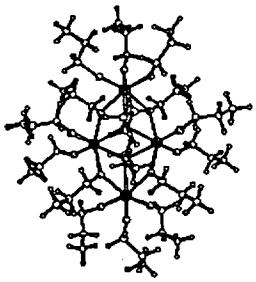
TC010776G Oct 22



Crystal Structure Analysis Report

Compound Formula: $Zr_4[OCH_2CH_2CH_3]_{16}$

Reference Code: WKS2-0899

Description of Single-Crystal Sample and Mounting Used for Data Collection:

1) Color: Colorless

2) Shape: Parallelepiped

3) Dimensions: 0.40 mm. x 0.48 mm. x 0.62 mm.

4) Indices of Faces:

5) Crystal Mount: Crystal was sealed under a N_2 atmosphere inside a sealed thin-walled glass capillary containing mother liquor.

6) Crystal Orientation: Crystal was oriented with one of its longer edges nearly parallel to the phi axis of the diffractometer.

7) Comments: Another crystal of $Zr_4(OPr^n)_{16}$ which was frozen with Paratone N oil to the end of a thin glass fiber fractured when cooled to -70°C.

Space Group and Cell Data:

1) Crystal System: Triclinic Space Group and Number[1]: $P_I - C_i^1$ (No. 2)

2) Number of Computer-Centered Reflections Used in the Least-Squares Refinement of the Cell Dimensions: 2078 measured at: 20±2 °C

3) Lattice Constants with esd's:

a = 12.115(1) Å	α = 64.369(2)°	V = 1776.7(3) Å^3
b = 12.675(1) Å	β = 81.369(3)°	Z = 1 tetranuclear formula unit
c = 13.869(1) Å	γ = 67.737(3)°	λ = 0.71073 Å

4) Molecular Weight: 1310.24 amu* Calculated Density: 1.225 g·cm^{-3}

5) Linear Absorption Coefficient[2a]: 0.62 mm^{-1} F(000) = 688.*

6) Comments:* These values are based on a molecular formula of $Zr_4[OC_3H_7]_{16}$.

Description of Data Collection[3]:

1) Instrument: Bruker SMART CCD Single Crystal Diffraction System
2) X-ray Source: Sealed normal focus X-ray tube
3) Radiation: MoKα Power: 50 kV 40 mA
4) X Monochromator: X Graphite ___Other (Specify:)
   ___Filter: ___Nickel ___Niobium ___Other (Specify:)
5) Incident Beam Collimator Diameter: 0.8 mm Temperature: 20±2 °C
6) Scan Axis: X Omega ___ Phi
7) Scan Width: 0.50° 2θ Range of Data : 3.26° - 45.00°
8) Sample to Detector Distance: 5.024 cm
9) Portion of Ewald Sphere Collected: Hemisphere
10) Number of frames collected: 810 Seconds/frame: 10
11) Total Number of Reflections Collected: 5833
12) Number of Independent Reflections Collected: 4049
13) Data Collected: $-14 \le h \le 14$; $-14 \le k \le 15$; $-5 \le l \le 16$ R_{int}[4] = 0.060

Data Reduction[3]:

1) Lorentz and Polarization Corrections? Yes
2) Absorption Correction: Yes Range of relative transmission factors: 0.783 - 1.000
   XX Empirical Correction using Measurements for Equivalent Reflections
   (1077 Reflections used)
   ____ Face-Indexed Gaussian Grid Correction
3) Comments:

Structure Solution[5]:

1) Method(s) Used in Structure Solution
   ___Heavy-atom Patterson Techniques
   XX Direct Methods
   a) XX SHELXTL/PC
   b) ___Other
   ___Other Techniques
2) Hydrogen Atom Positions Located? Yes
   After Refinement Cycle # 3 by ___Difference Fourier
   XX Calculated
3) Comments:

Structure Refinement[5]: (see next page for summary of refinement cycles)

1) Final Scale Factor: 0.316(2)
2) Extinction Parameter[6] Refined? No Final Value:
   Form: $k[1+0.001(x)(F_c^2)(\lambda^3)/\sin(2\theta)]^{-1/4}$
3) Anomalous Dispersion Corrections[2b] for Which Atoms: Zr, O, C
4) Variable Occupancies for Which (Nonhydrogen) Atoms? C_{21}, C_{51}, C_{14}, C_{44}, C_{15}, C_{45}, C_{16}, C_{46}, C_{17}, C_{47}, C_{28}, C_{58}, C_{38}, C_{68}

Atom	Final Occupancy	Atomic Form Factor[2c] Used
C_{21}, C_{51}, C_{14}, C_{44}, C_{15}, C_{45}	0.50, 0.50, 0.40, 0.60, 0.50, 0.50	C, C, C, C, C, C
C_{16}, C_{46}, C_{17}, C_{47}, C_{28}, C_{58}	0.50, 0.50, 0.50, 0.50, 0.70, 0.30	C, C, C, C, C, C
C_{38}, C_{68}	0.50, 0.50	C, C

5) Refinement Constraints/Restraints: The O-C and C-C bond lengths for the disordered n-propoxide ligands were restrained to have common values which were included as free variables in the least-squares refinement; the final refined values were 1.46(1)Å and 1.47(2)Å, respectively. The O-C-C and C-C-C angles for the disordered ligands were also restrained to nearly tetrahedral values. Normalized occupancy factors for these disordered carbons were assigned by varying the relative occupancies to give nearly equal equivalent isotropic thermal parameters for both positions. The anisotropic thermal parameters for 14 of the partial-occupancy methyl and methylene carbon atoms and 2 full-occupancy methyl carbon atoms were restrained to pseudoisotropic values.

