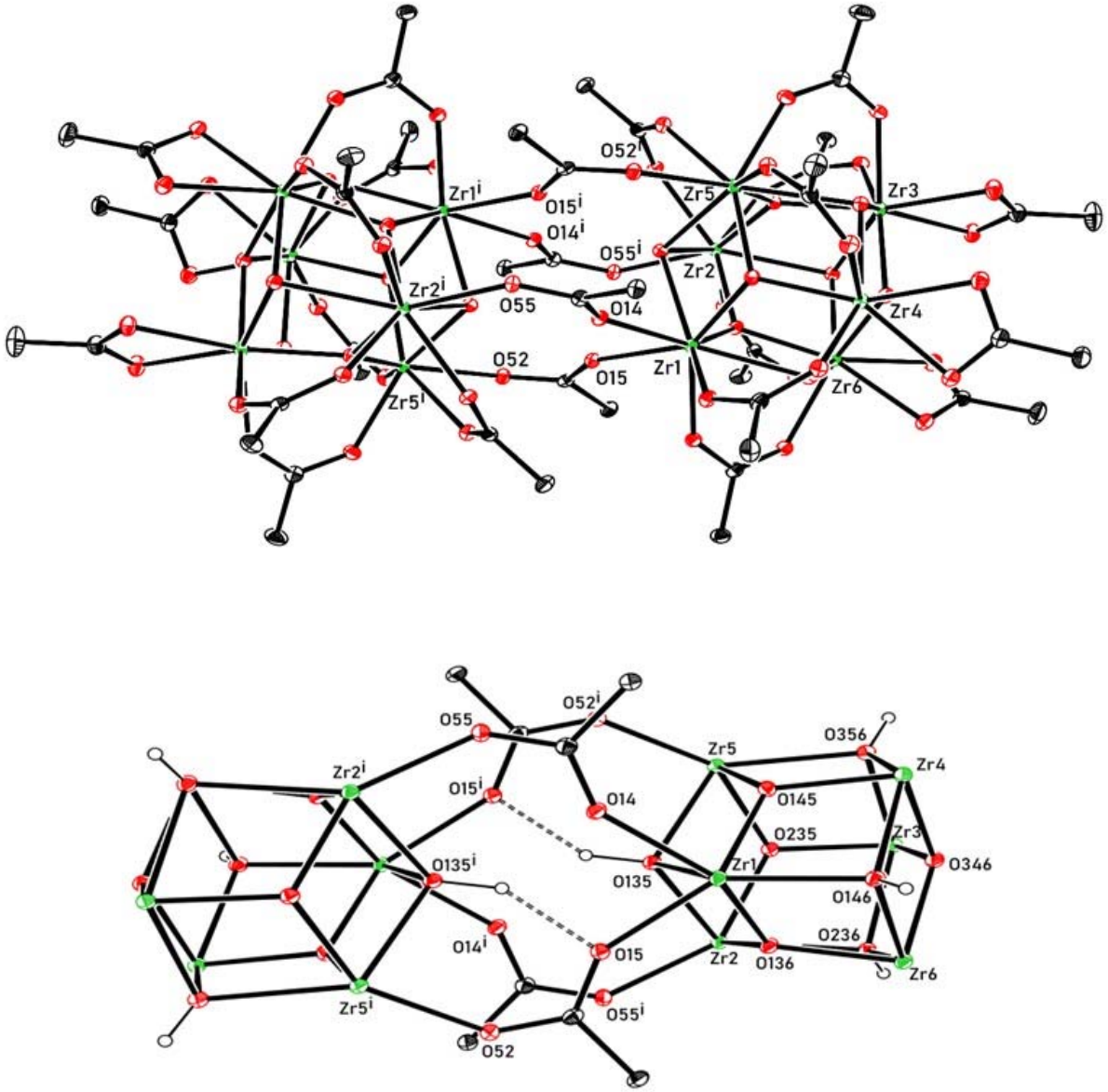

Figure S1. ORTEP views of the $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ structure. In the top structure, all H atoms are omitted for clarity. In the bottom structure, all acetates are removed except for the intercluster-bridging ones. The H atoms of the μ_3-OH ligands are explicitly shown to clarify the topology of the $[Zr_6O_4(OH)_4]$ cores.

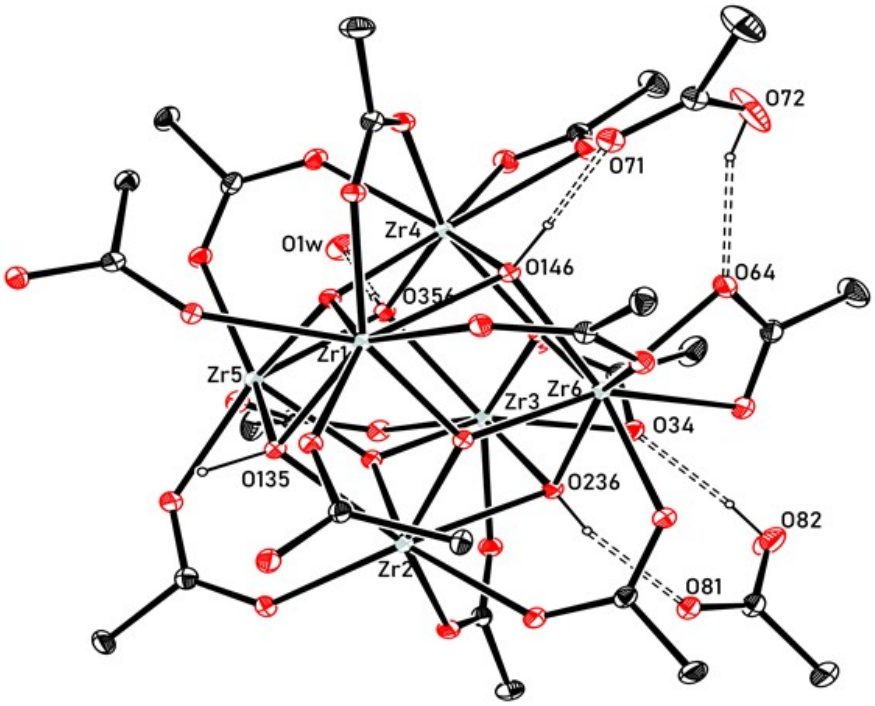

Figure S2. ORTEP view of one Zr_6 subunit of the $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ structure, highlighting the intermolecular H-bonding interactions of the cluster with two acetic acid molecules and with one water molecule.

3. Room-temperature ^{1}H NMR of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ in different solvents

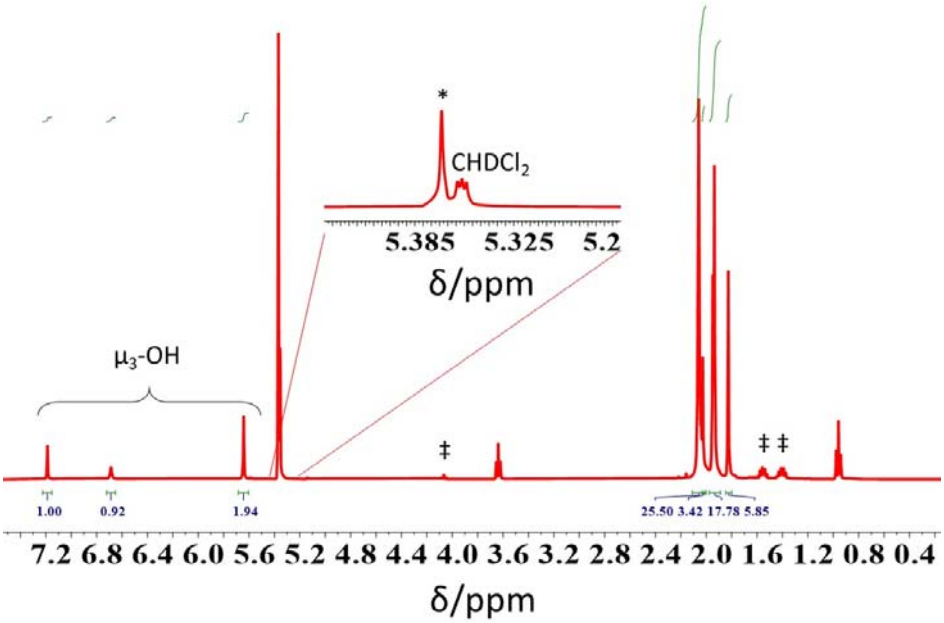

Figure S3. Room temperature ^{1}H NMR spectrum (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (5.3 mg) in CD_2Cl_2 (0.8 mL). * = co-crystallized CH_2Cl_2; ‡ = co-crystallized butanol from the compound synthesis.

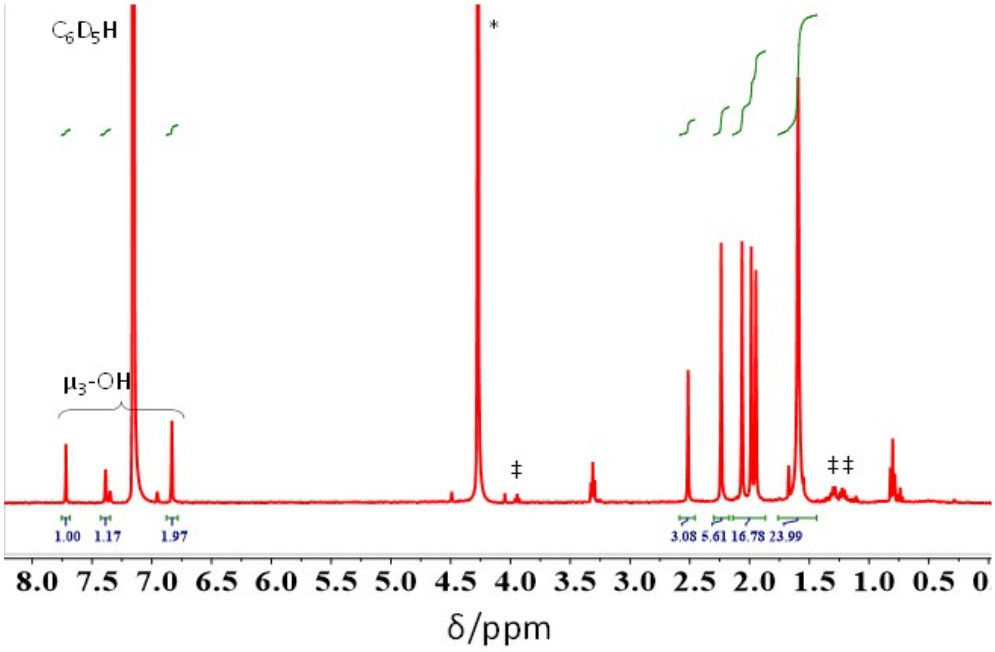

Figure S4. Room temperature ^{1}H NMR spectrum (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (8.0 mg) in C_6D_6 (0.8 mL). * = co-crystallized CH_2Cl_2; ‡ = co-crystallized butanol from the compound synthesis.

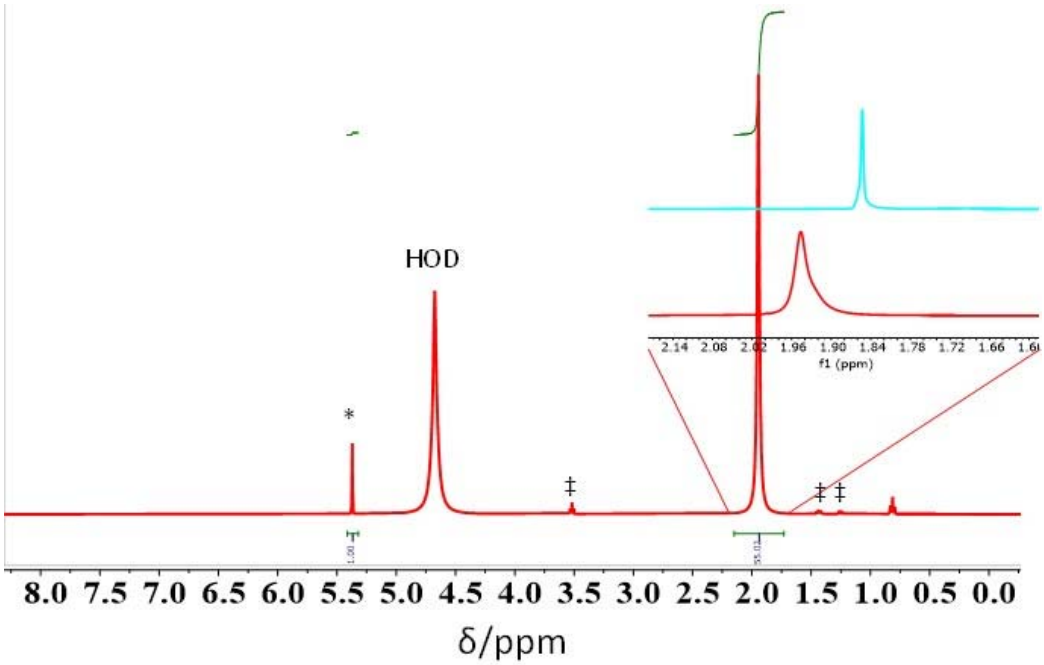

Figure S5. Room temperature ^{1}H NMR spectrum (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (15 mg) in D_2O (0.8 mL). * = co-crystallized CH_2Cl_2; ‡ = co-crystallized butanol from the compound synthesis. The blue spectrum in the inset corresponds to free CH_3COOH in the same solvent and conditions.

