Observed hydrolysis of fluorine substituted bis(β-diketonato)-dichlorotitanium(IV) complexes

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Supplementary Information

Table S1. ^{1}H NMR chemical shift data of the methine protons (CH) for the chelated and uncoordinated β-diketones in Ti(β-diketonato)$_2$Cl$_2$ and Hβ-diketone respectively.

Ti(β-diketonato)$_2$Cl$_2$					Free β-diketone
Compound	**Colour**	**^{1}H / ppm CH**	**Δ (A-B)**	**Δ (A-Hβ) Δ (B-Hβ)**	**^{1}H / ppm CH (Hβ)**
(a) CF$_3$-β-diketones:					
Ti(tfaa)$_2$Cl$_2$	Yellow	**A** = 6.40 **B** = 6.24	0.16	0.40 0.24	6.00
Ti(hfaa)$_2$Cl$_2$	Yellow	**A** = 6.80 **B** = 6.70	0.10	0.40 0.30	6.40
Ti(tfth)$_2$Cl$_2$	Red	**A** = 6.82 **B** = 6.63	0.19	0.37 0.18	6.45
Ti(tffu)$_2$Cl$_2$	Red	**A** = 6.93 **B** = 6.74	0.19	0.44 0.25	6.49
b) Non-CF$_3$-β-diketones					
Ti(acac)$_2$Cl$_2$	Orange	*cis* 6.00	-	0.50	5.50
Ti(ba)$_2$Cl$_2$	Red	*cis* 6.67	-	0.48	6.19
Ti(dbm)$_2$Cl$_2$	Red	*cis* 7.35	-	0.50	6.85

Table S2. ^{1}H and ^{19}F NMR chemical shifts of the methine proton (CH) and CF$_3$ of *cis*-Ti(β-diketonato)$_2$Cl$_2$ complexes, at T = -60 °C. Values shown in blue are the relative contributions of the indicated signals (%) of the three *cis*-isomers.

Compound	**^{1}H / CH ppm**	**№ of Peaks**	**^{19}F / CF$_3$ ppm**	**№ of Peaks**
(a) Symmetric$_3$-β-diketones				
Ti(hfaa)$_2$Cl$_2$	6.85 (100)	1	-73.39, -73.49 (50.0), (50.0)	2
(b) Unsymmetric-β-diketones				
Ti(tffu)$_2$Cl$_2$	--	--	-73.48, -73.57, -73.62, -74.55 (15.3), (11.5), (22.7), (50.5)	4
Ti(tfth)$_2$Cl$_2$	--	--	-73.31, -73.52, -74.39, -74.43 (14.3), (57.1), (14.3), (14.3)	4
Ti(tfaa)$_2$Cl$_2$	6.52, 6.51, 6.50, 6.49 (26.3), (26.3), (23.7), (23.7)	4	-73.66, -73.72, -74.80, -74.83 (24.3), (30.8), (24.3), (20.6)	4
Ti(ba)$_2$Cl$_2$	6.77, 6.76 (27.9), (72.1)	2*	**^{1}H / CH$_3$**: 2.48, 2.47, 2.37 (17.4), (27.9), (54.7)	3*

* Temperature lowering below -60 °C, needed for complete peak slitting, is limited by the freezing point of CDCl$_3$ (-63.5 °C).

Table S3. Crystal data and structure refinement data for dimeric $\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O)$ and tetrameric, $[Ti(hfaa)_2(\mu\text{-}O)]_4$ structures.

