

Supplementary Information

Investigation of Titanium(IV)-Oxo Complexes Stabilized with α -Hydroxy Carboxylate Ligands: Structural Analysis And DFT Studies

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Table S1. Crystal data and structure refinement for (1) and (2).

Empirical formula	C ₅₈ H ₈₆ O ₁₇ Ti ₄ (1)	C ₈₀ H ₇₆ O ₃₀ Ti ₆ (2)
Formula weight	1246.86	1804.80
Temperature	100(2) K	100(2) K
Wavelength [Å]	1.54184	1.54184
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions [Å] and [°]	a = 22.4667(4) b = 12.6262(2) c = 23.0730(5) $\alpha = 90$ $\beta = 106.0037(19)$ $\gamma = 90$	a = 12.4059(10) b = 12.5243(11) c = 17.3816(13) $\alpha = 77.520(7)$ $\beta = 69.528(8)$ $\gamma = 63.331(9)$
Volume [Å ³]	6291.4(2)	2255.3(4)
Z, calculated density [Mg/m ³]	4, 1.316	1, 1.329
Absorption coefficient [mm ⁻¹]	4.707	4.956
F(000)	2632	928
Crystal size [mm ³]	0.080 × 0.040 × 0.020	0.120 × 0.060 × 0.040
Theta range for data collection [°]	3.986 to 74.492	3.960 to 74.443
Index ranges	-26 ≤ h ≤ 27 -15 ≤ k ≤ 15 -27 ≤ l ≤ 28	-14 ≤ h ≤ 15 -12 ≤ k ≤ 15 -21 ≤ l ≤ 21
Reflections collected/unique	29621/ 6404 [R(int) = 0.0474]	27429/ 8652 [R(int) = 0.0968]
Completeness to theta	67.684° 99.9 %	67.684° 97.8 %
Absorption correction	Numerical	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.746	1.00000 and 0.65108
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	6404 / 0 / 397	8652 / 3 / 531
Goodness-of-fit on F2	1.095	1.019
Final R indices [I > 2σ(I)]	R1 ^a = 0.0428, wR2 ^b = 0.1131	R1 ^a = 0.0941, wR2 ^b = 0.2558

R indices (all data)	R1 ^a = 0.0498, wR2 ^b = 0.1169	R1 ^a = 0.1461, wR2 ^b = 0.2977
Extinction coefficient	0.00009(2)	nd
Largest diff. peak and hole	0.470 and -0.630 e·Å ⁻³	0.851 and -0.953 e·Å ⁻³

$$^a R1 = \frac{\sum ||F_o| - |F_d||}{\sum |F_o|} \quad ^b wR2 = \left[\frac{\sum w(F_o^2 - F^2)^2}{\sum (w(F_o^2)^2)} \right]^{1/2}$$

Table S2. Experimental and theoretical (B3LYP/6-31G(d,p)) values of bond lengths [Å] and angles [°] for **1** and **2**.