   Hydrogen atoms were included in the structural model as idealized atoms (assuming sp^3-hybridization of the carbon atom and a C-H bond length of 0.96 or 0.97 Å) "riding" on their respective carbon. The isotropic thermal parameters of these idealized hydrogen atoms were fixed at values 1.2 (methylene) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

6) Shift/Error Analysis for Final Least-Squares Cycle[7]:
   Maximum Shift for all Parameters: 0.003 σ_p Mean Shift for all Parameters: 0.000 σ_p

7) Peaks found in Final Difference Fourier Map: There were no peaks present in the final difference Fourier map above the background level (0.41 $e^-/Å^3$). The minimum and mean electron density in the final difference Fourier were -0.26 and 0.00 $e^-/Å^3$, respectively. The rms deviation from the mean electron density was 0.08 $e^-/Å^3$.

Summary of Full Matrix Least-Squares Refinement[8] Cycles

Cycle Number	sin θ/λ		Anisotropic[9] Atoms	Isotropic Atoms			# Refined Parameters	R_1 (unweighted,based on F)			R_2 (weighted,based on F^2)[10]			Extinction Correction
	Minimum	Maximum	Number and Type	Number and Type	Positions Refined	Thermal Parameters		R_1[11]	# Observed Reflections	$F_o/\sigma(F_o)$ Cutoff	R_2[12]	Total # Independent Reflections	'Goodness-of-fit' (Good)[13]	
1	0.00	0.54	2 Zr	8 O	X	X	51	0.183	2228	4.0	0.465	3234	2.054	
2	0.00	0.54	2 Zr	8 O, 31 C	X	X	177	0.119	2228	4.0	0.312	3234	1.307	
3	0.00	0.54	2 Zr, 8 O 31 C				372	0.100	2228	4.0	0.267	3234	1.136	
4	0.00	0.54	2 Zr, 8 O 31 C	*108 H			372	0.097	2228	4.0	0.258	3234	1.099	

* See Item 5 on page 3 regarding the treatment of the hydrogen atoms.

Final Statistics from Cycle #4 for All of the Reflection Data: R_1 = 0.160; wR_2 = 0.339; GOOF = 1.302 for 4049 reflections

References and Notes

1. "International Tables for X-Ray Crystallography", Vol. A, Kluwer Academic Publishers, Dordrecht, 1995.

2. "International Tables for X-Ray Crystallography", Vol. C, Kluwer Academic Publishers, Dordrecht, 1992; a) Tables 4.2.4.2 pp. 193-199; b) Tables 4.2.6.8 pp 219-222; c) Tables 6.1.1.4 pp 500-502.

3. Data acquisition and reduction was accomplished using standard versions of Bruker software for the diffraction system.

4. $R_{int} = \Sigma|F_o^2 - F_o^2(mean)| \; / \; \Sigma[F_o]^2$

5. All structure determination and refinement calculations were performed on an IBM compatible 586 personal computer using the Bruker SHELXTL Version 5.0 PC interactive software package.

6. A. C. Larson in "Crystallographic Computing", **1970**, Ed. F. R. Ahmed, Munksgaard, Copenhagen, pp 291-294.

7. σ_p is the estimated standard deviation of the parameter in question.

8. Refinement on F^2 for all reflections except for 815 with negative F^2 or flagged by the user for potential systematic errors. Weighted R-factors wR_2 and all goodnesses of fit S are based on F^2, conventional R-factors R_1 are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating "R-factor obs" etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on all data will be even larger.

9. The anisotropic thermal parameter is of the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

10. The weighting scheme used is defined as: $w = 1 / [\sigma^2(F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)]$ where $P = [F_o^2 + 2F_c^2]/3$. In this case, a= 0.1123, b= 4.6061, d = 0 and e = 0.

11. $\underline{R}_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

12. $w\underline{R}_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

13. GooF = S = $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$ where n is the total number of reflections and p is the number of parameters refined.

14. The value of the "Flack absolute structure parameter", x, should be 0.00 for the correct enantiomorphic description and 1.00 for the inverted description: a) H. D. Flack, *Acta Cryst.*, **1983**, *A39*, 876-881; b) G. Bernardinelli and H. D. Flack, *Acta Cryst.*, **1985**, *A41*, 500-511.

Table S-1. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $Zr_4(OPr^n)_{16}$ [a]