	$\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O)$	**$[Ti(hfaa)_2(\mu\text{-}O)]_4$**
Formula	$Ti_2O_9C_{20}H_4Cl_2F_{24}$	$Ti_4O_{20}C_{40}H_8F_{48}$
Formula weight	1010.93	1912.06
Crystal colour/habit	Yellow, cuboid	Yellow, cuboid
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/a$	$P2_1/n$
Unit cell dimension /Å / °	a = 23.1255(4) b = 23.1255(4) c = 12.3948(5) α = 90 β = 90 γ = 90	a = 13.7394(4) b = 16.4156(4) c = 28.3400(7) α = 90 β = 99.7990(10) γ = 90
Volume / Å^3	6628.6(3)	
Z	8	6298.6(3)
Density$_{calc}$ / Mg m^{-3}	2.026	4
Temperature / ℃	-173(2)	2.016
Wavelength / Å	0.71073	-173(2)
Absorption coefficiet / mm^{-1}	0.825	0.71073
F(000)	3920	0.700
Crystal size / mm^3	0.29 x 0.20 x 0.18	0.40 x 0.35 x 0.29
Theta range for data collection / °	2.49 to 28.27	1.44 to 28.35
Index ranges	-30 ≤ h ≤ 29, -29 ≤ k ≤ 30, -16 ≤ l ≤ 15	-17 ≤ h ≤ 18, -21 ≤ k ≤ 15, -35 ≤ l ≤ 37
Reflections collected	34 701	55 209
Independent reflections	4105[R(int) = 0.0399]	15 535[R(int) = 0.0301]
Completeness to theta = 28.35 / %	100.0	98.7
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8657 and 0.7958	0.8227 and 0.7670
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4105 / 0 / 259	15 535 / 0 / 1007
Goodness-of-fit on F^2	1.017	1.030
Final R indices [I>2sigma(I)]	R_1 = 0.0357, wR_2 = 0.0812	R_1 = 0.0465, wR_2 = 0.1189
R indices (all data)	R_1 = 0.0454 wR_2 = 0.0871	R_1 = 0.0608 wR_2 = 0.1333
Largest diff. peak and hole / e.Å^{-3}	0.524 and -0.377	1.953 and -1.241

Table S4. Hydrogen bonds for $\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O)$ and $[Ti(hfaa)_2(\mu\text{-}O)]_4$ (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Dimer				
C(8)-H(8)...Cl#1	0.95	2.89	3.840(2)	176.2
Tetramer				
C(8)-H(8)...F(42)#2	0.95	2.42	3.367(2)	172.0
C(23)-H(23)...F(38)#3	0.95	2.49	3.195(3)	130.8
C(33)-H(33)...F(3)#4	0.95	2.34	3.281(3)	168.9

Symmetry transformations used to generate equivalent atoms:
#1 -y+3/4,x-3/4,z+1/4 #2 -x,-y+1,-z+1 #3 -x,y+1/2,-z+3/2 #4 x-1,y,z

Crystallography

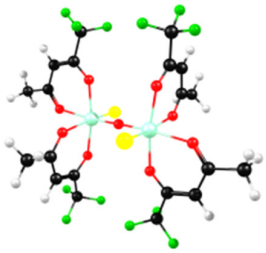
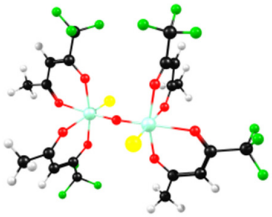
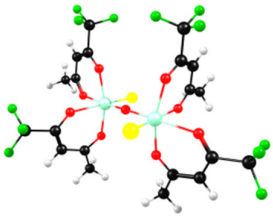
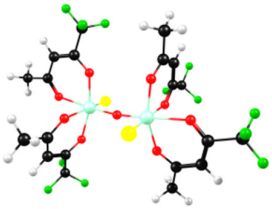
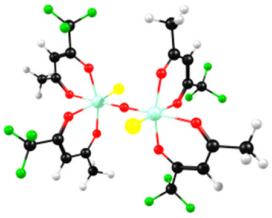
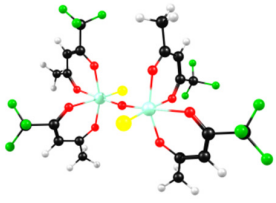
The initial unit cell and data collection were achieved by the Apex2 software[1] utilizing COSMO[2] for optimum collection of more than a hemisphere of reciprocal space. A total of 1143 and 1335 frames were collected at exposure times of 35 and 8 s.frame^{-1} for $\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O)$ and $[Ti(hfaa)_2(\mu\text{-}O)]_4$ respectively. Both collections were done with a 0.5° scan width in φ and ω. The frames were integrated using a narrow-frame integration algorithm and reduced with the SAINT-Plus[3] and XPREP[3] software packages respectively. Analysis of the data sets showed no significant decay during the data collection. Data were corrected for absorption effects using the multi-scan technique SADABS[4]. Both structures were solved by the direct methods package SIR97[5] and refined using the WinGX software package[6] incorporating SHELXL.[7]