[Ti ₄ O(O ⁱ Pr) ₁₀ (O ₃ C ₁₄ H ₈) ₂] (1)			[Ti ₆ O ₄ (O ⁱ Pr) ₂ (O ₃ C ₁₄ H ₈) ₄ (O ₂ CEt) ₆] (2)		
Parameter	Distances [Å]		Parameter	Distances [Å]	
	Exp.	Calc.		Exp.	Calc.
Ti(1)-O(31)	1.7921(15)	1.793	Ti(1)-O(17)	1.794(5)	1.800
Ti(1)-O(41)	1.8195(16)	1.821	Ti(1)-O(16)	1.884(4)	1.901
Ti(1)-O(16)	1.8293(7)	1.824	Ti(1)-O(21)	1.929(4)	1.884
Ti(1)-O(21)	2.0940(15)	2.139	Ti(1)-O(61)	2.008(5)	2.055
Ti(1)-O(1)	2.1801(15)	2.212	Ti(1)-O(52)	2.028(4)	2.036
Ti(1)-O(2)#1	2.2274(15)	2.283	Ti(1)-O(23)	2.093(5)	2.147
Ti(1)-Ti(2)	3.3510(5)	3.419	Ti(1)-Ti(3)	3.1182(18)	3.163
Ti(2)-O(61)	1.778(2)	1.788	Ti(2)-O(17)#1	1.800(4)	1.802
Ti(2)-O(51)	1.7819(19)	1.796	Ti(2)-O(16)	1.894(4)	1.895
Ti(2)-O(3)	1.8773(16)	1.873	Ti(2)-O(1)	1.936(5)	1.881
Ti(2)-O(21)	1.9695(16)	1.973	Ti(2)-O(41)	2.010(5)	2.042
Ti(2)-O(1)	2.0651(15)	2.106	Ti(2)-O(62)#1	2.022(5)	2.052
O(1)-C(2)	1.299(2)	1.301	Ti(2)-O(3)	2.094(4)	2.169
O(2)-C(2)	1.226(3)	1.234	Ti(2)-Ti(3)	3.1185(15)	3.164
C(3)-O(3)	1.393(3)	1.401	Ti(3)-O(71)	1.728(5)	1.740
			Ti(3)-O(3)	1.940(4)	1.962
			Ti(3)-O(23)	1.953(4)	1.972
			Ti(3)-O(42)	2.002(6)	2.040
			Ti(3)-O(51)	2.006(6)	2.050
			Ti(3)-O(16)	2.077(4)	2.070
			O(1)-C(2)	1.323(9)	1.331
			O(2)-C(2)	1.205(8)	1.207
			C(3)-O(3)	1.435(8)	1.423
Angles [°]			Angles [°]		
	Exp.	Calc.		Exp.	Calc.
O(31)-Ti(1)-O(41)	98.34(7)	98.6	O(17)-Ti(1)-O(16)	105.82(19)	104.9
O(31)-Ti(1)-O(16)	100.86(7)	102.0	O(17)-Ti(1)-O(21)	101.6(2)	104.1
O(41)-Ti(1)-O(16)	101.60(6)	100.1	O(16)-Ti(1)-O(21)	152.6(2)	150.8
O(31)-Ti(1)-O(21)	103.26(7)	102.6	O(17)-Ti(1)-O(61)	90.4(2)	89.9
O(41)-Ti(1)-O(21)	91.45(7)	91.9	O(16)-Ti(1)-O(61)	89.64(19)	88.9
O(16)-Ti(1)-O(21)	150.51(8)	150.6	O(21)-Ti(1)-O(61)	89.14(19)	88.0
O(31)-Ti(1)-O(1)	166.71(7)	165.2	O(17)-Ti(1)-O(52)	90.5(2)	93.5
O(41)-Ti(1)-O(1)	91.67(6)	92.9	O(16)-Ti(1)-O(52)	89.70(19)	89.1
O(16)-Ti(1)-O(1)	85.54(6)	85.1	O(21)-Ti(1)-O(52)	91.11(19)	92.4
O(21)-Ti(1)-O(1)	67.58(6)	67.4	O(61)-Ti(1)-O(52)	179.0(2)	176.4
O(31)-Ti(1)-O(2)#1	84.84(7)	85.3	O(17)-Ti(1)-O(23)	175.8(2)	178.5
O(41)-Ti(1)-O(2)#1	171.77(7)	172.5	O(16)-Ti(1)-O(23)	76.33(18)	75.1
O(16)-Ti(1)-O(2)#1	85.16(5)	85.2	O(21)-Ti(1)-O(23)	76.37(19)	75.9
O(21)-Ti(1)-O(2)#1	80.41(6)	81.1	O(61)-Ti(1)-O(23)	93.29(19)	91.6
O(1)-Ti(1)-O(2)#1	84.12(6)	82.3	O(52)-Ti(1)-O(23)	85.85(18)	85.0
O(31)-Ti(1)-Ti(2)	136.14(5)	134.8	O(17)-Ti(1)-Ti(3)	142.97(14)	141.8
O(41)-Ti(1)-Ti(2)	82.29(5)	85.5	O(16)-Ti(1)-Ti(3)	40.32(13)	39.1
O(16)-Ti(1)-Ti(2)	122.13(5)	121.7	O(21)-Ti(1)-Ti(3)	113.44(14)	113.1
O(21)-Ti(1)-Ti(2)	33.26(4)	32.2	O(61)-Ti(1)-Ti(3)	101.36(15)	99.3
O(1)-Ti(1)-Ti(2)	36.68(4)	36.6	O(52)-Ti(1)-Ti(3)	77.67(14)	77.2
O(2)#-Ti(1)-Ti(2)	90.15(4)	87.2	O(23)-Ti(1)-Ti(3)	37.97(12)	37.8
O(61)-Ti(2)-O(51)	107.54(10)	108.2	O(17)#1-Ti(2)-O(16)	106.52(19)	106.7
O(61)-Ti(2)-O(3)	106.21(8)	106.0	O(17)#1-Ti(2)-O(1)	100.76(19)	103.2