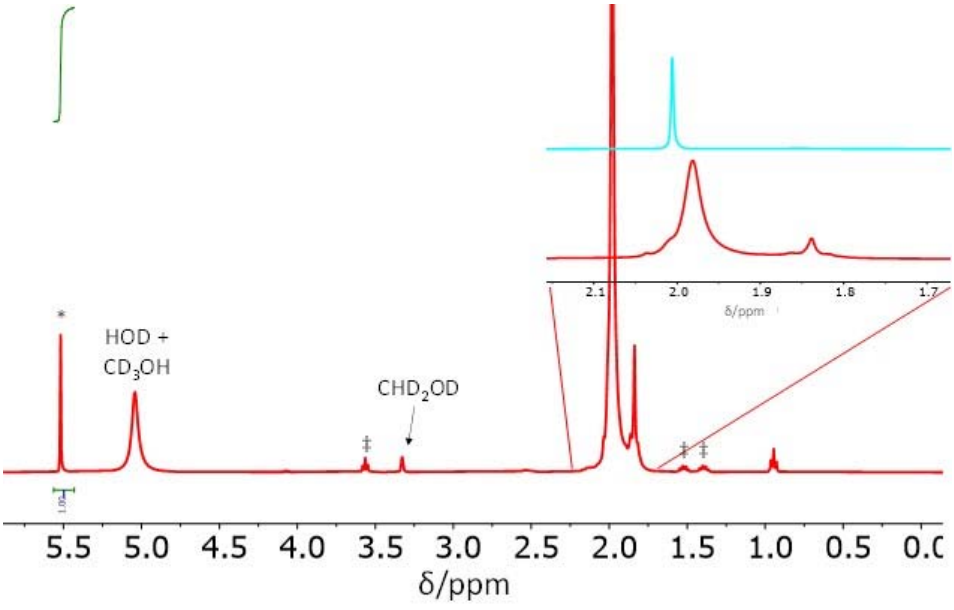

Figure S6. Room temperature ^{1}H NMR spectrum (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (15 mg) in CD_3OD (0.8 mL). * = co-crystallized CH_2Cl_2; ‡ = co-crystallized butanol from the compound synthesis. The blue spectrum in the inset corresponds to free CH_3COOH in the same solvent and conditions.

4. Variable-temperature NMR studies in CD_2Cl_2

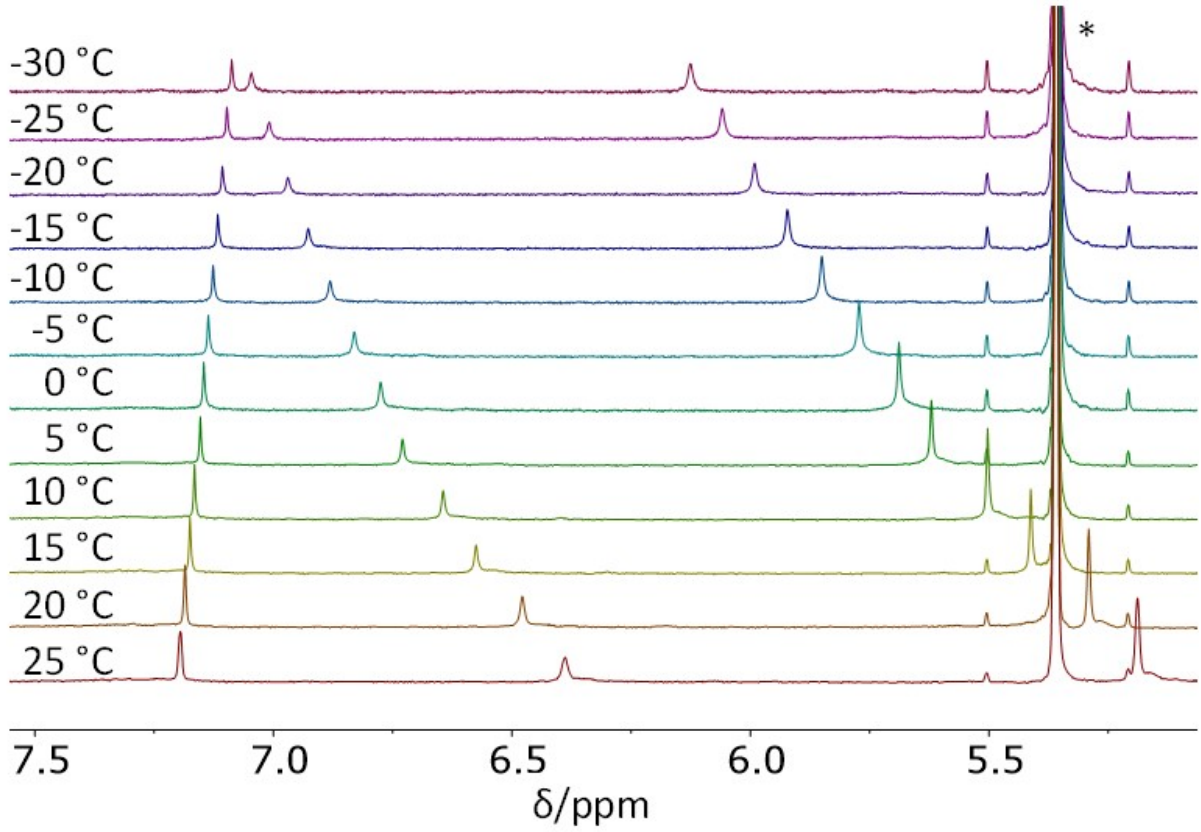

Figure S7. Variable-temperature ^{1}H NMR spectra (600 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (5.3 mg) in CD_2Cl_2 (0.8 mL) between 25 and -30 °C. (a) Acetate Me resonance region. (b) μ_3-OH region (the starred resonance, with its spinning side bands, belongs to the residual $CHDCl_2$ in the solvent).

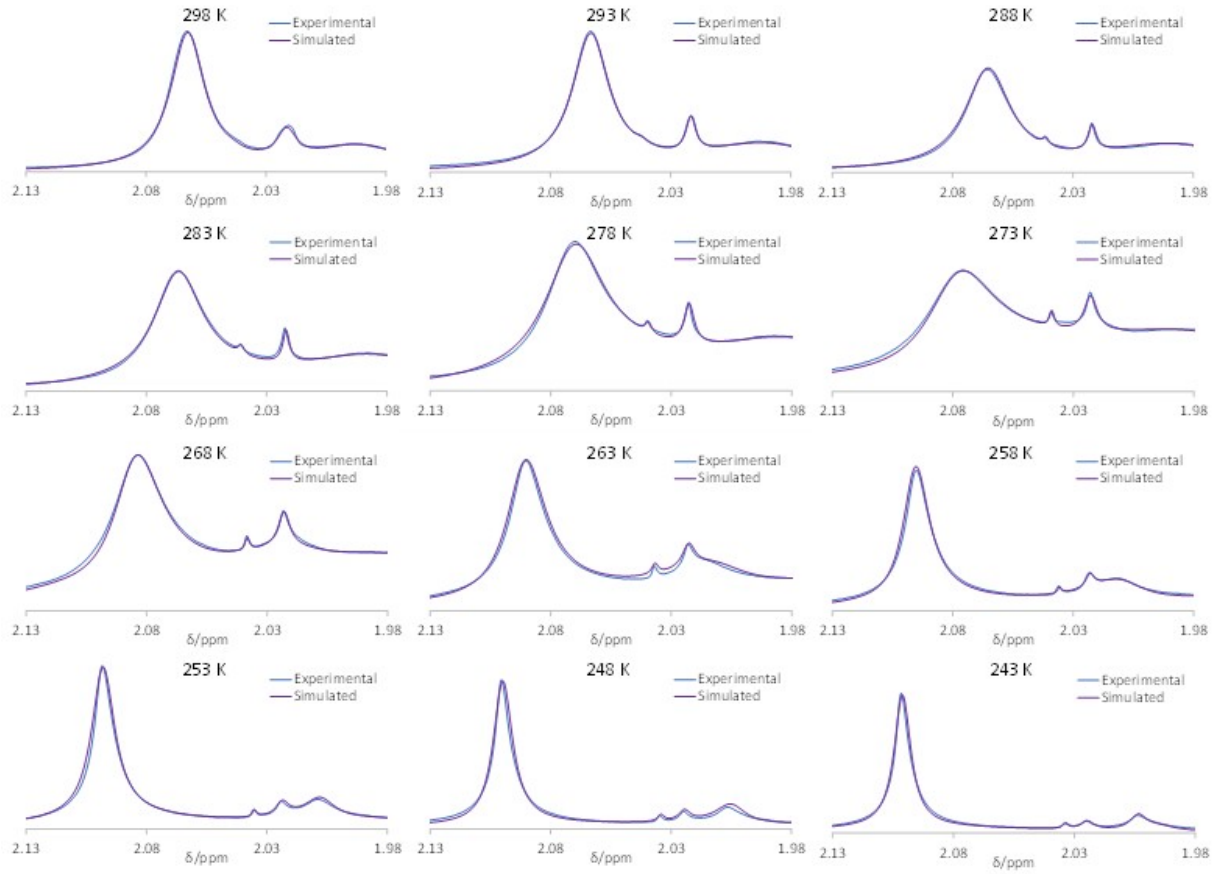

Figure S8. Simulations of the spectra recorded in CD_2Cl_2 at different temperatures (Figure S7a), highlighting the chelating acetate exchange dynamics with free acetic acid.

Table S3. Rate constants obtained from line-shape simulations of the site exchange between free acetic acid and the chelating acetate ligands of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ at different temperatures in CD_2Cl_2 (Figure S7).

T/K	T^{-1}/K^{-1}	k/s^{-1}	$\ln(k \cdot h \cdot (1/T)/k_B)$
248	0.004032	15	-26.564
253	0.003953	30	-25.891
258	0.003876	60	-25.218
263	0.003802	90	-24.831
268	0.003731	150	-24.339
273	0.003663	250	-23.847
278	0.003597	550	-23.077
283	0.003534	800	-22.720
288	0.003472	1200	-22.332

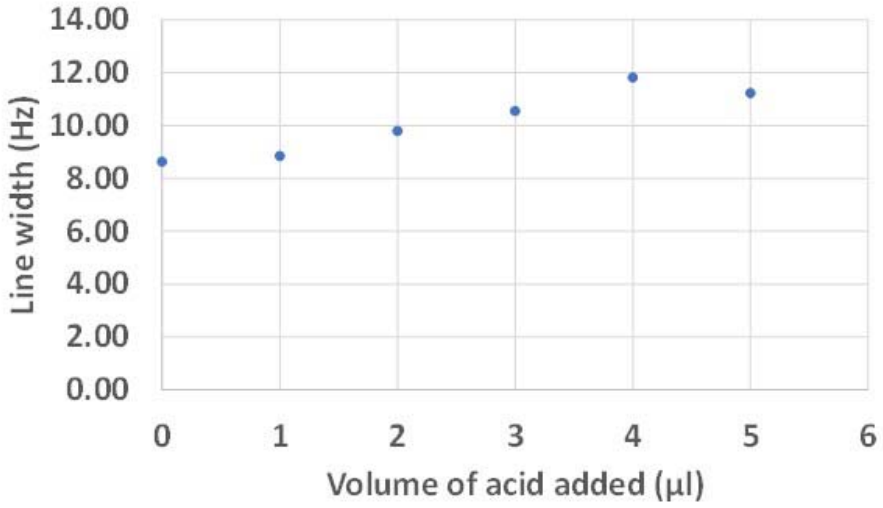

Figure S9. Dependence of the linewidth of the δ 2.00 resonance in Figure 4b on the amount of added free acetic acid.

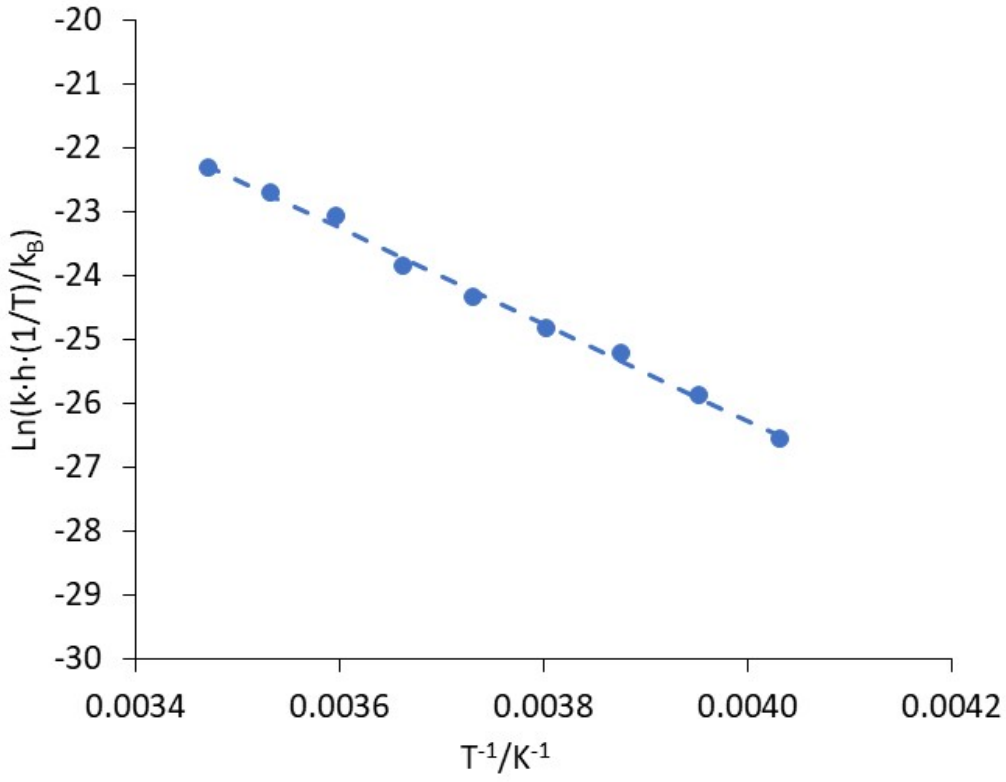

Figure S10. Eyring plot of the temperature-dependent rate constant (Table S3) for the site exchange of the chelating acetate ligands in the $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ molecule with free MeCOOH, measured in the -30 – +25 °C range in CD_2Cl_2 (Figure 4a).