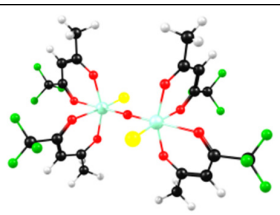
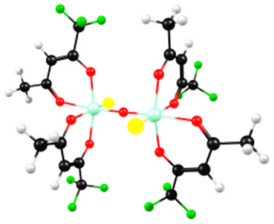
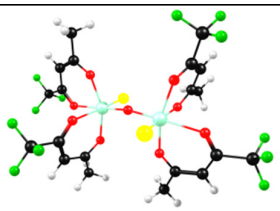
The structure of $[Ti(hfaa)_2(\mu\text{-}O)]_4$ showed large thermal ellipsoids on some of the peripheral CF_3 groups, especially for C38, F43, F44 and F45. The fluorides for this group was subsequently refined as disordered over two positions with their occupancies (50.26% and 49.74%) linked to a free variable to add to unity. Anisotropic displacement parameters of the disordered fluoride atoms had to be restrained (SIMU and DELU) with the default parameters of these adjusted to avoid serious alerts from the checkCIF routines. C–F bond distances, varying from 1.242 Å to 1.334 Å, were not restrained as these remained stable and within bounds during refinement. Four discrepant reflections were also removed during the final refinement cycles as these showed up as serious alerts. The final refinement of $[Ti(hfaa)_2(\mu\text{-}O)]_4$ showed only minor alerts, of note are the thermal ellipsoids for a few fluoride atoms. As these are signs of minor disorders, they were not further treated by refinement as it is believed that addressing these will not add to the significance of the paper. A similar approach was taken during the refinement of $\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O$, which also showed signs of minor disorder in the CF_3 regions.

Both data sets were evaluated online with the latest checkCIF routines, and showed no serious errors. The final refinement cycles yielded electron density maps with the highest peak value of 0.52 e.Å^{-3} at 1.15 Å from F2 and the deepest hole -0.38 e.Å^{-3} at 0.81 Å from F3 for $\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O)$, and the highest peak value of 0.86 e.Å^{-3} at 0.69 Å from F45B and the deepest hole -0.71 e.Å^{-3} at 0.13 Å from F43B for $[Ti(hfaa)_2(\mu\text{-}O)]_4$.

For both structures the aromatic H atoms were placed in geometrically idealized positions (C–H = 0.95 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography Volume C.[8] The molecular plot was drawn using the DIAMOND program[9] with a 30% thermal envelope probability for non-hydrogen atoms. Hydrogen atoms were drawn as arbitrary sized spheres with radius of 0.135 Å.

Table S5. Optimized geometry, relative energy of the 10 possible isomers of $\{Ti(tfaa)_2Cl\}_2(\mu\text{-}O)$. Color code used for atoms shown below:

Isomer number [a]	Optimized geometry	E_{rel} (eV)
1111		0.060
1112 (enantiomer 2111)		0.001
1212 (enantiomer 2121)		0.039
1122 (enantiomer 2211)		0.002
1221		0.000
1222 (enantiomer 2221)		0.025

2222		0.026
1121 (enantiomer 1211)		0.012
2212 (enantiomer 2122)		0.026
2112		0.017

a The isomers are referred to by 4 numbers indicating the groups that occupy the 4 *trans* positions: 1 = CF_3 and 2 = R (CH_3, C_4H_3S and C_4H_3O). For the higher symmetry isomers 1111 and 2222, 2 ring H and 2 CF_3 NMR signals are expected while for the other isomers 4 ring H and 4 CF_3 NMR signals are expected.