O(51)-Ti(2)-O(3)	95.72(8)	93.6	O(16)-Ti(2)-O(1)	152.5(2)	150.1
O(61)-Ti(2)-O(21)	102.92(8)	104.6	O(17)#1-Ti(2)-O(41)	91.5(2)	90.7
O(51)-Ti(2)-O(21)	97.16(8)	99.1	O(16)-Ti(2)-O(41)	89.34(19)	88.6
O(3)-Ti(2)-O(21)	142.74(7)	141.1	O(1)-Ti(2)-O(41)	93.4(2)	93.1
O(61)-Ti(2)-O(1)	108.26(9)	107.6	O(17)#1-Ti(2)-O(62)#1	90.7(2)	90.2
O(51)-Ti(2)-O(1)	144.09(8)	144.2	O(16)-Ti(2)-O(62)#1	88.01(18)	89.2
O(3)-Ti(2)-O(1)	76.93(6)	75.8	O(1)-Ti(2)-O(62)#1	88.3(2)	88.6
O(21)-Ti(2)-O(1)	72.19(6)	72.5	O(41)-Ti(2)-O(62)#1	176.96(19)	177.8
O(61)-Ti(2)-Ti(1)	119.65(7)	118.1	O(17)#1-Ti(2)-O(3)	176.2(2)	175.3
O(51)-Ti(2)-Ti(1)	116.53(7)	119.8	O(16)-Ti(2)-O(3)	76.00(18)	74.8
O(3)-Ti(2)-Ti(1)	108.03(5)	107.5	O(1)-Ti(2)-O(3)	76.94(18)	75.6
O(21)-Ti(2)-Ti(1)	35.67(4)	35.3	O(41)-Ti(2)-O(3)	85.6(2)	84.8
O(1)-Ti(2)-Ti(1)	39.10(4)	38.7	O(62)#1-Ti(2)-O(3)	92.33(18)	94.4
Ti(1)#1-O(16)-Ti(1)	142.49(12)	144.9	O(17)#1-Ti(2)-Ti(3)	143.93(14)	142.4
			O(16)-Ti(2)-Ti(3)	40.38(13)	39.0
			O(1)-Ti(2)-Ti(3)	113.89(15)	112.6
			O(41)-Ti(2)-Ti(3)	77.24(14)	76.7
			O(62)#1-Ti(2)-Ti(3)	99.76(13)	101.4
			O(3)-Ti(2)-Ti(3)	37.60(11)	37.6
			O(71)-Ti(3)-O(3)	105.8(2)	106.4
			O(71)-Ti(3)-O(23)	103.5(2)	102.4
			O(3)-Ti(3)-O(23)	150.71(19)	151.2
			O(71)-Ti(3)-O(42)	94.6(3)	94.1
			O(3)-Ti(3)-O(42)	88.0(2)	88.4
			O(23)-Ti(3)-O(42)	88.81(19)	89.5
			O(71)-Ti(3)-O(51)	92.6(3)	93.4
			O(3)-Ti(3)-O(51)	90.9(2)	91.0
			O(23)-Ti(3)-O(51)	88.6(2)	87.4
			O(42)-Ti(3)-O(51)	172.8(2)	172.3
			O(71)-Ti(3)-O(16)	177.9(3)	177.8
			O(3)-Ti(3)-O(16)	75.47(17)	75.8
			O(23)-Ti(3)-O(16)	75.29(17)	75.4
			O(42)-Ti(3)-O(16)	87.09(19)	86.3
			O(51)-Ti(3)-O(16)	85.71(19)	86.1
			O(71)-Ti(3)-Ti(1)	142.43(19)	142.5
			O(3)-Ti(3)-Ti(1)	110.37(14)	109.9
			O(23)-Ti(3)-Ti(1)	41.27(13)	41.9
			O(42)-Ti(3)-Ti(1)	96.57(15)	96.2
			O(51)-Ti(3)-Ti(1)	77.09	76.8
			O(16)-Ti(3)-Ti(1)	35.94(12)	35.4
			O(71)-Ti(3)-Ti(2)	145.41(19)	147.0
			O(3)-Ti(3)-Ti(2)	41.21(13)	42.5
			O(23)-Ti(3)-Ti(2)	109.84(13)	109.3
			O(42)-Ti(3)-Ti(2)	77.49(14)	77.3
			O(51)-Ti(3)-Ti(2)	97.02(13)	97.1
			O(16)-Ti(3)-Ti(2)	36.21(12)	35.2
			Ti(1)-Ti(3)-Ti(2)	72.15(4)	70.6
			Ti(1)-O(16)-Ti(2)	152.8(2)	148.7
			Ti(1)-O(16)-Ti(3)	103.74(18)	105.6
			Ti(2)-O(16)-Ti(3)	103.4(2)	105.8
			Ti(1)-O(17)-Ti(2)#1	144.6(3)	146.1