Atom Type[b]	Fractional Coordinates 10^4x	10^4y	10^4z	Equivalent Isotropic Thermal Parameter, U, $Å^2 \times 10^3$ [c]
Zr_1	5925(1)	-891(1)	4234(1)	126(1)
Zr_2	3247(1)	1773(2)	3046(1)	140(1)
O_{1A}	4920(7)	1118(8)	4100(7)	112(3)
O_{1B}	4197(9)	-281(10)	3552(9)	146(3)
O_{2B}	2784(9)	1135(10)	4783(9)	139(3)
O_{1C}	6291(12)	-2597(13)	4477(12)	187(5)
O_{2C}	6813(11)	-398(15)	2944(12)	196(6)
O_{1D}	4111(13)	2029(13)	1702(11)	200(6)
O_{2D}	2647(13)	3503(12)	2909(11)	199(6)
O_{1E}	1835(11)	1681(13)	2646(10)	185(5)
C_{11}	5779(21)	1764(18)	3857(17)	196(9)
C_{21}	5316(30)	3019(24)	3362(42)	194(18)
C_{51}	5815(51)	2554(48)	2858(27)	233(24)
C_{31}	6414(28)	3454(26)	2898(26)	331(19)
C_{12}	3695(22)	-1083(22)	3329(24)	271(18)
C_{22}	3827(33)	-1054(34)	2340(29)	335(22)
C_{32}	3346(30)	-2013(31)	2359(26)	328(20)
C_{13}	1591(22)	928(26)	5090(20)	257(16)
C_{23}	707(26)	2020(27)	5045(24)	257(13)
C_{33}	-462(21)	1743(27)	5489(29)	321(22)
C_{14}	6118(47)	-3349(63)	3994(74)	352(64)
C_{44}	6498(42)	-3917(27)	4835(33)	279(30)
C_{24}	7145(48)	-4446(36)	4121(44)	432(36)
C_{34}	8137(51)	-4109(49)	3596(55)	481(46)
C_{15}	7372(52)	141(45)	1920(33)	300(39)
C_{45}	7960(46)	-574(100)	2358(51)	393(67)
C_{25}	7814(46)	-658(44)	1397(33)	447(39)
C_{35}	8551(51)	-62(58)	572(39)	608(59)

Table S-1. (continued)

Atom Type[b]	Fractional Coordinates 10^4x	10^4y	10^4z	Equivalent Isotropic Thermal Parameter, U, $Å^2 \times 10^3$ [c]
C_{16}	4512(64)	2937(62)	820(34)	315(46)
C_{46}	4806(41)	2093(46)	744(28)	210(24)
C_{26}	4269(54)	3154(56)	-222(32)	592(65)
C_{36}	3241(63)	2924(91)	-358(46)	682(78)
C_{17}	1676(38)	4709(32)	2796(41)	256(35)
C_{47}	2610(55)	4770(25)	2651(48)	256(29)
C_{27}	1828(53)	5565(30)	1740(32)	507(48)
C_{37}	1318(64)	6826(33)	1570(48)	671(59)
C_{18}	875(30)	1611(35)	2224(33)	357(25)
C_{28}	324(39)	2636(46)	1295(32)	288(27)
C_{58}	-135(52)	2774(55)	1959(65)	317(76)
C_{38}	-870(61)	2589(119)	1353(95)	609(104)
C_{68}	164(85)	3849(53)	1245(71)	408(62)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Figure 1.

[c] This is one-third of the trace of the orthogonalized U_{ij} tensor.

[d] Atom labels are used to specify disorder in the alkyl groups of the n-propoxide ligands. The following pairs of atom labels are used to represent alternate positions for a disordered carbon (x = 1-8 propyl groups): C_{1x}, C_{4x} (methylene); C_{2x}, C_{5x} (methylene); and C_{3x}, C_{6x} (methyl).

Table S-2. Anisotropic Thermal Parameters for Nonhydrogen Atoms in Crystalline $Zr_4(OPr^n)_{16}$ [a,b]

Atom Type[c]	Anisotropic Thermal Parameters ($Å^2 \times 10^3$) U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr_1	110(1)	125(1)	135(1)	-62(1)	-10(1)	-19(1)
Zr_2	126(1)	131(1)	131(1)	-34(1)	-29(1)	-24(1)
O_{1A}	96(6)	109(6)	118(7)	-27(5)	-11(5)	-42(5)
O_{1B}	144(8)	126(8)	160(9)	-51(7)	-31(7)	-39(6)
O_{2B}	87(6)	154(8)	165(9)	-63(7)	4(6)	-33(6)
O_{1C}	197(12)	153(11)	212(13)	-117(10)	-46(10)	5(8)
O_{2C}	137(9)	234(14)	172(12)	-91(10)	-14(9)	-4(9)
O_{1D}	204(13)	183(13)	134(10)	-17(9)	19(10)	-51(10)
O_{2D}	187(12)	131(10)	199(12)	-20(9)	-44(10)	-10(8)
O_{1E}	130(9)	213(13)	186(11)	-59(9)	-44(8)	-42(8)
C_{11}	267(27)	140(17)	164(18)	-42(14)	41(18)	-91(18)
C_{21}	190(24)	202(25)	191(24)	-66(18)	3(17)	-89(19)
C_{51}	235(29)	223(29)	242(30)	-82(20)	13(19)	-100(20)
C_{31}	348(39)	262(32)	346(40)	14(26)	-46(31)	-214(30)
C_{12}	225(24)	228(25)	377(40)	-201(27)	-200(28)	70(19)
C_{22}	304(39)	369(50)	433(60)	-285(48)	-82(39)	-49(34)
C_{32}	385(44)	391(44)	413(48)	-296(40)	-13(36)	-187(38)
C_{13}	224(29)	269(32)	167(20)	-89(21)	-39(19)	42(25)
C_{23}	261(34)	238(31)	252(31)	-108(25)	-51(27)	-36(27)
C_{33}	133(18)	310(36)	449(53)	-101(33)	79(25)	-97(21)
C_{14}	315(94)	394(106)	262(82)	-108(74)	-19(70)	-59(75)
C_{44}	311(52)	146(31)	387(65)	-153(38)	-201(48)	39(30)
C_{24}	437(90)	492(100)	417(84)	-210(72)	-25(73)	-175(83)
C_{34}	636(119)	411(71)	539(103)	-253(68)	171(81)	-324(76)
C_{15}	222(47)	388(75)	110(30)	-75(39)	82(34)	17(44)
C_{45}	508(118)	332(88)	375(106)	-163(80)	-97(80)	-126(80)
C_{25}	434(72)	484(77)	228(45)	-115(48)	84(44)	-27(54)
C_{35}	573(95)	731(121)	297(53)	-189(64)	245(60)	-114(77)
C_{16}	227(56)	263(71)	364(91)	-89(60)	6(62)	-40(52)