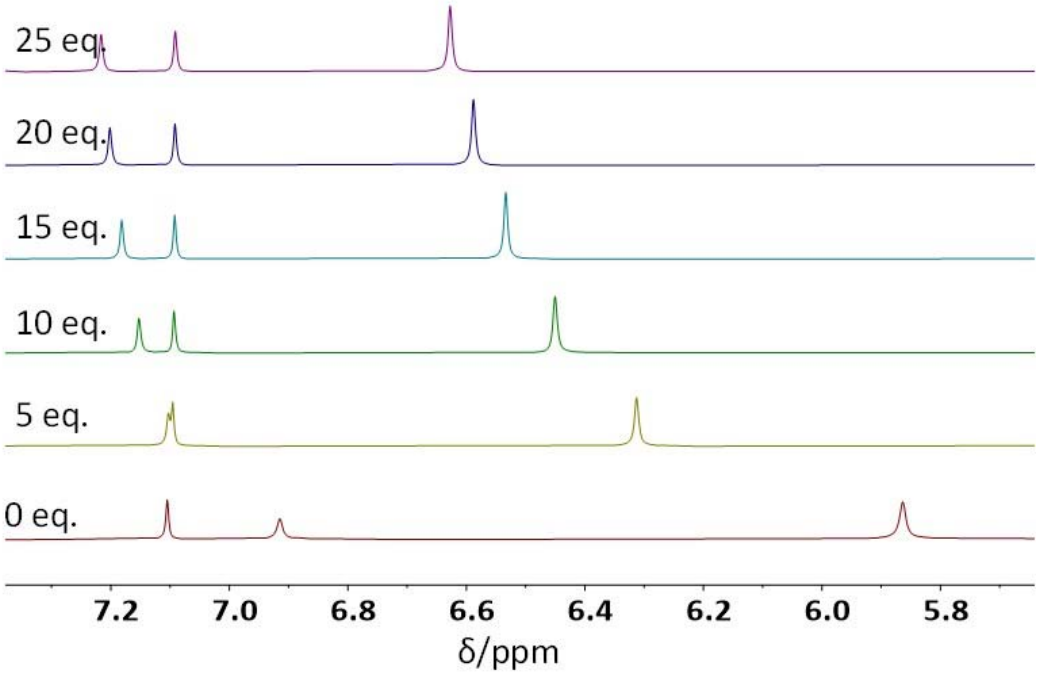

Figure S11. ^{1}H NMR spectra (600 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (5.3 mg) with different amounts of added free acetic acid at -20 °C in CD_2Cl_2 (0.8 mL) in the μ_3-OH region (1.14 µL = 5 equivalents of acetic acid per Zr_{12} unit).

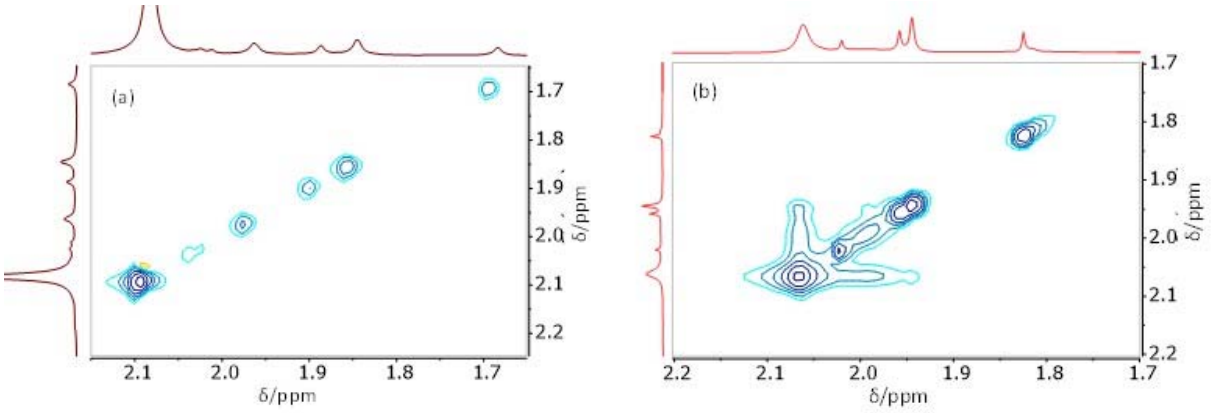

Figure S12. ^{1}H EXSY spectra (600 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (5.3 mg) in CD_2Cl_2 (0.8 mL) at 193 K (a) and 298 K (b), using 0.05 s as mixing time.

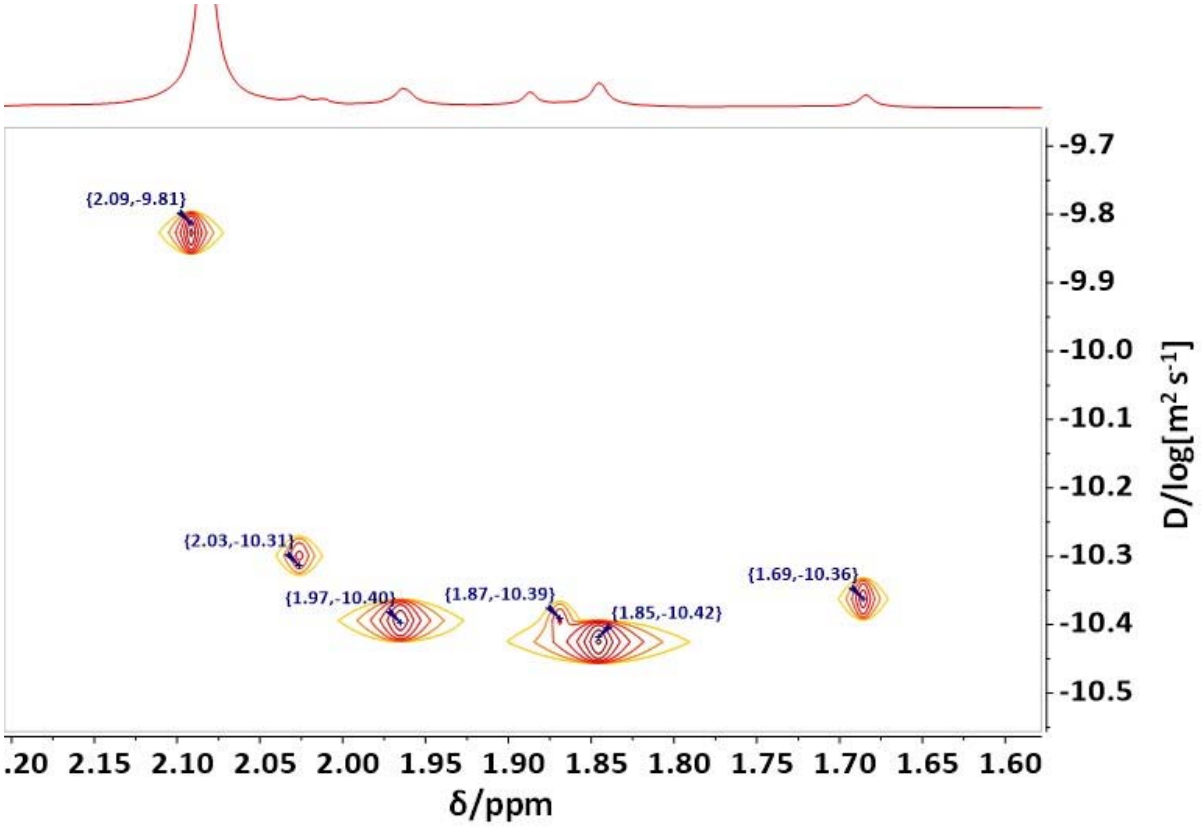

Figure S13. ^{1}H DOSY spectrum (600 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (5.3 mg) in CD_2Cl_2 (0.8 mL) at 193 K.

5. Variable-temperature NMR studies in C_6D_6

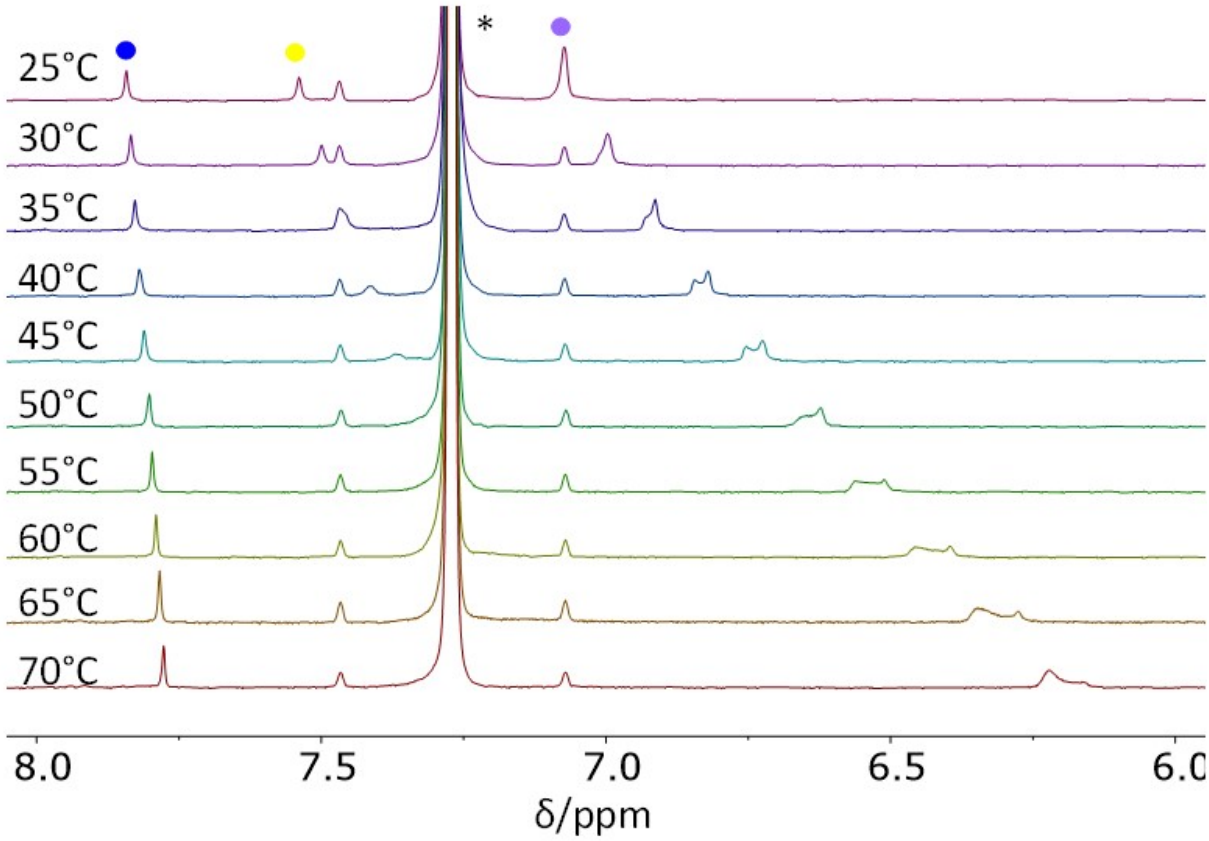

Figure S14. Variable-temperature ^{1}H NMR spectra (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (8.0 mg) in C_6D_6 (0.8 mL) between 25 and 70 °C in the μ_3-OH region (the starred resonance, with its spinning side bands, belongs to the residual C_6HD_5 in the solvent). The resonance assignments follow the same color coding used in Figure 5.

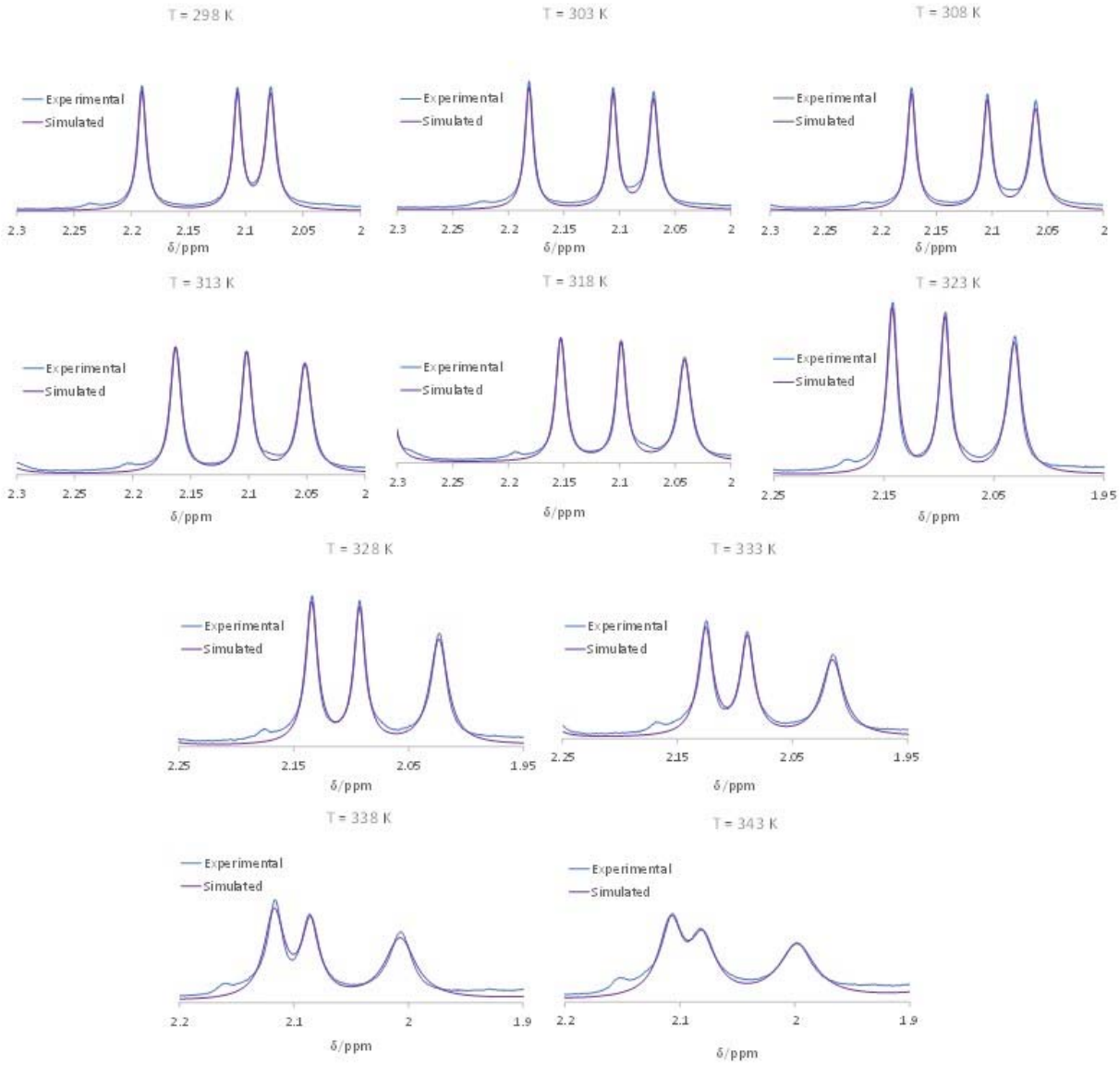

Figure S15. Simulations of the belt-bridging acetate resonances at different temperatures (spectra of Figure S14a).

