Short communication

The Crystal Structure of $[Li_8Ti_{10}F_{36}O_4(C_5Me_5)_4(thf)_8]$

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Dedicated to the memory of Professor Ljubo Golič

Abstract

The crystals of the cluster $[Li_8Ti_{10}F_{36}O_4(C_5Me_5)_4(thf)_8]$ **3** were isolated as the product of hydrolysis of $[\{(C_5Me_5)TiF_3\}_4(LiF)_2(thf)_2]$ **2**. The metal atoms in the cluster are six-coordinate (Ti and Li), or four-coordinate (Li). The oxido ligands form unsymmetrical oxido bridges Ti=O–Ti with a double-bond character. The mechanism of the cluster formation is proposed.

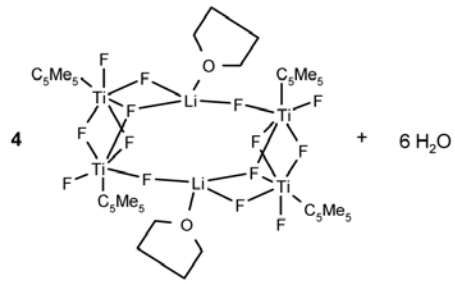
Keywords: Titanium, lithium, fluoride, X-ray structure

1. Introduction

The clusters with metal-oxido core attract interest due to their catalytic applications and as models of "bottom up" synthesis of nanosized materials.[1] The balance of positive and negative charges in the metal-oxido clusters favors metal atoms with high positive charges (+3, +4 and +5).[1d, 2] The heterometallic clusters incorporating metal ions with both low +1 or +2 charge and high charges are interesting as models for formation of nanosized perovskites ABX_3 (A, B = metal cations; X = anion). The –1 charge fluorido ligand instead of –2 oxido ligand allows the formation of clusters that incorporate low- and high-charge metals. Organotitanium fluoride $(C_5Me_5)TiF_3$ **1** is a useful starting compound for the metal fluorido clusters by the reaction of **1** with metal fluorides.[3] The structure of the Ba–Ti fluorido cluster that resembles the perovskite structure,[4] and the Li–Zr fluorido[5] and Li–Al fluorido[6] clusters were reported. We present now the structure of Li–Ti fluoride-oxido cluster $[Li_8Ti_{10}F_{36}O_4(C_5Me_5)_4(thf)_8]$ **3** obtained by hydrolysis of $[\{(C_5Me_5)TiF_3\}_4(LiF)_2(thf)_2]$ **2** (thf = tetrahydrofurane).[7]

2. Results and Discussion

The formation of **3** (Scheme 1) could be formally seen as the reaction of water molecules with $[\{(C_5Me_5)TiF_3\}_4(LiF)_2(thf)_2]$ **2** resulting in **3**, C_5Me_5H and insoluble TiF_4 and $TiOF_2$.



$$[Li_8Ti_{10}F_{36}O_4(C_5Me_5)_4(thf)_8] + 12\ (C_5Me_5)H + 4\ TiF_4 + 2\ TiOF_2$$

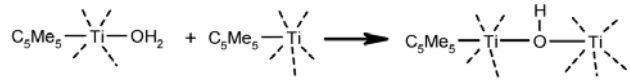
3

Scheme 1

The centrosymmetric structure of **3** consists of the $Li_8Ti_{10}F_{36}O_4$ core covered with four C_5Me_5 and eight thf ligands (Fig. 1, Table 1). All titanium atoms are six-coordinate: with C_5Me_5, four fluorines and oxygen (four Ti atoms), with five fluorines and with oxygen (four Ti atoms) or with six fluorines (two Ti atoms). Two lithium atoms are six-coordinate (with five fluorines and thf), oth-