Optimized Cartesian coordinates (Å)

DFT calculations: Geometries were optimized using the ADF (Amsterdam Density Functional) 2012 programme[10] with the OLYP (Handy-Cohen and Lee-Yang-Parr) GGA (Generalized Gradient Approximation) functional, the TZP (Triple ζ polarized) basis set, no symmetry constraint (C_1) in chloroform (ε_0 = 4.8) as solvent.[11,12,13,14,15]

1 $Ti(acac)_2Cl_2$

C	0.544831000	4.197759000	-0.893071000
C	0.794263000	2.726202000	-1.066725000
C	1.668169000	2.240271000	-2.040360000
C	1.945855000	0.869695000	-2.201530000
C	2.948994000	0.400866000	-3.221233000
C	-0.555535000	-4.203471000	-0.875290000
C	-0.799501000	-2.731914000	-1.057440000
C	-1.672008000	-2.249409000	-2.034697000
C	-1.947232000	-0.879580000	-2.203016000
C	-2.940519000	-0.412600000	-3.233093000
Cl	1.698676000	-0.250972000	1.575661000
Cl	-1.710454000	0.256199000	1.571268000
H	0.513362000	-4.411265000	-0.998704000
H	0.802750000	4.491354000	0.130526000
H	1.119080000	4.797812000	-1.599886000
H	2.176614000	2.951188000	-2.680981000
H	2.488357000	-0.354046000	-3.867058000
H	3.334133000	1.219890000	-3.829880000
H	3.782890000	-0.086563000	-2.703027000
H	-0.524077000	4.401104000	-1.023788000
H	-0.820555000	-4.490815000	0.148329000
H	-1.128035000	-4.805349000	-1.581990000
H	-2.180496000	-2.962720000	-2.672593000
H	-2.452150000	0.291926000	-3.915219000
H	-3.363833000	-1.239493000	-3.804567000
H	-3.747470000	0.133967000	-2.732314000
O	0.150372000	1.953615000	-0.249279000
O	1.388318000	-0.049642000	-1.501841000
O	-0.154428000	-1.957120000	-0.243749000
O	-1.391587000	0.041965000	-1.504124000
Ti	-0.004417000	-0.000144000	-0.003649000

2 $Ti(hfaa)_2Cl_2$

C	0.138525000	3.640585000	-2.413468000
C	0.360291000	2.803819000	-1.114339000
C	0.703775000	-3.377897000	2.694342000
C	0.842496000	3.406101000	0.044064000
C	1.081575000	-2.353767000	1.578233000
C	1.084863000	2.630473000	1.192129000
C	1.648564000	3.304836000	2.486176000

C	2.280681000	−2.474200000	0.881251000
C	2.618199000	−1.532813000	−0.107331000
C	3.967326000	−1.669717000	−0.886599000
Cl	−0.815895000	−1.331170000	−1.630268000
Cl	−2.048512000	0.569148000	0.929339000
F	0.419200000	4.955297000	−2.244281000
F	0.465440000	−2.730386000	3.863927000
F	0.751296000	3.176253000	3.499126000
F	0.929290000	3.166942000	−3.412260000
F	1.675166000	−4.296798000	2.912796000
F	1.907518000	4.624828000	2.322428000
F	2.799880000	2.694254000	2.868935000
F	3.711718000	−1.963050000	−2.190779000
F	4.655721000	−0.501256000	−0.849472000
F	4.765469000	−2.644882000	−0.388694000
F	−0.430332000	−4.042380000	2.347909000
F	−1.153369000	3.538481000	−2.820389000
H	1.055527000	4.465716000	0.053006000
H	2.961647000	−3.280602000	1.113947000
O	0.060951000	1.569063000	−1.258944000
O	0.188969000	−1.455785000	1.401345000
O	0.885428000	1.387377000	1.311698000
O	1.917848000	−0.544450000	−0.470692000
Ti	−0.072904000	0.003222000	0.018813000