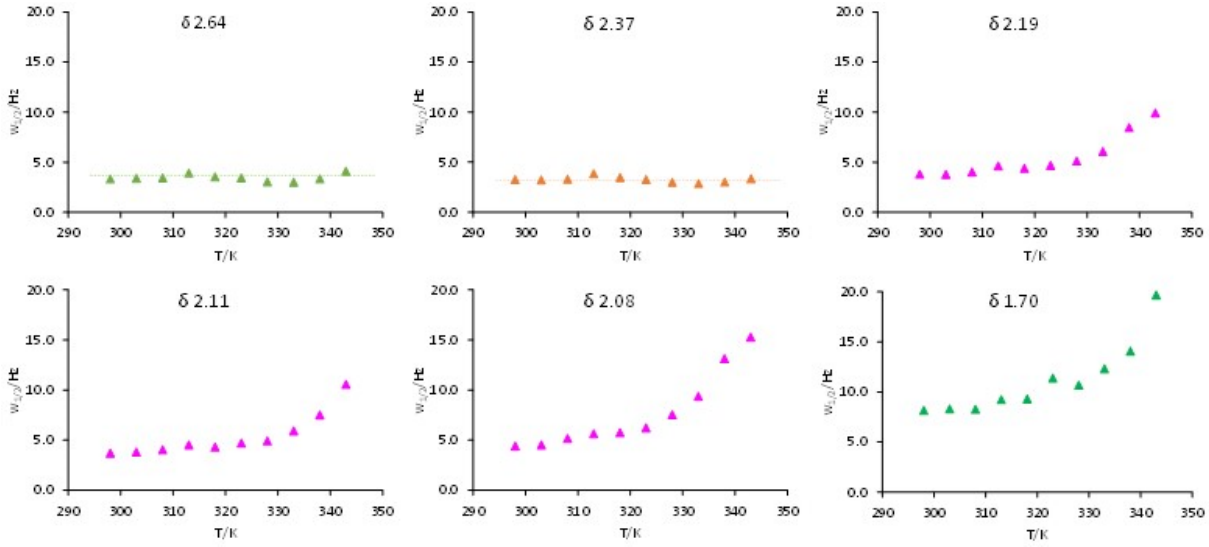

Figure S16. Temperature dependence of the linewidths of all Me resonances observed in the spectra of Figure 6a.

Table S4. Rate constants obtained from the linewidths of the belt-bridging acetate resonances[a] of the $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ spectra in C_6D_6 at different temperatures (Figure S15 and Figure S16).

		δ 2.19 resonance		δ 2.11 resonance		δ 2.08 resonance	
T/K	T^{-1}/K^{-1}	k/s^{-1}	$\ln(k\cdot h\cdot(1/T)/k_B)$	k/s^{-1}	$\ln(k\cdot h\cdot(1/T)/k_B)$	k/s^{-1}	$\ln(k\cdot h\cdot(1/T)/k_B)$
313	3.19E-03	2.37	-28.644	2.12	-28.75	2.98	-28.41
318	3.14E-03	1.64	-29.029	1.45	-29.15	3.29	-28.33
323	3.10E-03	2.56	-28.596	2.69	-28.55	4.82	-27.96
328	3.05E-03	3.94	-28.181	3.36	-28.34	8.90	-27.37
333	3.00E-03	6.92	-27.633	6.51	-27.69	14.64	-26.88
338	2.96E-03	14.44	-26.912	11.52	-27.14	26.51	-26.30
343	2.92E-03	19.00	-26.652	21.09	-26.55	33.22	-26.09

[a] $k = \pi\cdot(w_{1/2}-w_{1/2}°)$, where $w_{1/2}°$ was taken, for each resonance, as the average linewidth measured at 298, 303 and 308 K (assumed to be at the slow exchange limit).

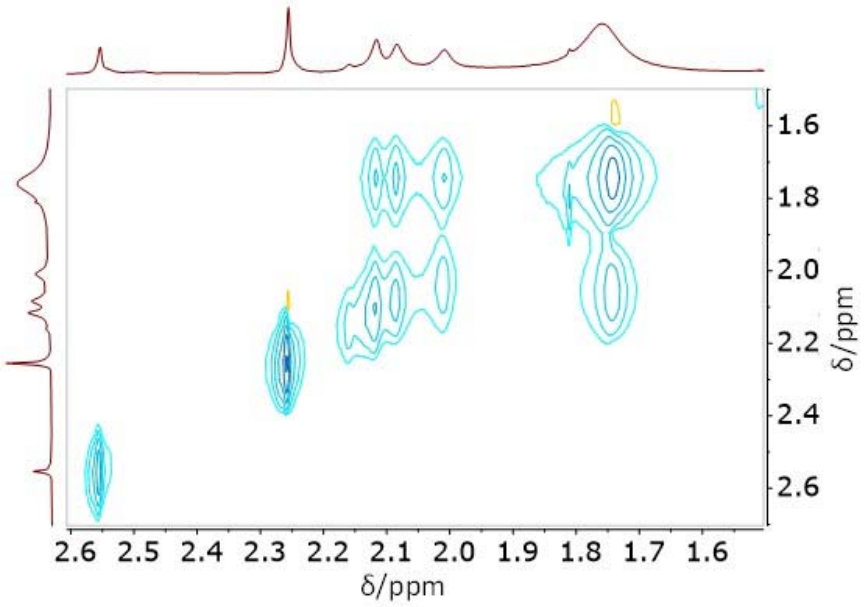

Figure S17. ^{1}H EXSY spectrum (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (8.0 mg) in C_6D_6 (0.8 mL) at 338 K, using 0.1 s as mixing time.

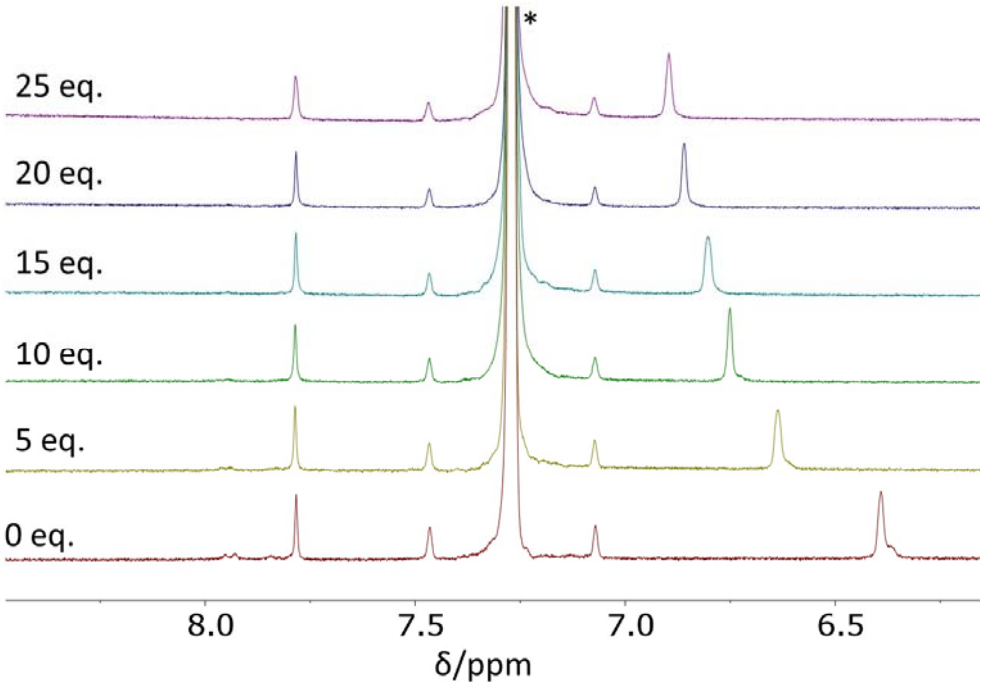

Figure S18. ^{1}H NMR spectra (400 MHz) of $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ (8.0 mg) with different amounts of added free acetic acid at 65 °C in C_6D_6 (0.8 mL) in the acetate Me resonance (a) and μ_3-OH (b) regions (1.14 μL = 5 equivalents of acetic acid per Zr_{12} unit).

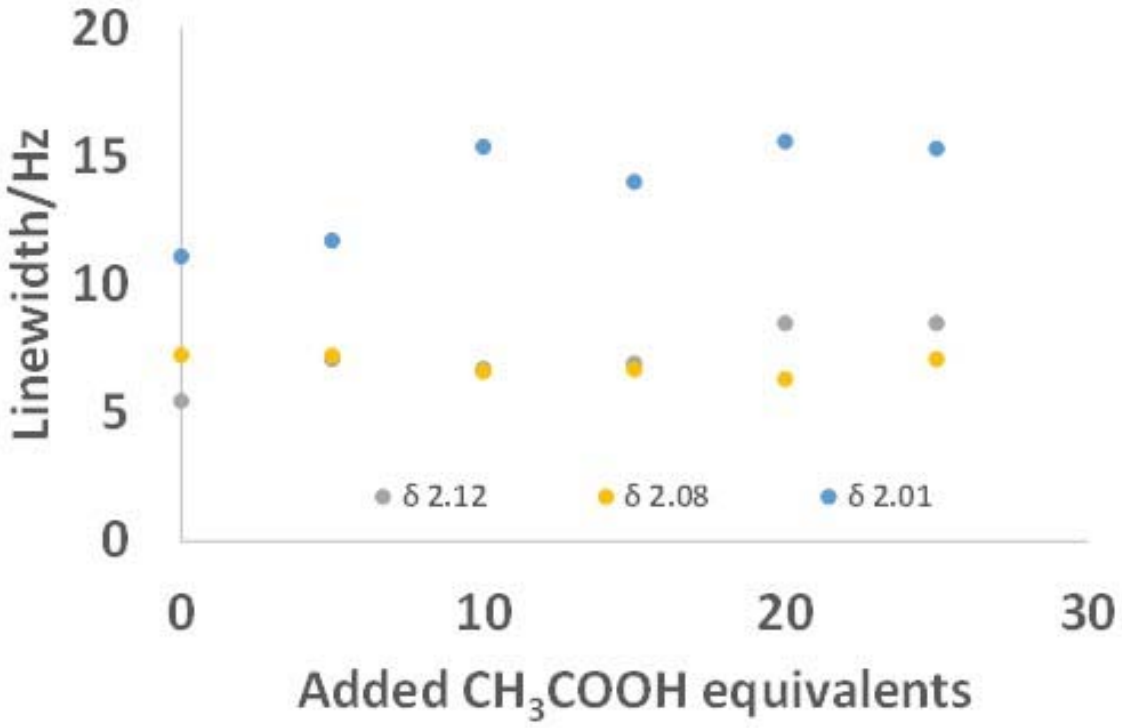

Figure S19. Dependence of the belt-bridging acetate resonance linewidth (Figure S18a) on the amount of added free acetic acid.

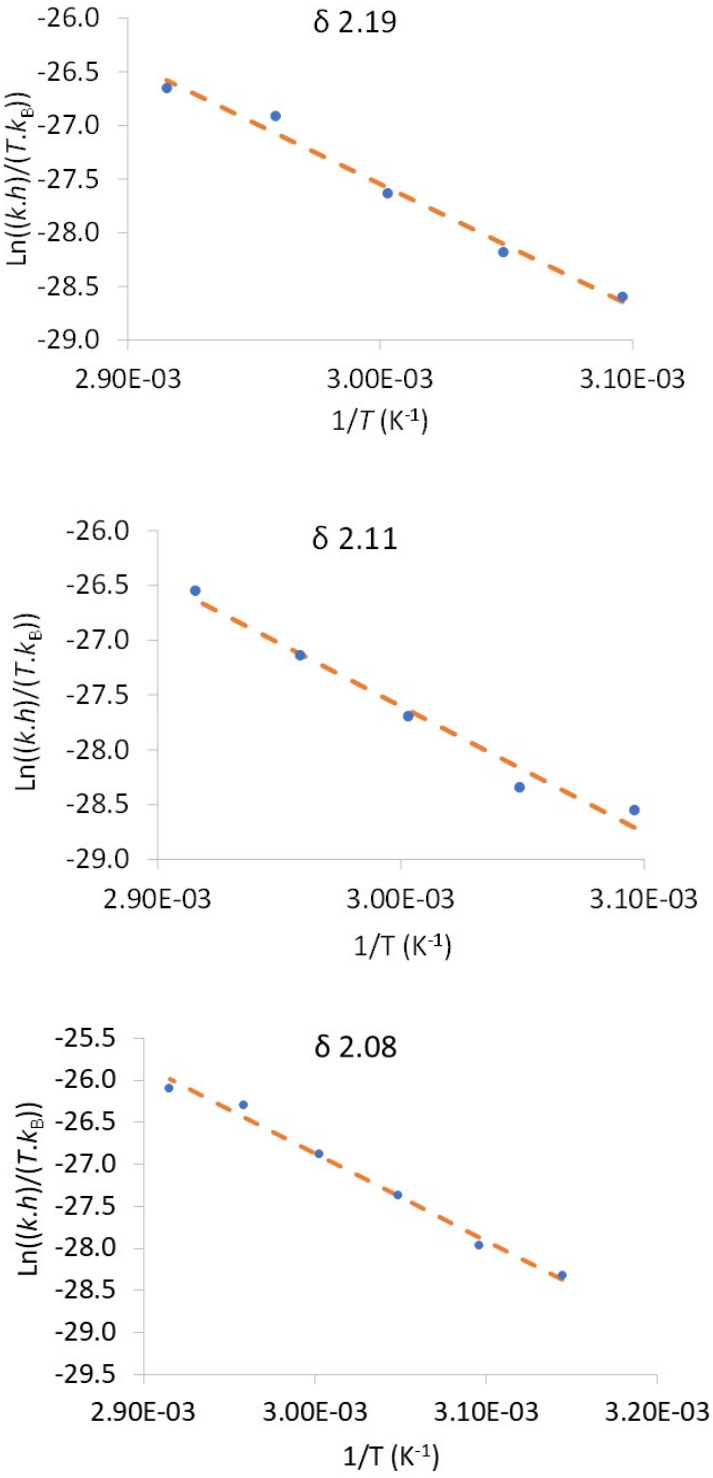

Figure S20. Eyring plot of the temperature-dependent rate constants (Table S4) for the site exchange of the belt-bridging acetate ligands in the $[Zr_6O_4(OH)_4(O_2CMe)_{12}]_2$ molecule with free MeCOOH, measured in the 25–70 °C range in C_6D_6 (Figure 6a).