er lithium atoms are four-coordinate: with four fluorines (two Li atoms), with three fluorines and thf (two Li atoms), or with two fluorines and two thf (two Li atoms). The Li–F distances for six-coordinate lithium atoms are on the average 2.024 Å, and for four-coordinate lithium 1.870 Å. All four oxido ligands bridge two titanium atoms. The Ti–O–Ti bridges are unsymmetrical with the longer Ti–O bridging distances 1.959(4) and 1.973(4) Å, and the corresponding shorter distances 1.716(4) and 1.699(4) Å. In the most of the reported Ti–O–Ti bridges both Ti–O bonds are very similar with the bridging Ti–O distances for six-coordinate titanium of 1.79–1.83 Å.[8] The unsymmetric oxygen bridges $X–Ti_a=O–Ti_b–Y$ were observed in titanoxanes with charge-depleted atom Ti_a.[9] The π bonding with donation of oxygen *p* electron density to *d* orbitals of Ti_a increases of the electron density on Ti_a and decreases the electron density on the oxygen. Additionally, the Ti_a *d* orbital used in the π bond is less accessible for ligand X bonded trans to oxygen. Consequently, the $X–Ti_a$ bond in trans position to oxygen and $O–Ti_b$ bond are weakened.[9] The structure of **3** suggest that the bonding in the bridge could also be described as $Ti_a=O–Ti_b$. The bond $Ti_a=O$ causes elongation of the trans Ti–F bond which is therefore longer (2.168(3) and 2.230(3) Å) than other Ti–F distances in **3**. The second distance in the bridge $O–Ti_b$ is longer than reported Ti–O bridging distances.[8] The reason for the unusual $Ti_a=O–Ti_b$ bridge is not clear. Due to rigidity of the fluorine and titanium atoms in the structure the unsymmetrical bridge with a double bond character is probably energetically more favourable than the symmetrical one.

The mechanism of formation of **3** could be suggested on the basis of equilibria observed by the variable-temperature NMR spectroscopy in solutions of **1**, **2**, and $[(\mathbf{1})_4(LiF)]$.[3, 10, 7, 11] The dissolution of **2** results in the equilibria of **2**, $[(\mathbf{1})_2(LiF)(thf)_x]$, $[(\mathbf{1})_4(LiF)]$, **1** and $[(\mathbf{1})_2]$. We assume that oxido ligands in **3** are formed upon the deprotonation of metal-coordinated water molecules. The coordination of the water molecule to the coordinatively unsaturated titanium atom was observed for $[(\mathbf{1})_2]$ with formation of $[(\mathbf{1})_2(H_2O)]$.[11] Water molecule can also exchange thf ligand coordinated to the lithium atoms in **2** and in $[(\mathbf{1})_2(LiF)(thf)_x]$.[12] The coordination of water molecules to the metal atoms increases its acidity.[13] With both Ti^{4+} and Li^+, having very similar ionic radii,[14] the acidity of the water molecule coordinated to titanium is higher than water coordinated to lithium. We propose as the first step in formation of **3** the deprotonation of $[(\mathbf{1})_2(H_2O)]$ by $(C_5Me_5)^-$ as a base and cleveage of $C_5Me_5–Ti$ bond, Scheme 2.



Scheme 2

+ C_5Me_5H

The hydroxide ligand is further deprotonated thus giving oxido ligand which acts as a bridge between two titanium atoms. In the structure of **3** there are six titanium atoms without C_5Me_5 ligands that were lost by the reaction according to the Scheme 2. These titanium atoms have available coordination sites and therefore act as glue in the growth of the larger species in the solution. The later process finally produces cluster **3**.

Table 1. Selected bond lengths (Å) and angles (°) for complex **3**.