3 $\{Ti(acac)_2Cl\}_2(\mu\text{-}O)$

C	2.121892000	2.676422000	3.310180000
C	2.158049000	2.248225000	1.865442000
C	2.261296000	−3.529372000	2.565229000
C	2.340174000	2.854653000	−0.516270000
C	2.346902000	3.192960000	0.840704000
C	2.532852000	3.903173000	−1.580939000
C	2.768226000	−2.394598000	1.713025000
C	4.129482000	−2.113080000	1.616839000
C	4.655076000	−1.087795000	0.792726000
C	6.149866000	−0.899197000	0.687217000
C	−2.132441000	−2.664760000	−3.320976000
C	−2.166353000	−2.242136000	−1.874654000
C	−2.258848000	3.537222000	−2.550775000
C	−2.345003000	−2.858023000	0.504977000
C	−2.355149000	−3.190655000	−0.853377000
C	−2.536249000	−3.910949000	1.565549000
C	−2.766366000	2.399850000	−1.702327000
C	−4.127786000	2.119538000	−1.605992000
C	−4.653609000	1.091546000	−0.785315000
C	−6.148472000	0.902636000	−0.681079000
Cl	1.983327000	−1.207145000	−2.157400000
Cl	−1.975163000	1.197313000	2.161634000
H	1.117992000	2.487290000	3.707685000
H	1.543132000	−3.140805000	3.295955000
H	1.674379000	3.890641000	−2.261565000
H	1.721834000	−4.244464000	1.933842000
H	2.363573000	3.732804000	3.436658000
H	2.489085000	4.232129000	1.113902000
H	2.650487000	4.903064000	−1.160711000
H	2.819313000	2.065644000	3.892501000
H	3.067556000	−4.046838000	3.087280000
H	3.417123000	3.654148000	−2.178572000

H	4.822532000	-2.733175000	2.174344000
H	6.405181000	0.130223000	0.960972000
H	6.455566000	-1.038532000	-0.355814000
H	6.705952000	-1.592096000	1.320599000
H	-1.127889000	-2.478705000	-3.718437000
H	-1.544403000	3.149942000	-3.285805000
H	-1.674654000	-3.904376000	2.242334000
H	-1.715244000	4.247664000	-1.917742000
H	-2.378732000	-3.719606000	-3.451533000
H	-2.499043000	-4.228557000	-1.130365000
H	-2.658952000	-4.908506000	1.141155000
H	-2.827921000	-2.048730000	-3.899965000
H	-3.065101000	4.059645000	-3.067840000
H	-3.417019000	-3.661802000	2.168234000
H	-4.820691000	2.742272000	-2.160760000
H	-6.403684000	-0.125273000	-0.960633000
H	-6.454456000	1.036191000	0.362617000
H	-6.704362000	1.598969000	-1.310853000
O	0.000824000	-0.001705000	-0.001409000
O	1.849333000	-1.731858000	1.083211000
O	1.996155000	0.994816000	1.653719000
O	2.168717000	1.652259000	-0.950748000
O	3.934269000	-0.297540000	0.102726000
O	-1.847579000	1.733381000	-1.076505000
O	-1.999649000	-0.990135000	-1.657958000
O	-2.168800000	-1.658143000	0.944063000
O	-3.933050000	0.298774000	-0.098061000
Ti	1.815187000	-0.108995000	-0.055252000
Ti	-1.813784000	0.106048000	0.055414000

4 $\{Ti(hfaa)_2Cl\}_2(\mu\text{-}O)$

C	0.427394000	0.662792000	-6.298197000
C	0.704165000	0.154820000	-4.840625000
C	1.719599000	-0.804774000	-4.620550000
C	1.978580000	-1.278773000	-3.343320000
C	2.669864000	1.056193000	2.494382000
C	2.919255000	-1.328172000	2.121018000
C	3.080223000	-2.359123000	-3.117295000
C	3.313056000	2.428329000	2.895643000
C	3.472846000	-0.099178000	2.471068000
C	3.813010000	-2.609813000	2.080523000
C	-0.410417000	-0.640051000	6.304371000
C	-0.694651000	-0.141155000	4.845101000
C	-1.708641000	0.819653000	4.624567000
C	-1.976280000	1.282794000	3.345071000
C	-2.670012000	-1.060478000	-2.509734000
C	-2.924985000	1.319670000	-2.115355000
C	-3.085818000	2.354603000	3.116372000
C	-3.309126000	-2.429011000	-2.929595000
C	-3.475741000	0.092929000	-2.476886000
C	-3.821656000	2.598639000	-2.058836000
Cl	1.303155000	2.242604000	-1.689505000
Cl	-1.309818000	-2.246849000	1.701825000
F	0.454013000	2.018778000	-6.336974000
F	0.827635000	-0.232483000	6.697748000
F	1.328554000	0.201344000	-7.201162000
F	2.528207000	-3.488828000	-2.599404000
F	2.844550000	3.429001000	2.115512000