6. DFT computational results

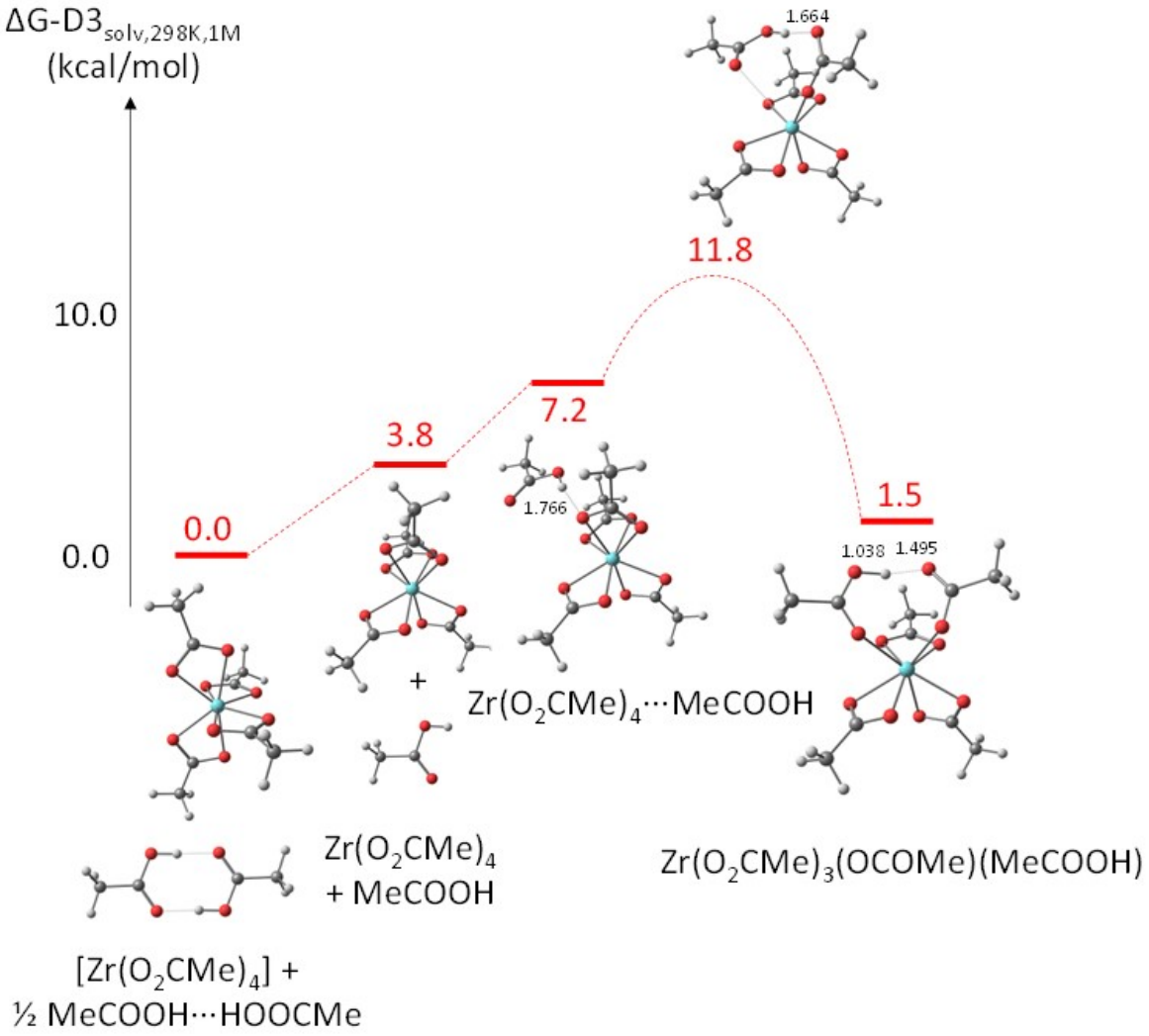

Figure S21. Gibbs energy profile of the alternative acetate exchange pathway with assistance of an acetic acid molecule.

Table S5. Cartesian coordinates (Å), energies (hartrees) and imaginary frequencies (for the TS) of all optimized geometries.

1. Small molecules

CH_3COOH

E_{DCM} = -229.102321953

$G_{298.15,DCM,1M}$ = -229.064064

1	1.874326000	0.367260000	0.000000000
8	1.244676000	-0.377878000	0.000000000
8	-0.198518000	1.351669000	0.000000000
6	0.000000000	0.153445000	0.000000000
6	-1.054687000	-0.917843000	0.000000000
1	-0.935322000	-1.554161000	0.882384000
1	-2.044821000	-0.462881000	0.000000000
1	-0.935322000	-1.554161000	-0.882384000

CH_3COO^-

E_{DCM} = -228.592082687

$G_{298.15,DCM,1M}$ = -228.567326

8	1.159740000	0.700257000	0.000000000
8	-1.104603000	0.811139000	0.000000000
6	0.000000000	0.206297000	0.000000000
6	-0.052061000	-1.351045000	0.000000000
1	0.474548000	-1.743940000	0.879417000
1	-1.077821000	-1.734802000	0.000000000
1	0.474548000	-1.743940000	-0.879417000

$(CH_3COOH)_2$

E_{DCM} = -458.233175577

$G_{298.15,DCM,1M}$ = -458.140370

1	0.386760000	1.109231000	0.000069000
8	1.393144000	1.157998000	-0.000592000
8	1.238877000	-1.089550000	0.000944000
6	1.913455000	-0.055405000	-0.000021000
6	3.414507000	-0.064468000	-0.000148000
1	3.782300000	0.460537000	0.886940000
1	3.784765000	-1.089060000	-0.008285000
1	3.783441000	0.475916000	-0.877325000
1	-0.386728000	-1.109215000	-0.000583000
8	-1.393105000	-1.157994000	-0.001039000
8	-1.238857000	1.089518000	0.000359000
6	-1.913512000	0.055400000	-0.000236000
6	-3.414529000	0.064489000	0.000418000
1	-3.782550000	-0.468560000	0.882529000
1	-3.784700000	1.089137000	0.001000000
1	-3.783282000	-0.467861000	-0.881800000

2. Mononuclear zirconium complexes

2A. Tetraacetate system

$[Zr(O_2CMe)_4]$

E_{DCM} = -961.383446391

$G_{298.15,DCM,1M}$ = -961.229047

40	0.000000000	0.000000000	0.004347000
8	-1.496971000	-0.501642000	-1.556233000
8	0.000000000	-1.986944000	-0.989631000
8	1.736138000	-0.974786000	0.994796000
8	1.163056000	1.052274000	1.570553000
6	-0.995513000	-1.673338000	-1.726478000
6	1.949350000	0.046330000	1.730727000
8	1.496971000	0.501642000	-1.556233000
6	0.995513000	1.673338000	-1.726478000
8	0.000000000	1.986944000	-0.989631000
8	-1.736138000	0.974786000	0.994796000
6	-1.949350000	-0.046330000	1.730727000
8	-1.163056000	-1.052274000	1.570553000
6	3.045743000	0.085549000	2.741132000
1	3.633066000	-0.832445000	2.715434000
1	3.683727000	0.952290000	2.542174000
1	2.604015000	0.222302000	3.733920000
6	-3.045743000	-0.085549000	2.741132000
1	-3.633066000	0.832445000	2.715434000
1	-3.683727000	-0.952290000	2.542174000
1	-2.604015000	-0.222302000	3.733920000
6	-1.528015000	-2.601278000	-2.765540000
1	-2.598549000	-2.440134000	-2.905858000
1	-1.018883000	-2.375957000	-3.710841000
1	-1.317401000	-3.637729000	-2.496706000
6	1.528015000	2.601278000	-2.765540000
1	2.598549000	2.440134000	-2.905858000
1	1.018883000	2.375957000	-3.710841000
1	1.317401000	3.637729000	-2.496706000

TS of Zr-O cleavage $[Zr(O_2CMe)_3(OCOMe)]$

E_{DCM} = -961.367817665

$G_{298.15,DCM,1M}$ = -961.212750

v = -80.3723i

40	-0.186446000	0.033756000	-0.050569000
8	3.049537000	0.510077000	-0.006247000
8	1.169360000	0.938508000	1.134877000
8	-1.266045000	-0.792411000	1.689185000
8	-1.940265000	-1.309547000	-0.325890000
6	2.501771000	0.993471000	0.973915000
6	-2.085366000	-1.434160000	0.943457000
8	-1.752748000	1.613338000	0.246341000
6	-1.383530000	2.208693000	-0.820314000
8	-0.433558000	1.648968000	-1.491736000
8	0.685941000	-0.895456000	-1.799487000
6	1.225883000	-1.848624000	-1.116071000
8	0.946812000	-1.888221000	0.127957000
6	-3.141033000	-2.318327000	1.516659000
1	-3.306376000	-2.091803000	2.570486000
1	-4.065876000	-2.211410000	0.944719000
1	-2.803577000	-3.357249000	1.420427000
6	2.153939000	-2.817857000	-1.760034000
1	1.776063000	-3.096559000	-2.746692000
1	3.119325000	-2.316448000	-1.897791000
1	2.292085000	-3.696708000	-1.129434000
6	3.218081000	1.693280000	2.096245000
1	4.290882000	1.725162000	1.903922000
1	2.824733000	2.709352000	2.203794000
1	3.021297000	1.166144000	3.035771000
6	-1.989903000	3.489301000	-1.278672000
1	-2.827318000	3.773147000	-0.641206000
1	-1.218873000	4.267484000	-1.254632000
1	-2.315846000	3.381934000	-2.317725000

$[Zr(O_2CMe)_3(OCOMe)]$

E_{DCM} = -961.369514176

$G_{298.15,DCM,1M}$ = -961.215481

40	-0.205532000	0.043062000	-0.094353000
8	3.357969000	0.993317000	0.183363000
8	1.178415000	1.251609000	0.623790000
8	-0.848124000	-0.936604000	1.769023000
8	-1.654468000	-1.646423000	-0.140450000
6	2.487073000	1.441635000	0.901269000
6	-1.605582000	-1.755526000	1.137830000
8	-1.948881000	1.349419000	0.442279000
6	-2.072242000	1.722767000	-0.772953000
8	-1.239439000	1.218354000	-1.618135000
8	0.836596000	-0.633788000	-1.877327000
6	1.552589000	-1.490885000	-1.229248000
8	1.292926000	-1.631670000	0.010203000
6	-2.397181000	-2.800305000	1.849755000
1	-2.257110000	-2.729087000	2.928359000
1	-3.455089000	-2.682642000	1.594861000
1	-2.079678000	-3.785794000	1.493281000
6	2.642014000	-2.244101000	-1.911238000
1	2.297156000	-2.592580000	-2.888111000
1	3.477859000	-1.554374000	-2.076178000
1	2.978689000	-3.078686000	-1.295479000
6	2.715588000	2.242352000	2.153880000
1	3.781529000	2.407663000	2.313284000
1	2.191674000	3.200647000	2.079710000
1	2.289358000	1.702569000	3.006562000
6	-3.111382000	2.695396000	-1.212922000
1	-3.763683000	2.969836000	-0.383828000
1	-2.612552000	3.585799000	-1.610577000
1	-3.692079000	2.252458000	-2.027983000

$[Zr(O_2CMe)_3]^+$

E_{DCM} = -732.675039236

$G_{298.15,DCM,1M}$ = -732.557359

40	0.009768000	-0.411915000	-0.773848000
8	-2.183851000	0.117418000	-0.597967000
8	-1.339275000	-1.545780000	0.525731000
8	1.378024000	-1.517701000	0.534902000
8	2.195483000	0.147948000	-0.605635000
6	-2.357454000	-0.797480000	0.280540000
6	2.382101000	-0.752739000	0.285320000
8	-0.019346000	1.775405000	-1.024211000
6	-0.028639000	1.971374000	0.237887000
8	-0.002156000	0.910361000	0.962759000
6	3.655415000	-0.855981000	1.045011000
1	3.645808000	-0.063322000	1.804373000
1	3.737572000	-1.822641000	1.542803000
1	4.505995000	-0.676205000	0.383919000
6	-0.082479000	3.334657000	0.823936000
1	-0.037136000	4.087250000	0.036182000
1	-1.016363000	3.436979000	1.386899000
1	0.747469000	3.461778000	1.525091000
6	-3.632502000	-0.936271000	1.031499000
1	-4.482315000	-0.761431000	0.368149000
1	-3.699835000	-1.912254000	1.513052000
1	-3.641590000	-0.156144000	1.803653000

