Electronic Supplementary Information

Titanium Thiosalicylate Complexes: Functional Metalloligands for the Construction of Redox-Active Heterometallic Architectures

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Crystal data for complexes 7·C_4H_8O: Crystal of **7** was mounted in a glass capillary. Intensity data were collected at 180 K on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite monochromated MoKα radiation source (λ = 0.71073 Å**).** Data were integrated using SAINT[1] and an absorption correction was performed with the program SADABS.[2] The structures were solved by direct methods[3] and refined by full-matrix least-squares methods based on F^2.

All crystals that we could have obtained for compound 7 have been weakly diffracting samples (20% nearly) resulting of very low quality. The poor quality of these crystals prevents doing a detailed structural analysis but it allows confirm, unambiguously, the existence of one H_2O molecule coordinated to Li atom. However, the structure is representative of the sample because several crystals were mounted with the same result. All molecules of THF are strongly disordered. Due to the low diffraction's intensity obtained in the experiment, it's very difficult to model the disorder and we have considered to stop only in the majority models assigning a chemical occupancy of 50% except for C25-C26 which have a value 60/40. This results in some high Uij for these molecules and they are refined isotropically. DELU, SIMU and SADI restraints have been used for these THF molecules. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions but It’s no possible to locate the hydrogen atoms in the H_2O molecule and they have been introduced with the CALC-OH (M. Nardelli, J. Appl. Cryst., 32, 563, 1999) program.

References

1. SAINT+ v8.37, Bruker-AXS (2016), APEX3 v2016.1.0. Madison, Wisconsin, USA.

2. SADABS, L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.,* 2015, **48**, 3-10.

3. (a) L. J. Farrugia, *J. Appl. Cryst*., 2012, **45**, 849-854; (b) G. M. Sheldrick, SHELX-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.

Table S1 Bond lengths [Å] and angles [°] for **7·C_4H_8O**.

Empirical formula	C_{64} H_{80} Li_2 O_{13} S_4 Ti_2
Formula weight	1295.20
Temperature (K)	180(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P n m a
a(Å)	22.77(2)
b(Å)	21.68(2)
c(Å)	14.279(16)
α(°)	90
β(°)	90
γ(°)	90
Volume($Å^3$)	7050(13)
Z	4
Density (calculated) (g/cm^3)	1.220
Absorption coefficient (mm^{-1})	0.401
F(000)	2728
Crystal size (mm^3)	0.12 x 0.09 x 0.05
Index ranges	-28≤h≤27, -26≤k≤26, -17≤l≤17
Reflections collected	46082
Independent reflections	7239 [R(int) = 0.3141]
Data / restraints / parameters	7239 / 103 / 384
Goodness-of-fit on F^2	0.669
Final R indices [I>2σ(I)]	R1 = 0.0819, wR2 = 0.1987
Largest diff. peak / hole, $e.Å^{-3}$	0.468 and -0.412

Table S2 Selected bond lengths [Å] and angles [°] for **7·C_4H_8O**.

Bond Length		*Angle*	
Ti(1)-O(1)	1.986(6)	O(1)-Ti(1)-O(3)	83.1(2)
Ti(1)-O(3)	2.016(5)	O(1)-Ti(1)-S(1)	82.6(2)
Ti(1)-S(1)	2.390(3)	O(3)-Ti(1)-S(2)	82.6(2)
Ti(1)-S(2)	2.414(3)	S(1)-Ti(1)-S(2)	79.7(1)
S(1)-C(6)	1.77(1)	O(2)-Li(1)-O(5)	114.1(7)
S(2)-C(8)	1.76(1)	O(2)-Li(1)-O(6)	103.1(8)
O(2)-Li(1)	1.87(1)	O(4)-Li(2)-O(7)	108.8(7)
O(5)-Li(1)	2.03(1)	O(4)-Li(2)-O(8)	107.9(7)
O(6)-Li(1)	1.90(2)		
O(4)-Li(2)	1.78(1)		
O(7)-Li(2)	1.97(2)		
O(8)-Li(2)	2.02(2)		

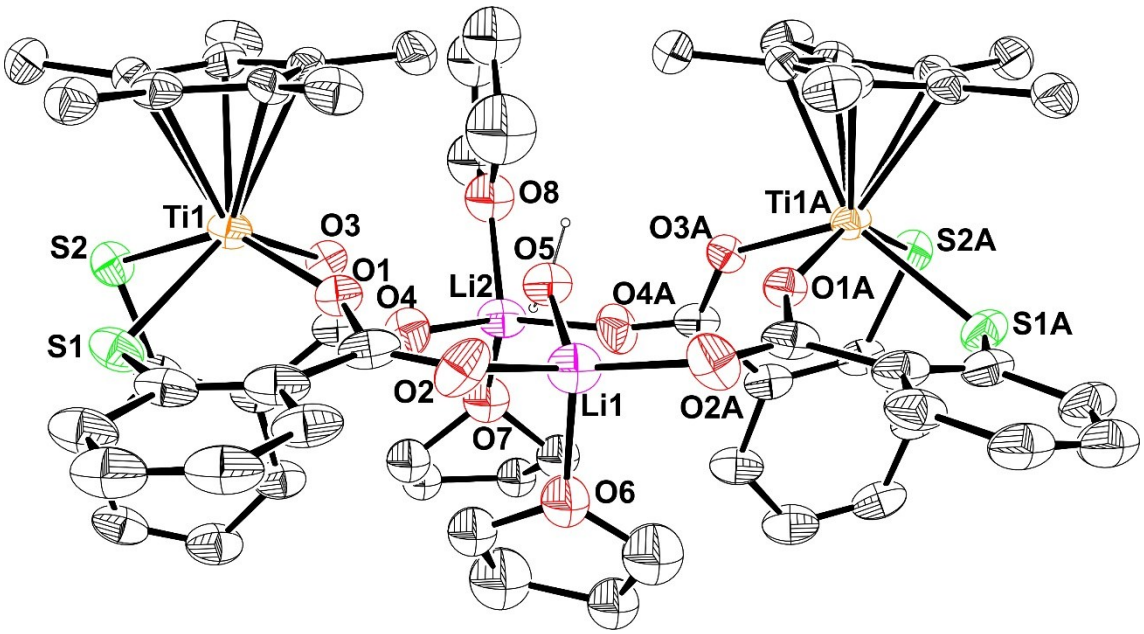

Figure S1 ORTEP of compound **7·C_4H_8O**.

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