Ti1–F1	2.028(4)	Ti4–O2a	1.699(4)	Ti1–F1–Ti2	115.41(17)
Ti1–F2	1.880(5)	Ti5–F13	1.993(4)	Ti1–F2–Li1	108.6(4)
Ti1–F9	2.171(3)	Ti5–F14	1.996(4)	Ti1–F9–Li1	93.4(3)
Ti1–F14	2.003(5)	Ti5–F15	1.886(4)	Ti1–O1–Ti3	150.2(3)
Ti1–O1	1.959(4)	Ti5–F16	1.779(5)	Ti1–F14–Ti5	150.7(2)
Ti2–F1	2.029(4)	Ti5–F17	1.792(5)	Ti2–F9–Li3	119.4(3)
Ti2–F3	1.887(4)	Ti5–F18	1.812(5)	Ti2–O2–Ti4a	147.1(2)
Ti2–F9	2.177(3)	Li1–F2	1.890(12)	Ti3–F8–Ti4	110.22(15)
Ti2–F13	1.997(4)	Li1–F3	1.947(11)	Ti3–F10–Li3	114.8(3)
Ti2–O2	1.973(4)	Li1–F4	2.140(11)	Ti4–F10–Li3	130.9(3)
Ti3–F4	1.914(4)	Li1–F5	2.109(12)	Ti4–F12–Li4	128.7(5)
Ti3–F6	1.857(4)	Li1–F9	2.036(13)	Ti5–F15–Li3	125.5(4)
Ti3–F8	2.168(3)	Li2–F4	1.829(12)	Li1–F9–Li3	117.8(5)
Ti3–F10	1.996(3)	Li2–F5	1.889(10)	Li1–F5–Li2	83.3(5)
Ti3–F11	1.876(4)	Li2–F7	1.917(11)	Li2–F4–Ti3	136.8(4)
Ti3–O1	1.716(4)	Li3–F7a	1.870(10)	F11–Li4–F12	110.2(6)
Ti4–F5a	1.889(3)	Li3–F9	1.901(10)		
Ti4–F7	1.924(3)	Li3–F10	1.894(10)		
Ti4–F8	1.928(3)	Li3–F15	1.827(12)		
Ti4–F10	2.230(3)	Li4–F11	1.814(15)		
Ti4–F12	1.877(3)	Li4–F12	1.864(14)		

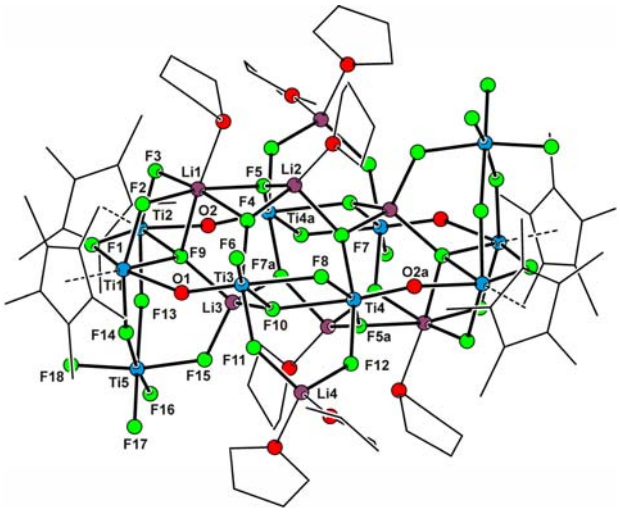


Figure 1. Molecular structure of **3** in the crystal. The solvate thf and Me_3SnCl molecules and hydrogen atoms of title complex are omitted for the reason of clarity.

3. Experimental

Crystals of **3** grew during the storage of thf solution of **2**[7] in a Schlenk flask at 4 °C for 15 months. We assume the diffusion of the moisture through the greased ground joint during the extended storage period. The crystals were characterized by X-ray diffraction.

3. 1. X-ray Determination

X-ray quality crystals of **3** were removed from the Schlenk flask and put into grease. A suitable crystal was selected then put on glass thread and immediately placed in the low temperature nitrogen stream of diffractometer. The intensity data sets were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer equipped with a Mo anode (Kα radiation, λ = 0.71073 Å) and graphite monochromator. A Cryostream Cooler (Oxford Cryosystems) was used for cooling the samle of **3**.

The structure was solved using WINGX[15] package by direct methods (SIR-92[16]) and refined by least-squares against F^2 (SHELX-97[17]).

Crystals of complex **3** crystallized with two molecules of Me_3SnCl and four molecule of THF. Complex presented severe disorder both in pentamethylcyclopentadienyl carbon atoms and in all non-coordinated THF molecules. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The bridging oxygen atoms O1 and O2 and other bridging fluorine atoms in this compound are not discernible in the refinement process. Their respective asignments have been made on the basis of the statistical database analyses of the Ti–O and Ti–F bond distances. Corresponding histograms show that the average bridging Ti–O distance for **3** (1.837 Å) lie in the region of the typical bridging Ti–O bond distances.