$[Zr(O_2CMe)_3(OCOCH_3)(CH_3COOH)]$ start

E_{DCM} = -1190.50799631

$G_{298.15,DCM,1M}$ = -1190.296878

40	0.413671000	-0.002133000	-0.087124000
8	-2.864886000	-1.186686000	-0.659259000
8	-0.832156000	-0.850479000	-1.539240000
8	1.824213000	-1.488123000	-1.016098000
8	2.286933000	-0.642805000	0.941985000
6	-1.974781000	-1.464354000	-1.489856000
6	2.603697000	-1.443686000	-0.008549000
8	1.694859000	1.341618000	-1.226557000
6	1.839695000	2.194608000	-0.262342000
8	1.272220000	1.932382000	0.836475000
8	-0.677290000	-0.012073000	1.793290000
6	-0.775169000	-1.300664000	1.865576000
8	-0.200956000	-1.970990000	0.957699000
6	3.830856000	-2.291519000	0.084599000
1	4.014406000	-2.815866000	-0.853782000
1	4.688131000	-1.663886000	0.345191000
1	3.695145000	-3.018638000	0.892699000
6	-1.563934000	-1.930838000	2.963976000
1	-1.276580000	-1.490228000	3.922667000
1	-2.623687000	-1.706292000	2.798241000
1	-1.415945000	-3.011016000	2.975661000
6	-2.165561000	-2.568597000	-2.492410000
1	-3.193862000	-2.930899000	-2.486729000
1	-1.890062000	-2.213686000	-3.489702000
1	-1.483514000	-3.387707000	-2.237867000
6	2.649616000	3.431169000	-0.481486000
1	3.648965000	3.151152000	-0.828766000
1	2.180036000	4.025782000	-1.272436000
1	2.718766000	4.017990000	0.434862000
1	-2.930420000	0.183944000	-0.066729000
8	-3.152290000	1.149595000	0.242257000
8	-1.071594000	1.650336000	-0.438055000
6	-2.192885000	1.988621000	0.005474000
6	-2.476247000	3.423911000	0.314243000
1	-1.993725000	3.656741000	1.271237000
1	-2.022323000	4.058470000	-0.449843000
1	-3.546329000	3.615367000	0.394933000

TS of proton transfer for $[Zr(O_2CMe)_3(OCOCH_3)(CH_3COOH)]$

E_{DCM} = -1190.50772797

$G_{298.15,DCM,1M}$ = -1190.298647

v = -616.0195i

40	0.417940000	0.086602000	-0.011771000
8	-2.675069000	-1.383175000	-1.318506000
8	-0.517827000	-0.855776000	-1.684766000
8	1.755786000	-1.696344000	-0.480222000
8	2.159525000	-0.447477000	1.259358000
6	-1.578898000	-1.522764000	-1.933899000
6	2.485355000	-1.456974000	0.532766000
8	1.733117000	1.053458000	-1.483941000
6	1.906129000	2.108150000	-0.757666000
8	1.341958000	2.126532000	0.378906000
8	-0.401876000	0.454263000	2.061951000
6	-0.875034000	-0.726622000	2.123296000
8	-0.685229000	-1.484991000	1.101779000
6	3.684638000	-2.281535000	0.871239000
1	3.715317000	-3.189970000	0.268741000
1	4.582765000	-1.683827000	0.678010000
1	3.673195000	-2.526604000	1.936881000
6	-1.647959000	-1.214215000	3.303814000
1	-1.378677000	-2.250342000	3.522689000
1	-1.474775000	-0.575510000	4.170834000
1	-2.713498000	-1.191870000	3.046607000
6	-1.493782000	-2.551255000	-3.025991000
1	-2.482943000	-2.912304000	-3.308537000
1	-0.975840000	-2.128749000	-3.890882000
1	-0.890153000	-3.388878000	-2.658139000
6	2.726658000	3.246395000	-1.267822000
1	3.707405000	2.873876000	-1.579030000

1	2.236680000	3.663886000	-2.154230000
1	2.837142000	4.019021000	-0.506468000
1	-2.844189000	-0.435830000	-0.523031000
8	-3.220254000	0.475436000	0.111711000
8	-1.255235000	1.430244000	-0.351037000
6	-2.454180000	1.493478000	0.066886000
6	-2.977537000	2.813662000	0.540580000
1	-2.752437000	3.579936000	-0.206674000
1	-4.048910000	2.772672000	0.736357000
1	-2.440175000	3.083150000	1.456638000

[Zr(O_2CMe)$_3$($OCOCH_3$)(CH_3COOH)] end

E_{DCM} = -1190.5099324

$G_{298.15,DCM,1M}$ = -1190.297227

40	0.416657000	0.114186000	0.007982000
8	-2.716247000	-1.420298000	-1.297466000
8	-0.562801000	-0.884385000	-1.691007000
8	1.640768000	-1.756810000	-0.439130000
8	2.129354000	-0.513053000	1.284533000
6	-1.595731000	-1.555159000	-1.929396000
6	2.386127000	-1.550322000	0.570241000
8	1.756800000	0.967763000	-1.514285000
6	2.010324000	2.019075000	-0.808137000
8	1.479119000	2.085507000	0.343678000
8	-0.362271000	0.538590000	2.089137000
6	-0.922089000	-0.601964000	2.143803000
8	-0.786521000	-1.371078000	1.118705000
6	3.517933000	-2.457792000	0.930251000
1	3.598501000	-3.282002000	0.220937000
1	4.448060000	-1.880296000	0.943804000
1	3.357083000	-2.845460000	1.941506000
6	-1.705971000	-1.053692000	3.331018000
1	-1.266883000	-1.978806000	3.718127000
1	-1.712716000	-0.287234000	4.106479000
1	-2.729392000	-1.280223000	3.015398000
6	-1.561778000	-2.606411000	-2.993431000
1	-2.566038000	-2.904785000	-3.294626000
1	-0.989460000	-2.241408000	-3.849025000
1	-1.032998000	-3.476213000	-2.585952000
6	2.874669000	3.105970000	-1.356345000
1	3.787829000	2.671662000	-1.773025000
1	2.338100000	3.597953000	-2.175561000
1	3.114402000	3.837690000	-0.584294000
1	-2.759114000	-0.630678000	-0.618704000
8	-3.148398000	0.574715000	0.174284000
8	-1.169506000	1.449293000	-0.376961000
6	-2.393212000	1.560233000	0.036995000
6	-2.858044000	2.951973000	0.364482000
1	-2.631367000	3.620914000	-0.470885000
1	-3.925571000	2.968522000	0.585638000
1	-2.292473000	3.309516000	1.232122000

[Zr(O_2CMe)$_4$]···CH_3COOH

E_{DCM} = -1190.49921492

$G_{298.15,DCM,1M}$ = -1190.287770

40	0.800177000	0.036160000	0.109305000
8	-0.902940000	-1.217663000	0.824134000
8	0.682457000	-0.702655000	2.227600000
8	2.631300000	0.922573000	0.991982000
8	2.165358000	1.269470000	-1.111367000
6	-0.433778000	-1.270984000	2.031649000
6	2.961622000	1.461765000	-0.118111000
8	2.036125000	-1.782524000	-0.126753000
6	1.521423000	-2.040491000	-1.278343000
8	0.644514000	-1.218734000	-1.711247000
8	-0.772369000	1.113827000	-1.024113000
6	-0.971063000	1.935384000	-0.066489000
8	-0.248334000	1.778526000	0.987432000
6	4.203699000	2.270019000	-0.274580000
1	4.726518000	2.369502000	0.676770000
1	4.850876000	1.781229000	-1.010715000
1	3.940345000	3.255625000	-0.670922000
6	-2.003598000	3.007094000	-0.139278000
1	-2.339006000	3.151409000	-1.166714000
1	-2.850766000	2.694757000	0.480585000
1	-1.603785000	3.936518000	0.273903000
6	-1.200945000	-1.957469000	3.107021000
1	-2.161335000	-1.445091000	3.231346000
1	-1.414466000	-2.984718000	2.795567000
1	-0.647934000	-1.949604000	4.046117000
6	1.935947000	-3.245039000	-2.051565000
1	1.718991000	-4.137848000	-1.455606000
1	1.411673000	-3.293542000	-3.005968000
1	3.018315000	-3.211288000	-2.211949000
1	-2.529698000	-0.600038000	0.523124000
8	-3.309093000	-0.001861000	0.433513000
8	-3.534572000	-1.130349000	-1.505078000
6	-3.893797000	-0.240925000	-0.757447000
6	-5.019551000	0.720377000	-1.032728000
1	-4.606934000	1.723356000	-1.184423000
1	-5.561198000	0.411623000	-1.926894000
1	-5.697998000	0.768455000	-0.176000000

TS of Zr-O bond cleavage in [Zr(O_2CMe)$_4$]···CH_3COOH

E_{DCM} = -1190.49338109

$G_{298.15,DCM,1M}$ = -1190.280382

v = -61.8043i

40	-0.608148000	0.014151000	-0.038534000
8	2.364693000	-0.041383000	2.491707000
8	0.405145000	0.510611000	1.590236000
8	-2.239267000	-0.851995000	1.176001000
8	-2.306014000	-1.030597000	-0.999575000
6	1.242420000	0.445516000	2.610531000
6	-2.848978000	-1.281750000	0.137403000
8	-1.974848000	1.775723000	0.101950000
6	-1.524792000	2.248461000	-0.999820000
8	-0.628447000	1.550323000	-1.598960000
8	0.694208000	-0.905711000	-1.530087000
6	0.818060000	-2.005038000	-0.868071000
8	0.158411000	-2.092939000	0.219458000
6	-4.115518000	-2.062799000	0.230703000
1	-4.540291000	-1.995147000	1.232529000
1	-4.826123000	-1.703943000	-0.518456000
1	-3.888523000	-3.110496000	0.001311000
6	1.727101000	-3.084477000	-1.343570000
1	1.663431000	-3.176989000	-2.430240000
1	2.749762000	-2.786633000	-1.085125000
1	1.492993000	-4.030808000	-0.854587000
6	0.713473000	1.011459000	3.896139000
1	1.466534000	0.951407000	4.682065000
1	0.416529000	2.053000000	3.735498000
1	-0.184081000	0.456800000	4.189534000
6	-1.987362000	3.556878000	-1.541638000
1	-3.044637000	3.706449000	-1.313172000
1	-1.414972000	4.349229000	-1.043783000
1	-1.804202000	3.613613000	-2.615555000
1	2.919468000	-0.267475000	0.939321000
8	3.350992000	-0.405158000	0.044758000

8	2.311212000	1.534058000	-0.432409000
6	3.055325000	0.619878000	-0.762331000
6	3.701800000	0.497540000	-2.114625000
1	3.174472000	-0.282299000	-2.674466000
1	3.618650000	1.441335000	-2.654143000
1	4.749036000	0.198438000	-2.022340000

2B. Triacetate system

[$Zr(O_2CMe)_3(OH)(H_2O)$]
E_{DCM} = -885.155411894
$G_{298.15,DCM,1M}$ = -885.008277

40	-0.038620000	-0.299977000	0.372394000
8	-2.242152000	0.338055000	0.221477000
8	-1.455755000	-1.299274000	-0.993364000
8	1.450992000	-0.996057000	-1.263891000
8	2.156935000	0.056490000	0.520560000
6	-2.449715000	-0.552815000	-0.660576000
8	0.075502000	1.508145000	-0.959303000
8	-0.017730000	1.799797000	1.203818000
8	-0.401003000	-0.769161000	2.261972000
8	0.521954000	-2.556984000	0.702045000
6	-3.780557000	-0.727655000	-1.319633000
1	-4.046158000	-1.788014000	-1.341440000
1	-4.548476000	-0.150020000	-0.803888000
1	-3.699781000	-0.383525000	-2.357174000
1	-0.753514000	-0.079955000	2.844190000
1	1.203215000	-2.969911000	0.147957000
1	0.690820000	-2.782483000	1.631646000
6	2.411296000	-0.454407000	-0.630861000
6	3.788119000	-0.366750000	-1.211429000
1	3.874680000	0.594337000	-1.732607000
1	4.539620000	-0.393057000	-0.419559000
1	3.954314000	-1.167994000	-1.933521000
6	0.022062000	2.311393000	0.036626000
6	-0.025990000	3.791761000	-0.174820000
1	0.631074000	4.074224000	-1.000801000
1	-1.051451000	4.065264000	-0.450351000
1	0.249221000	4.322974000	0.737427000

TS of Zr-O bond cleavage in [$Zr(O_2CMe)_3(OH)(H_2O)$]
E_{DCM} = -885.139549641
$G_{298.15,DCM,1M}$ = -884.995189
v = -92.6647i

40	-0.119181000	-0.441234000	0.004427000
8	-0.024951000	-1.294553000	2.116996000
8	-1.971652000	0.237929000	-1.145945000
8	-2.165012000	-0.891474000	0.715409000
8	-0.462917000	1.589651000	1.103259000
8	0.493653000	1.474576000	-0.870199000
6	-2.730244000	-0.306478000	-0.284329000
8	1.904394000	-0.414837000	0.681164000
8	2.474327000	-0.690724000	-1.459348000
8	0.003586000	-2.070826000	-1.055764000
6	-4.219363000	-0.287720000	-0.400837000
1	-4.644847000	0.149526000	0.507947000
1	-4.533455000	0.280118000	-1.277040000
1	-4.582601000	-1.318217000	-0.472533000
1	0.771465000	-2.236468000	-1.624872000
6	0.059111000	2.187511000	0.110573000
6	0.146623000	3.679945000	0.041427000
1	1.078716000	3.982618000	-0.441115000
1	-0.685211000	4.042336000	-0.574412000
1	0.064941000	4.116928000	1.037754000
6	2.795762000	-0.459940000	-0.287657000
6	4.217966000	-0.193362000	0.137440000
1	4.294047000	0.839457000	0.495334000
1	4.487961000	-0.848840000	0.971145000
1	4.905668000	-0.343146000	-0.695800000
1	0.778971000	-1.076579000	2.619054000
1	-0.798968000	-1.176056000	2.693174000