Table S-2. (continued)

Atom Type[c]	Anisotropic Thermal Parameters ($Å^2 \times 10^3$) U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C_{26}	491(113)	898(172)	238(56)	-135(78)	7(61)	-207(103)
C_{46}	301(63)	190(44)	140(33)	-70(30)	64(38)	-105(42)
C_{36}	601(123)	912(150)	472(114)	-148(92)	174(87)	-425(117)
C_{17}	230(54)	280(73)	312(68)	-118(52)	-67(47)	-125(51)
C_{47}	331(66)	54(22)	313(62)	-39(28)	-53(52)	-17(29)
C_{27}	828(117)	117(23)	455(72)	-36(32)	-302(77)	-20(42)
C_{37}	879(137)	522(97)	741(121)	-315(88)	-217(102)	-231(99)
C_{18}	233(33)	387(51)	400(52)	-42(40)	-158(35)	-137(34)
C_{28}	209(37)	434(68)	229(40)	-92(39)	-102(33)	-133(42)
C_{58}	245(90)	352(105)	281(100)	-51(68)	122(79)	-164(77)
C_{38}	411(130)	770(190)	702(190)	-290(137)	102(128)	-315(132)
C_{68}	498(121)	348(89)	515(122)	-204(81)	-192(91)	-186(83)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.
[b] The form of the anisotropic thermal parameter is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.
[c] Atoms are labeled in agreement with Figure 1.
[d] Atom labels are used to specify disorder in the alkyl groups of the n-propoxide ligands. The following pairs of atom labels are used to represent alternate positions for a disordered carbon (x = 1-8 propyl groups): C_{1x}, C_{4x} (methylene); C_{2x}, C_{5x} (methylene); and C_{3x}, C_{6x} (methyl).

Table S-3. Atomic Coordinates for Hydrogen Atoms in Crystalline $Zr_4(OPr^n)_{16}$ [a]

Atom Type[b]	Fractional Coordinates 10^4x	10^4y	10^4z
H_{11a}	6158	1539	4522
H_{11b}	6396	1459	3411
H_{11c}	5602	2217	4307
H_{11d}	6570	1134	4061
H_{21a}	4891	3373	3865
H_{21b}	4769	3277	2792
H_{51a}	5016	3030	2550
H_{51b}	6285	2108	2430
H_{31a}	6138	4349	2532
H_{31b}	6826	3092	2405
H_{31c}	6947	3187	3472
H_{31d}	6462	4052	2185
H_{31e}	7201	2969	3206
H_{31f}	5940	3886	3325
H_{12a}	4066	-1943	3831
H_{12b}	2850	-834	3480
H_{22a}	4661	-1263	2148
H_{22b}	3383	-226	1823
H_{32a}	3424	-2024	1663
H_{32b}	2521	-1795	2550
H_{32c}	3792	-2827	2874
H_{13a}	1397	656	4603
H_{13b}	1652	279	5808
H_{23a}	577	2642	4311
H_{23b}	939	2345	5469
H_{33a}	-1087	2499	5462
H_{33b}	-328	1132	6216
H_{33c}	-689	1428	5063

Table S-3. (continued)

Atom Type[b]	Fractional Coordinates 10^4x	10^4y	10^4z
H_{14a}	5439	-3598	4319
H_{14b}	5938	-2842	3237
H_{44a}	6926	-4373	5515
H_{44b}	5733	-4030	4956
H_{24a}	7334	-4957	4876
H_{24b}	6975	-4935	3824
H_{24c}	6591	-4239	3575
H_{24d}	7428	-5348	4514
H_{34a}	8818	-4851	3686
H_{34b}	8313	-3636	3898
H_{34c}	7952	-3611	2847
H_{34d}	8487	-4537	3138
H_{34e}	8719	-4338	4118
H_{34f}	7877	-3222	3175
H_{15a}	6789	917	1458
H_{15b}	8021	337	2050
H_{45a}	8214	125	2189
H_{45b}	8572	-1332	2807
H_{25a}	7174	-698	1084
H_{25b}	8286	-1495	1879
H_{25c}	6983	-244	1168
H_{25d}	8054	-1529	1517
H_{35a}	8907	-540	154
H_{35b}	9166	-22	904
H_{35c}	8064	769	117
H_{35d}	8459	-111	-81
H_{35e}	9373	-482	801
H_{35f}	8307	799	455
H_{16a}	4157	3728	888

Table S-3. (continued)