F	2.988963000	2.714989000	4.188432000
F	3.432726000	-3.466042000	3.066479000
F	3.672888000	-3.248813000	0.892982000
F	3.724347000	-2.697669000	-4.260918000
F	4.009875000	-1.907574000	-2.234627000
F	4.665799000	2.416285000	2.799663000
F	5.128608000	-2.331888000	2.253339000
F	-0.435989000	-1.995691000	6.351534000
F	-0.808848000	0.258406000	-6.700231000
F	-1.307312000	-0.173783000	7.209264000
F	-2.545800000	3.480879000	2.578996000
F	-2.833557000	-3.440198000	-2.167877000
F	-2.989135000	-2.692722000	-4.228272000
F	-3.450847000	3.464357000	-3.039485000
F	-3.674261000	3.226838000	-0.866169000
F	-3.721125000	2.703942000	4.261649000
F	-4.020835000	1.886304000	2.248121000
F	-4.661473000	-2.424051000	-2.827943000
F	-5.138351000	2.319276000	-2.223475000
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H	4.525884000	-0.029645000	2.705574000
H	-2.279393000	1.199666000	5.460066000
H	-4.528219000	0.023315000	-2.714286000
O	0.044995000	-0.656809000	3.970783000
O	1.394799000	-0.924361000	-2.254542000
O	1.433399000	1.115276000	2.244926000
O	1.700069000	-1.554297000	1.815075000
O	-0.004000000	-0.005506000	0.000777000
O	-0.042371000	0.662112000	-3.967420000
O	-1.397436000	0.921717000	2.255961000
O	-1.434619000	-1.119569000	-2.255324000
O	-1.705906000	1.546281000	-1.808916000
Ti	0.011999000	-0.418059000	1.773813000
Ti	-0.016273000	0.412752000	-1.771034000

5 $[Ti(acac)_2(\mu\text{-}O)]_4$

C	1.032401000	4.701779000	1.890329000
C	1.329853000	3.349983000	2.500817000
C	1.373765000	3.196078000	3.888818000
C	1.584740000	1.898643000	6.052037000
C	1.600638000	1.956549000	4.536247000
C	1.926889000	-1.506797000	-6.038622000
C	1.932020000	-4.422381000	-1.917802000
C	1.945886000	-1.582596000	-4.523756000
C	1.952000000	-3.029843000	-2.508844000
C	1.972156000	-2.851253000	-3.894437000
C	2.804149000	4.086192000	-2.666254000
C	3.110651000	2.619656000	-2.455247000
C	3.528080000	-3.475751000	2.730725000
C	3.551304000	-1.979197000	2.509157000
C	4.431979000	2.165139000	-2.465197000
C	4.764736000	-1.285691000	2.500265000
C	4.799389000	0.813019000	-2.252926000
C	4.871793000	0.108548000	2.272362000
C	6.241110000	0.760701000	2.306245000
C	6.265406000	0.426485000	-2.307492000
C	-1.006238000	-4.701007000	1.887692000
C	-1.308514000	-3.350926000	2.499869000