[$Zr(O_2CMe)_2(OCOCH_3)(OH)(H_2O)$]
E_{DCM} = -885.144992355
$G_{298.15,DCM,1M}$ = -885.000188

40	-0.220406000	-0.342187000	-0.000138000
8	0.045079000	-1.465982000	1.960982000
8	-2.183431000	0.359857000	-0.930135000
8	-2.180347000	-1.138525000	0.660649000
8	-0.319515000	1.644806000	1.106789000
8	0.351927000	1.567471000	-0.980450000
6	-2.847017000	-0.424363000	-0.182736000
8	1.848757000	-0.345672000	0.493886000
8	2.866318000	-1.241357000	-1.306282000
8	0.219499000	-1.512006000	-1.463673000
6	-4.333347000	-0.543307000	-0.260480000
1	-4.760921000	-0.388000000	0.734868000
1	-4.744720000	0.176775000	-0.968143000
1	-4.588520000	-1.561668000	-0.572978000
1	1.194456000	-1.584777000	-1.647880000
6	0.097988000	2.260396000	0.065467000
6	0.265832000	3.746889000	0.067531000
1	0.770373000	4.084794000	-0.838124000
1	-0.726080000	4.208718000	0.128441000
1	0.827001000	4.050593000	0.955711000
6	2.909673000	-0.650005000	-0.219113000
6	4.217516000	-0.211761000	0.394036000
1	4.240433000	0.882930000	0.432895000
1	4.285790000	-0.575995000	1.423617000
1	5.064018000	-0.574856000	-0.190061000
1	0.883167000	-1.386840000	2.445799000
1	-0.678915000	-1.660037000	2.579020000

2C. Diacetate system

[$Zr(O_2CMe)_2(OH)_2(H_2O)_2$]
E_{DCM} = -808.91439525
$G_{298.15,DCM,1M}$ = -808.779256

40	-0.005990000	0.253101000	0.053546000
8	-2.309565000	0.689983000	-0.224417000
8	-1.508575000	-1.354158000	-0.178235000
8	1.517618000	-1.256949000	-0.796465000
8	2.193522000	0.539327000	0.264244000
6	-2.515104000	-0.556169000	-0.297582000
8	-0.090227000	0.803862000	-1.868483000
8	0.231049000	2.608733000	0.112632000
8	-0.542256000	0.787878000	1.941265000
8	0.576470000	-1.492049000	1.721337000
6	-3.882109000	-1.127518000	-0.527330000
1	-4.107434000	-1.859211000	0.254646000
1	-4.637359000	-0.340694000	-0.535426000
1	-3.889549000	-1.657731000	-1.485638000
1	-1.244928000	1.439400000	2.068692000
1	-0.780811000	1.407581000	-2.174462000
1	0.119005000	-2.314552000	1.484700000
1	0.048249000	-1.077892000	2.428867000
1	0.681681000	2.896598000	0.924588000
1	0.782916000	2.903708000	-0.631395000

6	2.475972000	-0.548522000	-0.364101000
6	3.908303000	-0.943823000	-0.556813000
1	4.438438000	-0.139563000	-1.076757000
1	4.377531000	-1.066930000	0.424998000
1	3.985193000	-1.871594000	-1.124733000

TS of Zr-O bond cleavage in [Zr(O$_2$CMe)$_2$(OH)$_2$(H$_2$O)$_2$]
E_{DCM} = -808.908368586
$G_{298.15,DCM,1M}$ = -808.774595
v = -85.1898i

40	0.078159000	0.391900000	-0.022412000
8	-2.741875000	0.528160000	-0.558620000
8	-1.445351000	-1.131147000	0.158877000
8	1.285151000	-1.594358000	-0.307687000
8	2.293157000	0.327625000	-0.053067000
6	-2.604004000	-0.659012000	-0.201058000
8	-0.205899000	0.579903000	-1.951782000
8	0.917896000	2.631229000	-0.202511000
8	-0.869880000	1.494422000	1.370463000
8	0.585767000	-0.621557000	2.154678000
6	-3.758202000	-1.630964000	-0.165153000
1	-3.860840000	-2.042424000	0.844428000
1	-4.687574000	-1.143098000	-0.462188000
1	-3.548100000	-2.468768000	-0.838303000
1	-1.815719000	1.626805000	1.208393000
1	-1.066867000	0.776862000	-2.345749000
1	0.397021000	-1.573357000	2.118432000
1	-0.107927000	-0.224224000	2.708073000
1	0.698144000	3.104229000	0.616730000
1	1.872801000	2.727870000	-0.351291000
6	2.369134000	-0.943886000	-0.254934000
6	3.709169000	-1.593585000	-0.407262000
1	4.263812000	-1.095807000	-1.208593000
1	4.275655000	-1.456838000	0.520092000
1	3.604918000	-2.656782000	-0.625896000

[Zr(O$_2$CMe)(OCOMe)(OH)$_2$(H$_2$O)$_2$]
E_{DCM} = -808.915569902
$G_{298.15,DCM,1M}$ = -808.783916

40	0.180085000	0.465750000	-0.235581000
8	-3.300539000	0.318551000	0.548859000
8	-1.527126000	-0.783866000	-0.296126000
8	1.054005000	-1.661189000	0.025017000
8	2.422362000	0.043959000	-0.003163000
6	-2.789928000	-0.683826000	0.028063000
8	0.289383000	0.699694000	-2.165529000
8	1.398217000	2.445437000	0.171095000
8	-1.066855000	1.847379000	0.460867000
8	0.304830000	0.023550000	2.129008000
6	-3.610273000	-1.915372000	-0.284697000
1	-3.166910000	-2.786147000	0.208974000
1	-4.644383000	-1.789142000	0.039256000
1	-3.581156000	-2.104950000	-1.362987000
1	-1.984575000	1.500926000	0.564753000
1	-0.153360000	1.192640000	-2.866324000
1	0.314047000	-0.916879000	2.372094000
1	-0.439014000	0.433032000	2.600222000
1	0.853274000	3.052728000	0.698576000
1	2.266269000	2.357680000	0.596084000
6	2.250034000	-1.221385000	0.049773000
6	3.419769000	-2.157007000	0.098342000
1	3.674037000	-2.440366000	-0.930012000
1	4.286644000	-1.667577000	0.546144000
1	3.159906000	-3.064529000	0.647334000

2D. Monoacetate system

[Zr(O$_2$CMe)(OH)$_3$(H$_2$O)$_3$]
E_{DCM} = -732.680322969
$G_{298.15,DCM,1M}$ = -732.557383

40	0.480814000	-0.070490000	-0.042211000
8	-1.675122000	-1.144874000	-0.051526000
8	-1.481413000	1.044825000	0.037154000
8	0.775391000	1.827892000	1.481869000
8	2.498549000	0.015709000	0.036905000
6	-2.222742000	-0.005616000	-0.013736000
8	0.223713000	-0.668713000	1.930953000
8	1.027775000	-2.401848000	-0.035018000
8	0.272888000	-0.513989000	-2.003579000
8	0.910110000	1.960210000	-1.284672000
6	-3.716707000	0.156230000	-0.048198000
1	-4.000990000	0.613500000	-1.002519000
1	-4.216823000	-0.807720000	0.055554000
1	-4.033661000	0.835444000	0.748679000
1	-0.249952000	-1.287976000	-2.251544000
1	-0.580913000	-1.157280000	2.149856000
1	2.941327000	0.411533000	0.799406000
1	0.465407000	1.235730000	2.200252000
1	0.041103000	2.438314000	1.305163000
1	1.878739000	2.033788000	-1.243413000
1	0.714654000	1.623866000	-2.177838000
1	1.948092000	-2.436485000	-0.347823000
1	1.082045000	-2.540472000	0.927573000

TS of Zr-O bond cleavage in [Zr(O$_2$CMe)(OH)$_3$(H$_2$O)$_3$]
E_{DCM} = -732.674660835
$G_{298.15,DCM,1M}$ = -732.553492
v = -81.5431i

40	-0.604079000	-0.012543000	0.043094000
8	2.052315000	-1.530116000	-0.148171000
8	1.503115000	0.636038000	-0.053582000
8	-0.373591000	1.728862000	-1.694858000
8	-2.468729000	0.703759000	-0.082375000
6	2.374407000	-0.335229000	-0.036038000
8	-0.336176000	-1.102085000	-1.641493000
8	-2.021850000	-1.989086000	0.219137000
8	-0.313244000	-0.613797000	1.930269000
8	-0.315637000	2.097153000	1.196856000
6	3.813758000	0.091720000	0.148980000
1	3.936515000	0.505124000	1.156486000
1	4.491251000	-0.753666000	0.020025000
1	4.063829000	0.885229000	-0.561957000
1	-0.333869000	-1.554500000	2.151493000
1	0.527526000	-1.546582000	-1.602560000
1	-2.619940000	1.604627000	-0.398625000
1	-0.343806000	1.143311000	-2.472163000
1	0.539428000	2.048991000	-1.596898000
1	-0.776269000	2.027604000	2.049927000
1	0.633172000	2.105252000	1.413086000
1	-2.931201000	-1.667500000	0.341440000
1	-1.962083000	-2.280952000	-0.707913000

[Zr(OCOMe)(OH)$_3$(H$_2$O)$_3$]
E_{DCM} = -732.677435019
$G_{298.15,DCM,1M}$ = -732.555511

40	-0.671440000	0.016452000	-0.028328000
8	2.540079000	1.517033000	0.434926000

8	1.486314000	-0.369404000	-0.203747000
8	0.107716000	-0.962057000	2.029058000
8	-2.367831000	-0.777413000	0.746733000
6	2.549490000	0.375340000	-0.045730000
8	-0.178233000	1.806386000	0.668571000
8	-2.535930000	1.551140000	-0.434801000
8	-0.826213000	-0.028476000	-2.026917000
8	-0.232929000	-2.319146000	-0.605163000
6	3.837654000	-0.274045000	-0.506707000
1	3.778713000	-0.463616000	-1.584114000
1	4.696213000	0.364761000	-0.294404000
1	3.962434000	-1.243125000	-0.012757000
1	-1.345758000	0.647385000	-2.481897000
1	0.798606000	1.921610000	0.719616000
1	-2.457553000	-1.711980000	0.973899000
1	1.028242000	-1.266305000	1.981386000
1	-0.414146000	-1.683936000	2.412529000
1	-0.636804000	-2.398524000	-1.486839000
1	0.724293000	-2.237627000	-0.774098000
1	-3.264898000	1.124607000	0.047502000
1	-2.278386000	2.336405000	0.077616000

3. Dinuclear zirconium complexes

***anti*-[Zr(O$_2$CMe)$_3$(OH)(H$_2$O)]$_2$**
E_{DCM} = -1770.36191249
$G_{298.15,DCM,1M}$ = -1770.044975

40	-2.219078000	0.075854000	-0.236451000
40	2.214442000	-0.062525000	-0.257248000
8	-3.610639000	1.914700000	-0.234223000
8	-1.355857000	1.401648000	1.299217000
8	-1.079645000	1.266836000	-1.496289000
8	1.473435000	1.575923000	-1.668758000
8	3.643217000	1.593471000	0.134871000
8	3.653046000	-0.197244000	-2.063685000
8	1.101988000	-1.120609000	-1.649069000
8	-1.434914000	-1.338592000	-1.835543000
8	1.327739000	-1.628019000	1.002001000
8	-0.856794000	-1.202012000	0.816765000
8	0.800617000	1.108906000	0.826682000
8	-3.406134000	-1.893132000	-0.076142000
8	-3.679399000	-0.344270000	1.442465000
8	-3.844985000	0.342470000	-1.730705000
8	3.264444000	0.242701000	1.817014000
6	3.828601000	1.283973000	1.374766000
6	4.659876000	2.173300000	2.247686000
1	5.540574000	2.519980000	1.701343000
1	4.062212000	3.053192000	2.513819000
6	4.310449000	-1.115736000	-1.484772000
8	3.916640000	-1.478636000	-0.315886000
6	5.504724000	-1.764001000	-2.111229000
1	5.364281000	-2.849168000	-2.120400000
1	6.386302000	-1.551191000	-1.497173000
6	0.116556000	-1.868561000	1.283194000
6	-0.205816000	-2.994359000	2.226529000
1	-0.900796000	-3.683629000	1.736761000
1	0.694656000	-3.524033000	2.537716000
6	-0.129437000	1.625957000	1.518012000
6	0.265522000	2.561619000	2.625682000
1	-0.598863000	2.872551000	3.212591000
1	1.004273000	2.067027000	3.263357000
6	-3.931518000	-1.527634000	1.025082000
6	-4.784441000	-2.454922000	1.834456000
1	-5.082092000	-3.325144000	1.247853000
1	-4.204367000	-2.786152000	2.703640000
6	-4.224652000	1.475507000	-1.251542000
1	-5.664276000	-1.922711000	2.205405000
1	-0.717218000	-2.582074000	3.102814000
1	4.953528000	1.653271000	3.160723000
1	0.748448000	3.440922000	2.185353000
1	5.662462000	-1.394538000	-3.125031000
6	-5.351708000	2.223041000	-1.893778000
1	-5.119712000	2.388516000	-2.950703000
1	-6.259005000	1.611534000	-1.847856000
1	-5.521851000	3.176920000	-1.393278000
1	-1.283664000	1.091011000	-2.428458000
1	1.377142000	-0.890045000	-2.550343000
1	-0.409962000	-1.326794000	-1.768998000
1	-1.733462000	-2.249203000	-1.682201000
1	0.455546000	1.559067000	-1.578147000
1	1.780267000	2.455273000	-1.395031000

TS of chelating Zr-O cleavage in *anti*-[Zr(O$_2$CMe)$_3$(OH)(H$_2$O)]$_2$
E_{DCM} = -1770.35269027
$G_{298.15,DCM,1M}$ = -1770.034334
ν = -92.9103i