Atom Type[b]	Fractional Coordinates 10^4x	10^4y	10^4z
H_{16b}	5368	2676	898
H_{46a}	5573	2105	854
H_{46b}	4954	1338	646
H_{26a}	4962	2632	-465
H_{26b}	4169	4017	-686
H_{26c}	4041	3931	-140
H_{26d}	4803	3180	-821
H_{36a}	3160	3101	-1095
H_{36b}	2541	3454	-146
H_{36c}	3335	2065	77
H_{36d}	2808	3586	-993
H_{36e}	2736	2891	250
H_{36f}	3492	2142	-422
H_{17a}	898	4633	2865
H_{17b}	1764	4976	3329
H_{47a}	2306	5002	3246
H_{47b}	3400	4821	2483
H_{27a}	2675	5369	1599
H_{27b}	1479	5442	1229
H_{27c}	2269	5512	1108
H_{27d}	1190	5249	1818
H_{37a}	1458	7338	848
H_{37b}	1671	6965	2058
H_{37c}	475	7039	1686
H_{37d}	810	7284	944
H_{37e}	1938	7160	1469
H_{37f}	856	6898	2179
H_{18a}	1172	870	2077
H_{18b}	275	1504	2770

Table S-3. (continued)

Atom Type[b]	Fractional Coordinates 10^4x	10^4y	10^4z
H_{18c}	641	926	2747
H_{18d}	1131	1452	1587
H_{28a}	731	2550	661
H_{28b}	296	3411	1296
H_{28c}	-453	2623	1220
H_{28d}	792	2538	688
H_{58a}	-760	2730	1630
H_{58b}	-446	2874	2613
H_{58c}	98	3494	1528
H_{58d}	-533	2865	2595
H_{38a}	-1334	3266	741
H_{38b}	-1246	2662	1993
H_{38c}	-814	1808	1364
H_{38d}	-1590	3306	1120
H_{38e}	-1064	1858	1798
H_{38f}	-440	2481	742
H_{68a}	-533	4590	1096
H_{68b}	457	3765	589
H_{68c}	769	3911	1572
H_{68d}	-220	4488	579
H_{68e}	928	3890	1294
H_{68f}	-321	3975	1827

[a] Hydrogen atoms were included in the structural model as fixed atoms (using idealized sp^3-hybridized geometry and C-H bond lengths of 0.96-0.97 Å) "riding" on their respective carbons. The isotropic thermal parameters of these idealized hydrogen atoms were fixed at values 1.2 (methylene) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

[b] Hydrogen atoms are labeled with the same numerical subscripts as the carbon atoms to which they are covalently bonded[c] and carry an additional

literal subscript (a, b, c, d, e or f) to distinguish between hydrogens bonded to the same carbon and/or to designate disorder.

[c] Atom labels are used to specify disorder in the alkyl groups of the n-propoxide ligands. The following pairs of atom labels are used to represent alternate positions for a disordered carbon (x = 1-8 propyl groups): C_{1x}, C_{4x} (methylene); C_{2x}, C_{5x} (methylene); and C_{3x}, C_{6x} (methyl).

Table S-4. Bond Lengths in Crystalline $Zr_4(OPr^n)_{16}$ [a]

Type[b,c]	Length, Å	Type[b,c]	Length, Å
Zr_1-O_{1A}	2.31(1)	Zr_2-O_{1A}	2.35(1)
Zr_1-O_{1A}'	2.32(1)	Zr_2-O_{1B}	2.23(1)
Zr_1-O_{1B}	2.15(1)	Zr_2-O_{2B}	2.24(1)
Zr_1-O_{2B}'	2.08(1)	Zr_2-O_{1D}	1.96(1)
Zr_1-O_{1C}	1.92(1)	Zr_2-O_{2D}	1.96(2)
Zr_1-O_{2C}	1.93(2)	Zr_2-O_{1E}	1.93(1)
Zr_1···Zr_2	3.624(2)	Zr_1···Zr_1'	3.678(3)
Zr_1···Zr_2'	3.624(2)		
O_{1A}-C_{11}	1.47(2)	O_{2C}-C_{45}	1.49(3)
O_{1B}-C_{12}	1.51(2)	O_{1D}-C_{16}	1.44(3)
O_{2B}-C_{13}	1.53(2)	O_{1D}-C_{46}	1.45(3)
O_{1C}-C_{14}	1.47(3)	O_{2D}-C_{17}	1.49(3)
O_{1C}-C_{44}	1.45(3)	O_{2D}-C_{47}	1.47(3)
O_{2C}-C_{15}	1.47(3)	O_{1E}-C_{18}	1.43(2)
C_{11}-C_{21}	1.35(2)	C_{25}-C_{35}	1.46(3)
C_{11}-C_{51}	1.32(2)	C_{16}-C_{26}	1.40(3)
C_{21}-C_{31}	1.57(2)	C_{46}-C_{26}	1.44(3)
C_{51}-C_{31}	1.59(3)	C_{26}-C_{36}	1.44(3)
C_{12}-C_{22}	1.34(3)	C_{17}-C_{27}	1.43(3)
C_{22}-C_{32}	1.52(2)	C_{47}-C_{27}	1.43(3)
C_{13}-C_{23}	1.38(2)	C_{27}-C_{37}	1.40(3)
C_{23}-C_{33}	1.56(2)	C_{18}-C_{28}	1.39(3)
C_{14}-C_{24}	1.43(3)	C_{18}-C_{58}	1.45(3)
C_{44}-C_{24}	1.41(3)	C_{28}-C_{38}	1.46(3)
C_{24}-C_{34}	1.42(3)	C_{28}-C_{68}	1.45(3)

Table S-4. (continued)

Type[b]	Length, Å	Type[b]	Length, Å
C_{15}-C_{25}	1.40(3)	C_{58}-C_{38}	1.45(3)
C_{45}-C_{25}	1.42(3)	C_{58}-C_{68}	1.44(3)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Figure 1. Atoms labeled with a prime(′) are related to those labeled without a prime by the crystallographic inversion center located at (1/2,0,1/2) in the unit cell.