Symmetry transformations used to generate equivalent atoms:

- (1) #1 -x+1, y, -z+3/2
- (2) #1 -x+1, -y+2, -z+1

Table S3. Hirshfeld atomic charges (in au.) obtained at the B3LYP/6-31G(d,p) level of theory for **1** and **2**.

[Ti ₄ O(O ⁱ Pr) ₁₀ (O ₃ C ₁₄ H ₈) ₂] (1)		[Ti ₆ O ₄ (O ⁱ Pr) ₂ (O ₃ C ₁₄ H ₈) ₄ (O ₂ CEt) ₆] (2)	
Atom	Charge	Atom	Charge
Ti1	0.581	Ti1	0.622
Ti2	0.601	Ti2	0.623
O16	-0.389	Ti3	0.595
O1	-0.197	O16	-0.369
O2	-0.193	O17	-0.349
O3	-0.287	O1	-0.238
O21	-0.254	O3	-0.249
O31	-0.253	O21	-0.239
O41	-0.273	O23	-0.250
O51	-0.266	O41	-0.217
O61	-0.272	O42	-0.208
		O51	-0.208
		O52	-0.218
		O61	-0.210
		O62	-0.212
		O2	-0.265
		O22	-0.266
		O71	-0.222

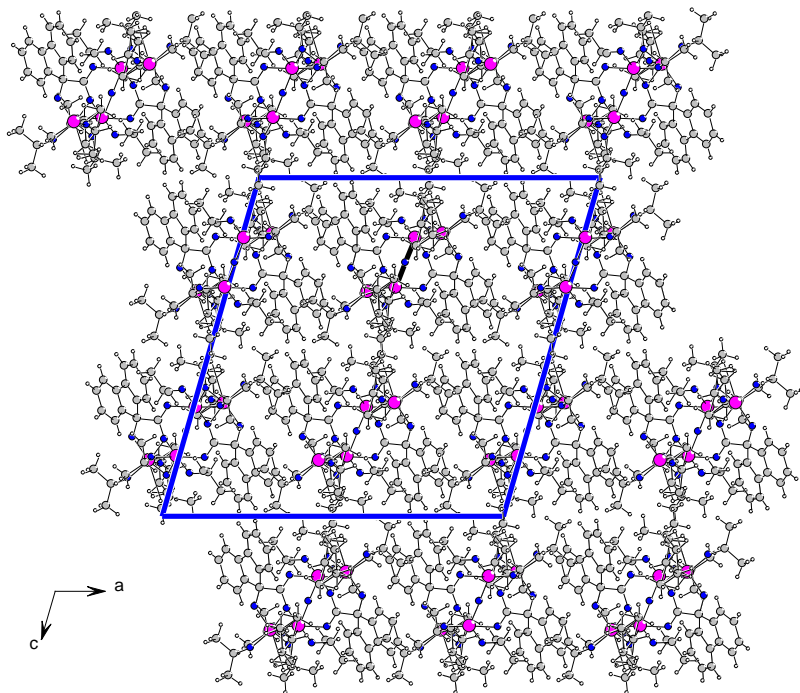


Figure S1. The TOCs packing in the crystal network of (1) along *b* axis.