40	-2.220964000	0.003023000	-0.274480000
40	2.143632000	0.053186000	-0.223255000
8	-3.981046000	1.310624000	-0.533371000
8	-1.385096000	1.799942000	0.640303000
8	-1.142351000	0.817866000	-1.864691000
8	1.332328000	1.175533000	-1.951709000
8	3.442570000	1.931053000	-0.388629000
8	3.482295000	-2.723358000	-0.326839000
8	1.143470000	-1.433600000	-1.218006000
8	-1.410092000	-1.807474000	-1.413864000
8	1.427654000	-1.014814000	1.547650000
8	-0.706186000	-0.858165000	0.958376000
8	0.837827000	1.526407000	0.702178000
8	-3.520618000	-1.645149000	0.432174000
8	-3.209302000	-0.005977000	1.849887000
8	-3.686045000	-0.241704000	-2.038166000
8	3.649025000	0.589746000	1.330223000
6	4.001360000	1.665063000	0.725469000
6	5.007347000	2.585382000	1.341027000
1	5.818321000	2.005820000	1.788969000
1	5.397006000	3.285730000	0.600898000
6	4.202355000	-1.954901000	-0.984954000
8	3.893289000	-0.695465000	-1.166641000
6	5.494447000	-2.398173000	-1.624115000
1	6.325039000	-1.834343000	-1.186198000
1	5.473247000	-2.169209000	-2.694441000
6	0.197141000	-1.252766000	1.754614000
6	-0.216480000	-2.039921000	2.962696000
1	-0.627966000	-2.999062000	2.628889000
1	0.626682000	-2.216440000	3.630460000
6	-0.216962000	2.189125000	0.944512000
6	-0.061514000	3.528442000	1.610771000
1	-1.011976000	3.883806000	2.009859000
1	0.691498000	3.466255000	2.400257000
6	-3.714944000	-1.138434000	1.605017000
6	-4.498017000	-1.907392000	2.623049000
1	-5.442769000	-2.241145000	2.184249000
1	-3.929099000	-2.801325000	2.902231000
6	-4.376085000	0.735755000	-1.614963000
1	-4.683928000	-1.300515000	3.509926000
1	-1.014678000	-1.502296000	3.482640000
1	4.514970000	3.148092000	2.142887000
1	0.301550000	4.241697000	0.861139000
1	5.655557000	-3.466314000	-1.473601000

6	-5.597086000	1.225774000	-2.325298000
1	-5.819009000	0.605418000	-3.194135000
1	-6.443043000	1.220882000	-1.630899000
1	-5.433790000	2.262691000	-2.637526000
1	-1.372769000	0.374259000	-2.696593000
1	1.608719000	-2.272471000	-1.044395000
1	-0.392776000	-1.731211000	-1.377219000
1	-1.656602000	-2.644467000	-0.988397000
1	0.289630000	1.082353000	-1.966876000
1	1.548287000	2.121986000	-1.920679000

$[Zr_2(O_2CMe)_5(OCOMe)(OH)_2(H_2O)_2]$ from *anti*

E_{DCM} = -1770.3592626

$G_{298.15,DCM,1M}$ = -1770.040902

40	2.205111000	-0.065401000	-0.220472000
40	-2.137544000	-0.246531000	-0.318346000
8	4.031827000	-1.300368000	-0.090664000
8	1.398929000	-1.631094000	1.089696000
8	1.231157000	-1.290724000	-1.587696000
8	-1.270000000	-1.688388000	-1.832309000
8	-3.651367000	-1.829413000	-0.570895000
8	-2.925723000	2.979000000	-1.484095000
8	-1.179752000	0.975999000	-1.604945000
8	1.375346000	1.380618000	-1.783693000
8	-1.531343000	1.134191000	1.282288000
8	0.606100000	0.993291000	0.713467000
8	-0.817443000	-1.511818000	0.802998000
8	3.423415000	1.754796000	0.120577000
8	3.084708000	0.494398000	1.879400000
8	3.737023000	-0.181852000	-1.941594000
8	-3.597889000	-0.871565000	1.399956000
6	-4.120163000	-1.728200000	0.631698000
6	-5.252518000	-2.609658000	1.056251000
1	-6.143519000	-2.336012000	0.480162000
1	-5.015746000	-3.651425000	0.820696000
6	-3.855673000	2.324239000	-0.991055000
8	-3.747469000	1.068941000	-0.626182000
6	-5.218996000	2.927155000	-0.762138000
1	-5.445846000	2.903558000	0.309144000
1	-5.976957000	2.321648000	-1.269295000
6	-0.315430000	1.459185000	1.449807000
6	0.057457000	2.444176000	2.517463000
1	0.354914000	3.381110000	2.032550000
1	-0.776624000	2.634685000	3.192969000
6	0.222485000	-2.040476000	1.311098000
6	0.026549000	-3.235155000	2.201731000
1	0.932760000	-3.459092000	2.765188000
1	-0.815602000	-3.059818000	2.875857000
6	3.566243000	1.555704000	1.389238000
6	4.261848000	2.582828000	2.227678000
1	5.223794000	2.837865000	1.773580000
1	3.653550000	3.494034000	2.246033000
6	4.452033000	-0.982853000	-1.264877000
1	4.406626000	2.219078000	3.245606000
1	0.924783000	2.065799000	3.064976000
1	-5.455561000	-2.496389000	2.121674000
1	-0.225481000	-4.095611000	1.570444000
1	-5.256954000	3.954606000	-1.125981000
6	5.736886000	-1.546194000	-1.782732000
1	5.927572000	-1.208401000	-2.801808000
1	6.553657000	-1.230116000	-1.125275000
1	5.691426000	-2.639312000	-1.748687000
1	1.519387000	-1.074986000	-2.489142000
1	-1.671602000	1.838298000	-1.674030000
1	0.360659000	1.267143000	-1.767783000
1	1.566112000	2.308262000	-1.569378000
1	-0.245749000	-1.596564000	-1.770046000
1	-1.492746000	-2.613698000	-1.640172000

***syn*-$[Zr(O_2CMe)_3(OH)(H_2O)]_2$**

E_{DCM} = -1770.36315032

$G_{298.15,DCM,1M}$ = -1770.040825

40	2.209352000	-0.063754000	-0.277045000
40	-2.205523000	0.055465000	-0.284489000
8	3.517718000	-1.948284000	-0.245183000
8	1.349538000	-1.332805000	1.342423000
8	1.127716000	-1.346156000	-1.492598000
8	-1.396938000	-1.253111000	-1.942612000
8	-3.283600000	-1.998269000	-0.106346000
8	-4.003197000	0.236487000	-1.591950000
8	-1.123786000	1.304696000	-1.534176000
8	1.403403000	1.201133000	-1.971227000
8	-1.348374000	1.373913000	1.294136000
8	0.802444000	1.215221000	0.717108000
8	-0.795236000	-1.190038000	0.742594000
8	3.293860000	1.989803000	-0.161923000
8	3.677996000	0.430309000	1.326067000
8	4.005109000	-0.291406000	-1.580095000
8	-3.671507000	-0.395109000	1.333870000
6	-3.867298000	-1.606560000	0.950748000
6	-4.728868000	-2.521914000	1.764235000
1	-4.996841000	-3.412618000	1.194221000
1	-4.167400000	-2.821161000	2.657062000
6	-4.285923000	1.419560000	-1.184539000
8	-3.521012000	1.935986000	-0.309738000
6	-5.484409000	2.139387000	-1.718715000
1	-5.513243000	3.168474000	-1.358864000
1	-6.386221000	1.609755000	-1.392095000
6	-0.124508000	1.649862000	1.469848000
6	0.273319000	2.528973000	2.622692000
1	0.961582000	3.302576000	2.270936000
1	-0.596900000	2.978251000	3.101800000
6	0.122818000	-1.590126000	1.525088000
6	-0.291170000	-2.403394000	2.719605000
1	0.573069000	-2.797141000	3.254938000
1	-0.876576000	-1.759341000	3.385710000
6	3.876319000	1.629209000	0.906918000
6	4.739183000	2.566648000	1.693198000
1	4.993155000	3.448913000	1.104094000
1	4.185911000	2.876239000	2.587539000
6	4.279083000	-1.465535000	-1.142013000
1	5.644722000	2.051460000	2.024020000
1	0.815466000	1.913844000	3.350116000
1	-5.626041000	-1.993534000	2.096694000
1	-0.944988000	-3.218214000	2.395453000
1	-5.466718000	2.118471000	-2.812449000
6	5.449112000	-2.224053000	-1.685487000
1	5.293613000	-2.398573000	-2.755481000
1	6.354525000	-1.618612000	-1.578204000
1	5.570683000	-3.176502000	-1.168435000
1	1.247128000	-2.271823000	-1.229728000
1	-1.251560000	2.237701000	-1.303064000
1	0.381300000	1.227528000	-1.893917000
1	1.712169000	2.116886000	-1.876209000
1	-0.374986000	-1.275592000	-1.859880000
1	-1.704022000	-2.166738000	-1.825141000

TS of bridging Zr-O cleavage in *syn*-$[Zr(O_2CMe)_3(OH)(H_2O)]_2$

E_{DCM} = -1770.34206939

$G_{298.15,DCM,1M}$ = -1770.024282

v = -81.4761i

40	2.334715000	-0.035834000	-0.367320000
40	-2.178208000	0.049878000	-0.266524000
8	3.693354000	-1.823483000	-0.368009000
8	0.843861000	-2.405773000	1.208428000
8	1.104224000	-1.337766000	-1.322928000
8	-1.346894000	-1.037777000	-2.075344000
8	-3.525349000	-1.816359000	-0.535913000
8	-3.827821000	0.672500000	-1.649861000
8	-0.915978000	1.418713000	-1.281896000
8	1.447021000	1.238399000	-1.887358000
8	-1.234016000	1.103795000	1.493274000
8	0.864971000	0.594786000	0.970472000
8	-1.105012000	-1.488083000	0.643721000
8	3.171671000	2.051585000	0.089720000
8	3.690928000	0.343579000	1.358998000
8	4.113084000	-0.110319000	-1.664087000
8	-3.849452000	-0.414988000	1.114719000
6	-4.174261000	-1.502656000	0.507953000
6	-5.291261000	-2.347711000	1.035991000
1	-5.382403000	-3.272854000	0.465799000
1	-5.111055000	-2.569131000	2.092294000
6	-3.999267000	1.804120000	-1.073484000
8	-3.262452000	2.072383000	-0.071595000
6	-5.039163000	2.758302000	-1.573078000
1	-5.012395000	3.693823000	-1.013256000
1	-6.025655000	2.293802000	-1.470846000
6	0.003436000	1.188381000	1.709882000
6	0.523692000	1.990481000	2.865532000
1	1.226734000	2.738132000	2.483511000
1	-0.286108000	2.474660000	3.411004000
6	-0.299533000	-2.027199000	1.511054000
6	-0.842131000	-2.152776000	2.913580000
1	-0.178862000	-2.748613000	3.541768000
1	-0.942346000	-1.146480000	3.336457000
6	3.784645000	1.600914000	1.112162000
6	4.590489000	2.486659000	2.007686000
1	4.537132000	3.525123000	1.679629000
1	4.219590000	2.393798000	3.033215000
6	4.439563000	-1.286351000	-1.249471000
1	5.631050000	2.145940000	2.002567000
1	1.083774000	1.326611000	3.532376000
1	-6.225774000	-1.779696000	0.972417000
1	-1.843221000	-2.593050000	2.889622000
1	-4.873554000	2.949544000	-2.637828000
6	5.653478000	-1.969612000	-1.787138000
1	6.538169000	-1.394400000	-1.492583000
1	5.728627000	-2.987132000	-1.402854000
1	5.612197000	-1.975542000	-2.880506000
1	0.950793000	-2.060111000	-0.675239000
1	-1.022175000	2.313321000	-0.923745000
1	0.370773000	1.319632000	-1.692392000
1	1.817255000	2.134062000	-1.946058000
1	-0.347647000	-1.154140000	-1.899905000
1	-1.720425000	-1.933927000	-2.114454000

$[Zr_2(O_2CMe)_5(OCOMe)(OH)_2(H_2O)_2]$ from *syn*

E_{DCM} = -1770.35123497

$G_{298.15,DCM,1M}$ = -1770.031375

40	-2.439171000	0.180251000	-0.313338000
40	2.124774000	-0.226352000	-0.125468000
8	-3.985256000	1.808923000	-0.585466000
8	0.294307000	3.280234000	0.544165000
8	-1.123999000	1.585984000	-0.981558000
8	1.099655000	0.787042000	-1.809168000
8	3.580797000	1.448657000	-0.774032000
8	3.441737000	-1.150495000	-1.676424000
8	0.656039000	-1.685018000	-1.061119000
8	-1.669259000	-0.953280000	-1.817512000
8	1.090472000	-1.096117000	1.636772000
8	-0.873411000	-0.221009000	1.096992000
8	1.457100000	1.414181000	0.937718000
8	-2.957954000	-1.965102000	0.442593000
8	-3.820020000	-0.210136000	1.427367000
8	-4.347445000	-0.159396000	-1.464346000
8	4.068232000	0.087485000	0.863029000
6	4.404361000	1.083146000	0.120031000
6	5.728123000	1.750858000	0.310270000
1	5.789995000	2.665143000	-0.280813000
1	5.884273000	1.967618000	1.370626000
6	3.554283000	-2.254346000	-1.034210000
8	2.963214000	-2.342560000	0.090617000
6	4.363337000	-3.381097000	-1.593973000
1	4.226157000	-4.288588000	-1.004896000
1	5.420678000	-3.093765000	-1.582104000
6	-0.128292000	-0.860134000	1.904716000
6	-0.714555000	-1.364173000	3.190175000
1	-1.394486000	-2.190000000	2.950644000
1	0.060883000	-1.718262000	3.869607000
6	1.276447000	2.703990000	1.029056000
6	2.351745000	3.454835000	1.775254000
1	2.021927000	4.464586000	2.023321000
1	2.638129000	2.910291000	2.679018000
6	-3.727583000	-1.486743000	1.332707000
6	-4.535787000	-2.365594000	2.237787000
1	-4.181932000	-3.396487000	2.195585000
1	-4.493185000	-1.985975000	3.262065000
6	-4.748559000	1.039175000	-1.259689000
1	-5.581961000	-2.330096000	1.912902000
1	-1.306887000	-0.573514000	3.658167000
1	6.515265000	1.057164000	-0.006158000
1	3.235841000	3.514346000	1.130284000
1	4.079400000	-3.554619000	-2.635900000
6	-6.044738000	1.527252000	-1.824508000
1	-5.881358000	1.797503000	-2.874597000
1	-6.792823000	0.731894000	-1.793240000
1	-6.392161000	2.409101000	-1.284207000
1	-0.721662000	2.266148000	-0.375882000
1	0.502496000	-2.476313000	-0.521873000
1	-0.245811000	-1.400475000	-1.448876000
1	-2.200537000	-1.723510000	-2.072669000
1	0.129992000	1.123669000	-1.555495000
1	1.597252000	1.550032000	-2.145971000

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[2] Sheldrick, G. M., SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015,** *71*, 3-8.

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