[c] Atom labels are used to specify disorder in the alkyl groups of the n-propoxide ligands. The following pairs of atom labels are used to represent alternate positions for a disordered carbon (x=1-8 propyl groups): C_{1x}, C_{4x} (methylene); C_{2x}, C_{5x} (methylene); and C_{3x}, C_{6x} (methyl).

Table S-5. Bond Angles in Crystalline $Zr_4(OPr^n)_{16}$ [a]

Type[b,c]	Angle, (deg)	Type[b,c]	Angle, (deg)
$O_{1A}Zr_1O_{1A}'$	74.8(3)	$O_{1B}Zr_2O_{1A}$	70.8(4)
$O_{1B}Zr_1O_{1A}$	73.0(4)	$O_{2B}Zr_2O_{1A}$	69.4(3)
$O_{1B}Zr_1O_{1A}'$	90.3(4)	$O_{1D}Zr_2O_{1A}$	95.2(5)
$O_{2B}'Zr_1O_{1A}$	90.7(4)	$O_{2D}Zr_2O_{1A}$	95.2(5)
$O_{2B}'Zr_1O_{1A}'$	72.6(4)	$O_{1B}Zr_2O_{2B}$	81.4(4)
$O_{1C}Zr_1O_{1A}'$	94.7(5)	$O_{1D}Zr_2O_{1B}$	88.1(5)
$O_{2C}Zr_1O_{1A}$	94.6(5)	$O_{1E}Zr_2O_{1B}$	91.4(5)
$O_{1C}Zr_1O_{1B}$	93.4(5)	$O_{2D}Zr_2O_{2B}$	89.4(5)
$O_{2C}Zr_1O_{1B}$	99.8(5)	$O_{1E}Zr_2O_{2B}$	93.1(5)
$O_{1C}Zr_1O_{2B}'$	99.6(5)	$O_{1D}Zr_2O_{2D}$	98.0(6)
$O_{2C}Zr_1O_{2B}'$	94.2(5)	$O_{1E}Zr_2O_{1D}$	99.8(6)
$O_{1C}Zr_1O_{2C}$	98.6(7)	$O_{1E}Zr_2O_{2D}$	100.7(6)
$O_{1C}Zr_1O_{1A}$	162.5(5)	$O_{1E}Zr_2O_{1A}$	156.3(4)
$O_{2C}Zr_1O_{1A}'$	162.7(6)	$O_{2D}Zr_2O_{1B}$	165.2(5)
$O_{2B}'Zr_1O_{1B}$	159.2(4)	$O_{1D}Zr_2O_{2B}$	163.5(5)
$Zr_1O_{1A}Zr_1'$	105.2(3)	$Zr_1O_{1B}Zr_2$	111.7(5)
$Zr_1O_{1A}Zr_2$	102.4(4)	$Zr_1'O_{2B}Zr_2$	114.0(5)
$Zr_1'O_{1A}Zr_2$	101.7(3)		
		$C_{12}O_{1B}Zr_1$	125.8(10)
$C_{11}O_{1A}Zr_1$	109.0(9)	$C_{12}O_{1B}Zr_2$	122.3(10)
$C_{11}O_{1A}Zr_1'$	111.2(10)	$C_{13}O_{2B}Zr_1'$	128.9(12)
$C_{11}O_{1A}Zr_2$	125.5(9)	$C_{13}O_{2B}Zr_2$	117.1(12)
$C_{14}O_{1C}Zr_1$	141(3)	$C_{46}O_{1D}Zr_2$	175(2)
$C_{44}O_{1C}Zr_1$	171(2)	$C_{17}O_{2D}Zr_2$	153(2)
$C_{15}O_{2C}Zr_1$	173(2)	$C_{47}O_{2D}Zr_2$	160(3)

Table S-5. (continued)

Type[b,c]	Angle, (deg)	Type[b,c]	Angle, (deg)
$C_{45}O_{2C}Zr_1$	150(4)	$C_{18}O_{1E}Zr_2$	172(2)
$C_{16}O_{1D}Zr_2$	143(3)		
$C_{21}C_{11}O_{1A}$	115(2)	$C_{25}C_{45}O_{2C}$	110(4)
$C_{51}C_{11}O_{1A}$	117(2)	$C_{26}C_{16}O_{1D}$	118(3)
$C_{22}C_{12}O_{1B}$	117(3)	$C_{26}C_{46}O_{1D}$	115(3)
$C_{23}C_{13}O_{2B}$	110(2)	$C_{27}C_{17}O_{2D}$	104(3)
$C_{24}C_{14}O_{1C}$	113(3)	$C_{27}C_{47}O_{2D}$	105(3)
$C_{24}C_{44}O_{1C}$	115(3)	$C_{28}C_{18}O_{1E}$	116(3)
$C_{25}C_{15}O_{2C}$	113(4)	$C_{58}C_{18}O_{1E}$	110(4)
$C_{11}C_{21}C_{31}$	106(2)	$C_{16}C_{26}C_{36}$	117(4)
$C_{11}C_{51}C_{31}$	106(3)	$C_{46}C_{26}C_{36}$	102(4)
$C_{12}C_{22}C_{32}$	107(3)	$C_{17}C_{27}C_{37}$	114(3)
$C_{13}C_{23}C_{33}$	109(2)	$C_{47}C_{27}C_{37}$	115(3)
$C_{14}C_{24}C_{34}$	110(4)	$C_{18}C_{28}C_{38}$	102(5)
$C_{44}C_{24}C_{34}$	119(5)	$C_{18}C_{58}C_{68}$	113(4)
$C_{15}C_{25}C_{35}$	102(3)	$C_{18}C_{28}C_{68}$	116(4)
$C_{45}C_{25}C_{35}$	109(4)	$C_{18}C_{58}C_{38}$	100(5)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