Crystal structure analysis for **3**: $C_{94}H_{174}Cl_2F_{36}Li_8O_{16}Sn_2Ti_{10}$, M = 3087.13 g mol^{-1}, monoclinic, $P2_1/n$, a = 15.4384(2) Å, b = 21.0638(3) Å, c = 20.5152(3) Å, β = 94.4826(6)°, V = 6650.96(16), Z = 2, $\rho_{calcd.}$ = 1.542 g cm^{-3}, $F(000)$ = 3136, 23,961 reflections measured, 12,522 were independent of symmetry, of which 8480 were observed ($I > 2\sigma(I)$), R_1 = 0.0700, wR_2 (all data) = 0.1764, 770 parameters.

Additional crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre with quotation number CCDC 695194 and are available free of charge on request.[18]

4. Acknowledgments

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5. References

1. (a) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171–198. (b) U. Schubert, *Chem. Mater.* **2001**, *13*, 3487–3494. (c) G. Kickelbick, M. P. Feth, H. Bertagnolli, M. Puchberger, D. Holzinger, S. Gross, *J. Chem. Soc., Dalton Trans.* **2002**, 3892–3898. (d) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev*. **1998**, *98*, 239 –271.
2. R. E. P. Winpenny, *Adv. Inorg. Chem.* **2001**, *52*, 1–111.
3. (a) F. Perdih, A. Pevec, S. Petriček, A. Petrič, N. Lah, K. Kogej, A. Demšar, *Inorg. Chem*. **2006**, *45*, 7915–7921. (b) A. Pevec, A. Demšar, V. Gramlich, S. Petriček, H. W. Roesky, *J. Chem. Soc., Dalton Trans*. **1997**, 2215–2216.
4. A. Pevec, *Inorg. Chem.* **2004,** *43*, 1250–1256.
5. A. Künzel, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *J. Chem. Soc. Chem. Commun.* **1995**, 2145–2146.
6. H. Hatop, M. Schiefer, H.W. Roesky, R. Herbst-Irmer, T. Labahn, *Organometallics* **2001**, *20*, 2643–2646.
7. A. Pevec, F. Perdih, J. Košmrlj, B. Modec, H. W. Roesky, A. Demšar, *Dalton Trans.* **2003**, 420–425.
8. (a) J. L. Lamboy, A. Pasquale, A. L. Rheingold, E. Meléndez, *Inorg. Chim. Acta* **2007**, *360*, 2115–2120. (b) N. Steunou, F. Robert, K. Boubekeur, F. Ribot, C. Sanchez, *Inorg. Chim. Acta* **1998**, *279*, 144–151. (c) B. A. Borgias, S. R. Cooper, Y. B. Koh, and K. N. Raymond, *Inorg. Chem.* **1984**, *23*, 1009–1016.
9. (a) F. Franceschi, E. Gallo, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamellotti, *Chem. Eur. J*. **1996**, *2*, 1466–1476. (b) Labels Ti_a and Ti_b are used in order to distinguish Ti atoms in X–Ti_a=O–Ti_b–Y.
10. A. Demšar, A. Pevec, L. Golič, S. Petriček, A. Petrič, H. W. Roesky, *Chem. Commun*. **1998**, 1029–1030.

11. F. Perdih, A. Pevec, A. Demšar, *J. Fluorine Chem*. **2005**, *126*, 1065–1071.
12. A. Pevec, A. Demšar, to be published.
13. F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th edition, Wiley, New York, **1988**, pp. 463–467.
14. R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.
15. L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837–838.
16. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* **1994**, *27*, 435.
17. G. M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, **1997**.
18. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: www.ccdc.cam.ac.uk/data_request/cif.

Povzetek

Izolirali smo kristale klastra $[Li_8Ti_{10}F_{36}O_4(C_5Me_5)_4(thf)_8]$ **3**, ki so nastali kot produkt hidrolize spojine $[\{(C_5Me_5)TiF_3\}_4(LiF)_2(thf)_2]$ **2**. Kovinski atomi v tem klastru imajo koordinacijsko število šest (Ti in Li) ali štiri (Li). Oksidni ligandi tvorijo nesimetrične oksidne mostove Ti=O–Ti. Predlagan je mehanizem tvorbe takšnega klastra.