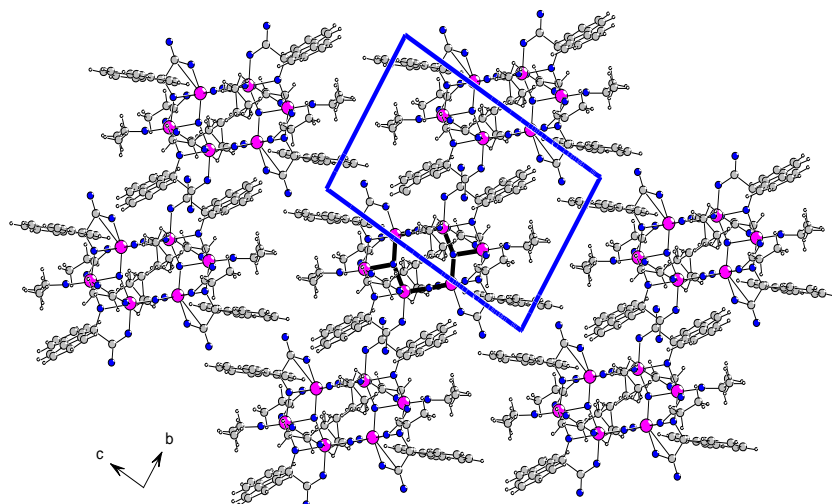


Figure S2. The differences in TOCs packing in the crystal network of (2) along *a* axis (b).

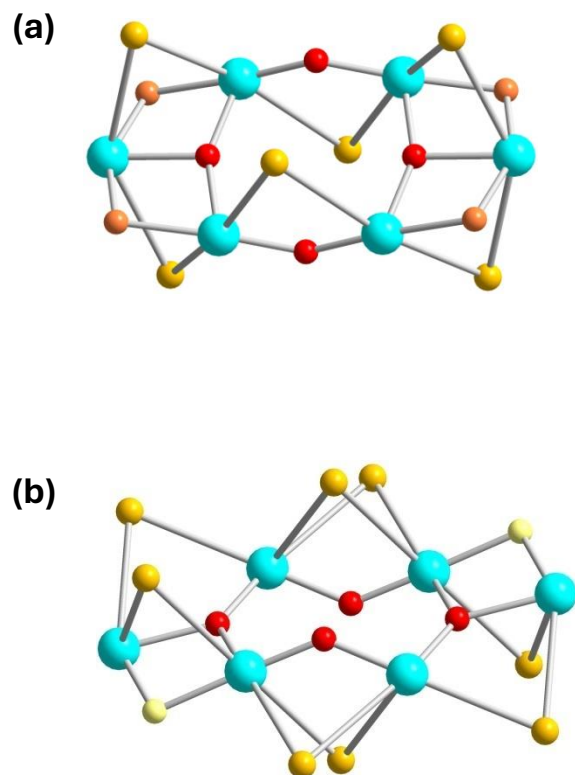


Figure S3. Cages of $[[\text{Ti}_6\text{O}_4(\text{O}^i\text{Pr})_2(\text{O}_3\text{C}_{14}\text{H}_8)_4(\text{O}_2\text{C}_3\text{H}_5)_6]$ (2) (a) and $[\text{Ti}_6\text{O}_4(\text{O}^i\text{Bu})_8(\text{O}_2\text{CC}_{13}\text{H}_9)_8] \cdot \text{Me}_2\text{CO}$ (b)¹. Titanium atoms in cyan, oxo bridges in red, orange – 9-hydroxy-9-fluorencarboxylate ligand, dark yellow – propionate, yellow – 9-fluorencarboxylate ligand, light yellow – bridging isobutanolate. The central part - $[\text{Ti}_6(\mu_3\text{-O})_2(\mu\text{-O})_2]$ is common but due to different complex content the connectivity of lateral ligands is distinct.