C	-1.347266000	-3.197261000	3.887986000
C	-1.566814000	-1.902514000	6.052020000
C	-1.584596000	-1.960156000	4.536344000
C	-1.935425000	1.512372000	-6.035628000
C	-1.953199000	4.424919000	-1.911882000
C	-1.954584000	1.586654000	-4.520691000
C	-1.968385000	3.033018000	-2.504661000
C	-1.980452000	2.855030000	-3.890446000
C	-2.776761000	-4.085764000	-2.685838000
C	-3.094484000	-2.622594000	-2.468132000
C	-3.533697000	3.468796000	2.730114000
C	-3.553977000	1.972036000	2.509512000
C	-4.419023000	-2.177292000	-2.484762000
C	-4.765991000	1.276220000	2.498567000
C	-4.798498000	-0.830078000	-2.262198000
C	-4.869604000	-0.119284000	2.275999000
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H	0.120235000	4.625434000	1.287908000
H	0.734372000	1.285866000	6.372798000
H	0.902690000	5.481671000	2.643360000
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H	2.274886000	4.470468000	-1.786928000
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H	2.723753000	-0.838332000	-6.380876000
H	2.773972000	-4.539541000	-1.226556000
H	2.878492000	-3.710461000	3.580756000
H	3.089485000	-3.959602000	1.850394000
H	3.704040000	4.681099000	-2.834086000
H	4.523619000	-3.887269000	2.908590000
H	5.219630000	2.890792000	-2.638477000
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H	6.258873000	1.522057000	3.094398000
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H	6.424165000	-0.262456000	-3.145359000
H	6.531420000	-0.114098000	-1.393519000
H	6.927002000	1.287018000	-2.427137000
H	7.047344000	0.045643000	2.482812000
H	-0.104110000	-4.616212000	1.271718000
H	-0.716991000	-1.288399000	6.371912000
H	-0.857586000	-5.478536000	2.639653000
H	-0.992238000	1.055085000	-6.355767000
H	-1.046810000	4.543184000	-1.307638000
H	-1.160516000	-4.071520000	4.502749000
H	-1.483870000	-2.888586000	6.513980000
H	-1.824771000	-4.993411000	1.220635000
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H	−2.743233000	0.857567000	−6.378880000
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H	−2.889215000	3.704834000	3.583738000
H	−3.091014000	3.952565000	1.851831000
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H	−5.200073000	−2.907634000	−2.668317000
H	−5.678446000	1.839019000	2.665268000
H	−6.263778000	−1.503413000	3.132529000
H	−6.396356000	−1.332440000	1.384673000
H	−6.424070000	0.284158000	−3.106121000
H	−6.553031000	0.018835000	−1.369956000
H	−6.917876000	−1.315593000	−2.496772000
H	−7.048504000	−0.057584000	2.450436000
O	0.000490000	0.000153000	1.953354000
O	1.521120000	2.403778000	1.648777000
O	1.808252000	0.859879000	3.935464000
O	1.923748000	−0.475523000	−3.906805000
O	1.942211000	−2.076912000	−1.643704000
O	2.038987000	0.173379000	0.018927000
O	2.078414000	1.871846000	−2.276584000
O	2.395497000	−1.439046000	2.338066000
O	3.889678000	0.876651000	2.042626000
O	3.979774000	−0.125626000	−2.021783000
O	−0.002844000	0.011641000	−1.906708000
O	−1.513668000	−2.406921000	1.648642000
O	−1.803026000	−0.865252000	3.936467000
O	−1.936145000	0.478755000	−3.904770000
O	−1.966833000	2.079308000	−1.640013000
O	−2.040291000	−0.176405000	0.021023000
O	−2.068982000	−1.868705000	−2.277437000
O	−2.396940000	1.434067000	2.342068000
O	−3.885691000	−0.885149000	2.047209000
O	−3.987925000	0.113246000	−2.018404000
Ti	1.770331000	0.404679000	1.803959000
Ti	1.811165000	−0.062868000	−1.771764000
Ti	−1.768522000	−0.407970000	1.805479000
Ti	−1.816389000	0.067218000	−1.769510000

6 $[Ti(hfaa)_2(\mu\text{-}O)]_4$

C	1.661087000	4.761170000	1.943895000
C	1.710018000	3.335528000	2.579783000
C	1.782601000	3.201159000	3.961383000
C	1.808155000	1.922187000	4.559271000
C	1.815358000	1.809400000	6.124752000
C	2.111549000	−1.407628000	−6.164346000
C	2.146756000	−1.509394000	−4.597223000
C	2.335964000	−2.928591000	−2.627801000
C	2.376469000	−2.773043000	−4.007252000
C	2.533637000	4.099576000	−3.181489000
C	2.579346000	−4.338603000	−2.002990000
C	2.981639000	2.657641000	−2.780513000
C	3.323793000	−3.525140000	3.112416000
C	3.467442000	−2.015724000	2.739579000
C	4.321298000	2.298750000	−2.879785000
C	4.703292000	−1.392402000	2.847192000
C	4.746959000	1.005655000	−2.506253000