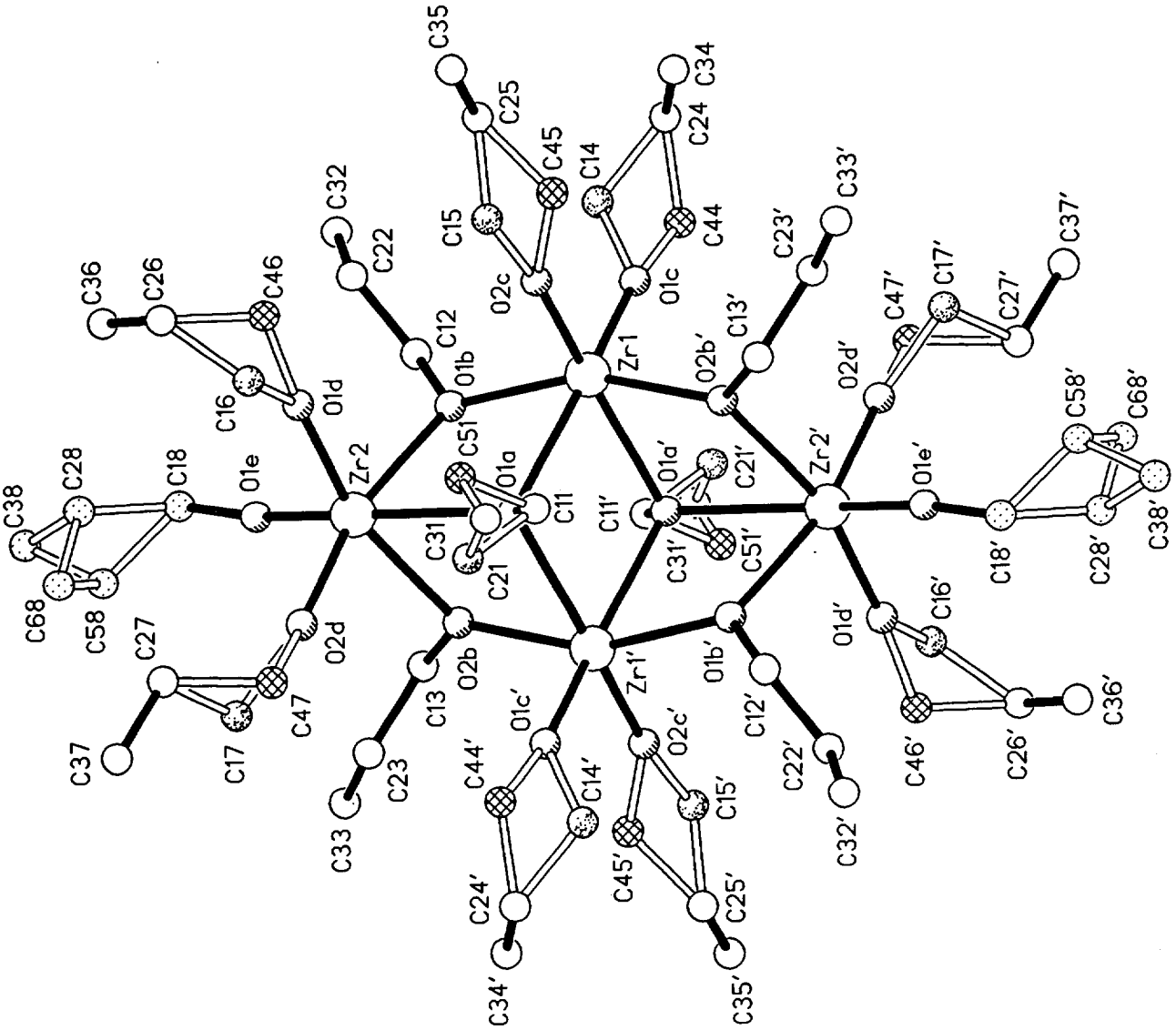
[b] Atoms are labeled in agreement with Figure 1. Atoms labeled with a prime(′) are related to those labeled without a prime by the crystallographic inversion center located at (1/2,0,1/2) in the unit cell.

[c] Atom labels are used to specify disorder in the alkyl groups of the npropoxide ligands. The following pairs of atom labels are used to represent alternate positions for a disordered carbon (x=1-8 propyl groups): C_{1x}, C_{4x} (methylene); C_{2x}, C_{5x} (methylene); and C_{3x}, C_{6x} (methyl).