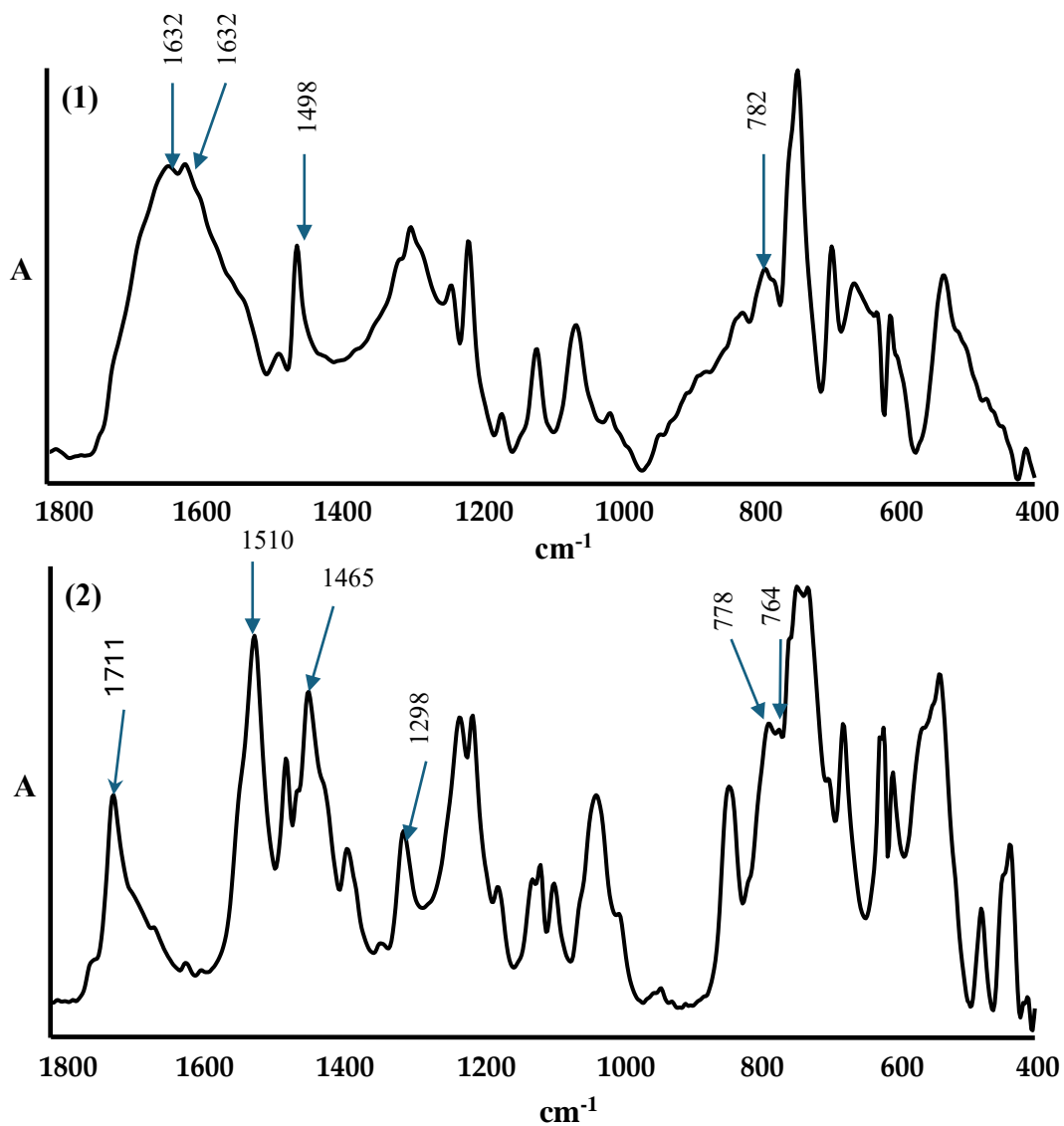


Figure S4. IR spectra of (1) and (2)

References

- 1 B. Kubiak, P. Piszczek, A. Radtke, T. Muzioł, G. Wrzeszcz and P. Golińska, *Crystals*, 2023, 13, 998.