C	4.855039000	-0.028792000	2.504120000
C	6.274665000	0.619312000	2.689762000
C	6.275213000	0.653953000	-2.572121000
C	-1.669505000	-4.761377000	1.936282000
C	-1.727542000	-3.338149000	2.574457000
C	-1.835044000	-3.206849000	3.952019000
C	-1.857398000	-1.928183000	4.556209000
C	-1.901111000	-1.862581000	6.125724000
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C	-2.334838000	2.928602000	-2.640457000
C	-2.385436000	2.766561000	-4.017741000
C	-2.519007000	-4.099568000	-3.164894000
C	-2.569988000	4.340842000	-2.018503000
C	-2.969539000	-2.657712000	-2.766449000
C	-3.270453000	3.541222000	3.114576000
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C	-4.670543000	1.422360000	2.846737000
C	-4.737612000	-1.007021000	-2.497651000
C	-4.834492000	0.059230000	2.510002000
C	-6.257821000	-0.576737000	2.705620000
C	-6.269433000	-0.667740000	-2.552773000
F	0.583325000	4.879890000	1.130418000
F	0.654807000	1.242843000	6.550632000
F	0.818296000	-1.394505000	-6.591855000
F	1.562482000	-4.673071000	-1.171762000
F	1.589370000	5.747348000	2.874498000
F	1.684856000	4.044817000	-4.243639000
F	1.878073000	4.695727000	-2.153797000
F	1.939870000	3.011915000	6.743673000
F	2.492557000	-3.666126000	4.180582000
F	2.686241000	-5.314599000	-2.941110000
F	2.703982000	-0.267021000	-6.590358000
F	2.736517000	-2.452085000	-6.768218000
F	2.777674000	4.977076000	1.197048000
F	2.790723000	-4.220681000	2.076117000
F	2.840815000	1.021611000	6.538668000
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F	4.509928000	-4.101783000	3.431833000
F	6.403303000	1.749884000	1.964277000
F	6.459493000	0.938524000	4.003847000
F	6.465698000	-0.502999000	-3.255677000
F	6.762640000	0.480390000	-1.312938000
F	7.016921000	1.618555000	-3.173559000
F	7.272375000	-0.230243000	2.326125000
F	-0.570353000	-4.885416000	1.152139000
F	-0.643110000	-2.008889000	6.629291000
F	-0.883337000	1.680945000	-6.632117000
F	-1.526875000	4.688289000	-1.225408000
F	-1.628812000	-5.749776000	2.866384000
F	-1.718008000	-4.048911000	-4.264209000
F	-1.810003000	-4.671645000	-2.159707000
F	-2.390957000	-0.680713000	6.557803000
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F	-2.481720000	0.174828000	-6.601387000
F	-2.674804000	-2.852537000	6.648256000
F	-2.712167000	4.232491000	2.089156000

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F	−6.983668000	−1.567100000	−3.276491000
F	−7.251188000	0.282083000	2.351344000
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H	−5.032188000	−3.027594000	−3.211278000
H	−5.522171000	1.995974000	3.186938000
O	0.004361000	0.004027000	−1.922771000
O	0.007584000	−0.006201000	1.907467000
O	1.675312000	2.396322000	1.710145000
O	1.805016000	0.816889000	3.962397000
O	1.925415000	−0.431957000	−3.992896000
O	2.011204000	1.924047000	−2.383254000
O	2.046563000	0.197232000	−0.009733000
O	2.116991000	−2.020282000	−1.750948000
O	2.364624000	−1.487399000	2.356173000
O	3.956112000	0.742383000	2.090784000
O	4.019948000	0.068789000	−2.089887000
O	−1.668521000	−2.394721000	1.708374000
O	−1.809250000	−0.822539000	3.966576000
O	−1.925655000	0.427150000	−3.998453000
O	−1.998886000	−1.919246000	−2.378597000
O	−2.036004000	−0.192042000	−0.009026000
O	−2.108459000	2.023268000	−1.760819000
O	−2.330923000	1.494132000	2.356985000
O	−3.943583000	−0.722005000	2.096799000
O	−4.011926000	−0.067265000	−2.086293000
Ti	1.787055000	0.369728000	1.789230000
Ti	1.825243000	−0.015728000	−1.808341000
Ti	−1.773946000	−0.372879000	1.787019000
Ti	−1.815864000	0.022265000	−1.807997000

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