FIGURE CAPTIONS

Figure S-1 shows a perspective drawing of the disordered solid-state structure for the $Zr_4(OPr^n)_{16}$ molecule. Ordered Ti, O and C atoms are represented by large open, medium-sized shaded and medium-sized open spheres, respectively. Disordered positions for carbon atoms of the alkyl groups are represented by medium-sized spheres with a cross-hatched pattern, a heavy random dot pattern with highlight or a light regular dot pattern. Hydrogen atoms are omitted for clarity. Atoms labeled with a prime(') are related to those labeled without a prime by the crystallographic inversion center located at (1/2, 0, 1/2) in the unit cell of the centrosymmetric space group used for structure refinement of the disordered structure. The following atom labels (x = 1-8 propyl groups) are used to indicate alternate (disordered) positions for carbon atoms in the n-propoxide ligands: C_{1x}, C_{4x} (methylene); C_{2x}, C_{5x} (methylene); and C_{3x}, C_{6x} (methyl). Disordered carbon atoms are connected to other atoms with hollow bonds.

Figure S-2 shows a perspective drawing of the disordered solid-state structure for the $Zr_4(OPr^n)_{16}$ molecule. The view and atom labeling scheme is as in Figure S-1 but nonhydrogen atoms are now represented by 30% probability thermal vibration ellipsoids. Hydrogen atoms are omitted for clarity.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Zr-1'
Zr-2'
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O1b
O1c
O1d
O1e
O2b
O2c
O2d
O1b'
O1c'
O1d'
O1e'
O2b'
O2d'
C11
C11'
C12
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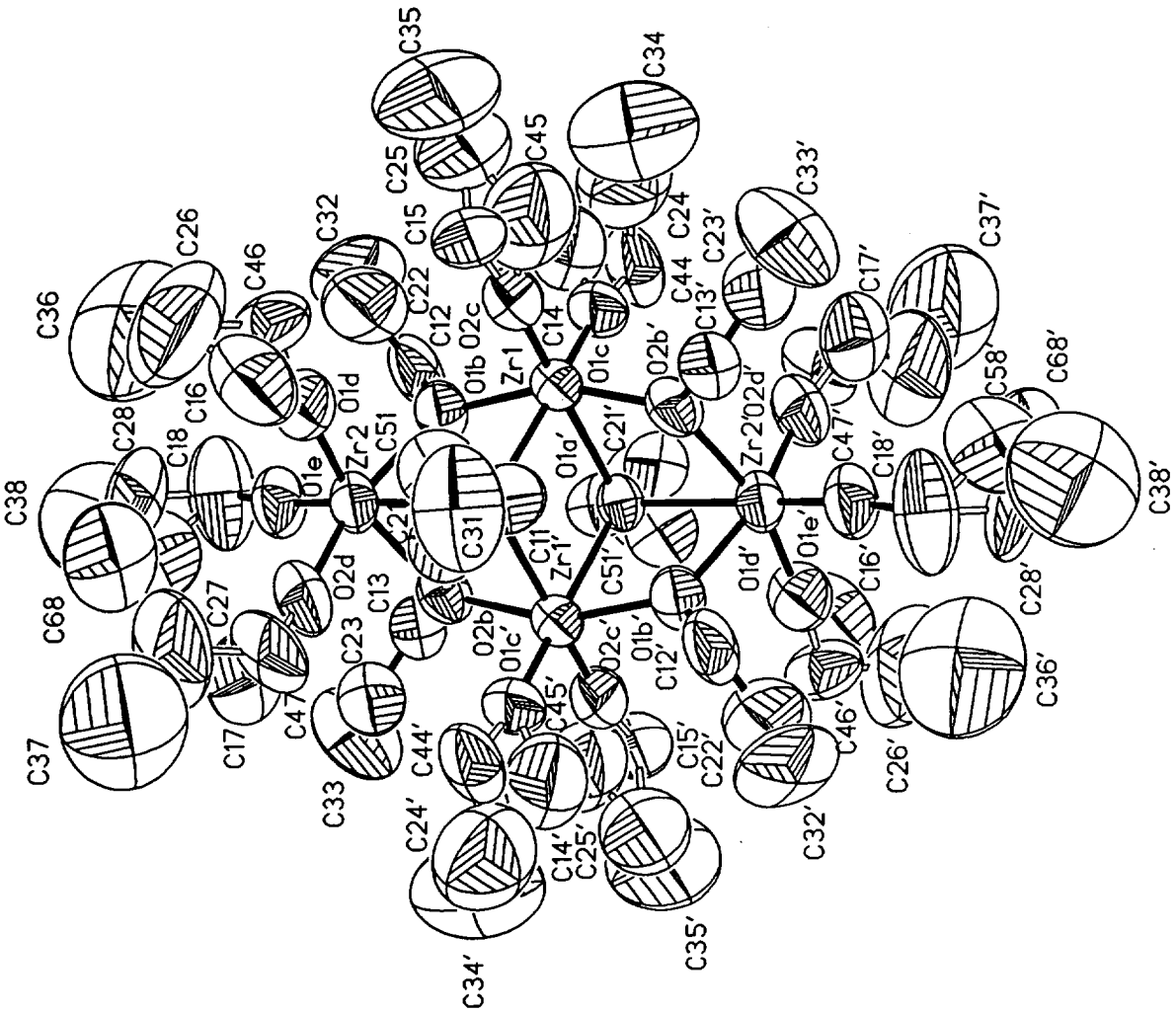
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C12
C13'
C17'
C28
C18
C16
O1d
O1b
O2c
Zr1
C14
O1c
O2b'
C58'
C68'
C38
O1e
Zr2
C51
C21'
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C18'
C31
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