Bis-Imide Derivatives of the Heterometallic Alkoxide $Li_4Ti_4O_4(O^iPr)_{12}$

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

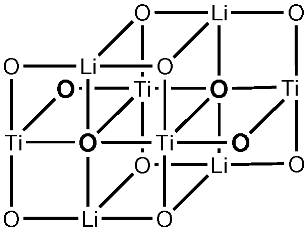
The imide derivatives $Li_4Ti_4O_2(NR)_2(O^iPr)_{12}$ (R = $CH_2C_6H_5$, C_6H_{11}, C_4H_9) were obtained either by reaction of the amine adduct $Ti_2(O^iPr)_8(H_2NR)_2$ with lithium di-*iso*-propylamide or butyllithium, or when the primary amine was first reacted with the base and then with $Ti(O^iPr)_4$. The structures of the imide derivatives are the same as that of $Li_4Ti_4O_4(O^iPr)_{12}$ (= $Li_4Ti_4(\mu_2\text{-}O)_2(\mu_5\text{-}O)_2(\mu_2\text{-}O^iPr)_4(\mu_3\text{-}O^iPr)_4(O^iPr)_4$) with the two μ_2-oxo groups replaced by two μ_2-NR groups.

Key words: Titanium Alkoxide Derivatives, Lithium Alkoxide Derivatives, Imide Ligands

Introduction

The heterometallic alkoxide $Li_4Ti_4O_4(O^iPr)_{12}$ (**1**) has been obtained previously by controlled hydrolysis of $Li_2Ti_2(O^iPr)_{10}$ [1]. The interesting structure of this compound can be described as a double (face-sharing) cube of the composition $Li_4Ti_2O_2(O^iPr)_6$ to which two $TiO(O^iPr)_3$ units are condensed, or as six condensed cubes with four missing corners (Scheme 1). The titanium atoms within the double cube are six-coordinate, while those outside are five-coordinate.

A formula taking the different bonding modes of the oxo and alkoxo ligands into account is $Li_4Ti_4(\mu_2\text{-}O)_2(\mu_5\text{-}O)_2(\mu_2\text{-}O^iPr)_4(\mu_3\text{-}O^iPr)_4(O^iPr)_4$. Each titanium atom is bonded to a terminal O^iPr ligand. The μ_2-O^iPr, μ_3-O^iPr and μ_5-oxo groups connect the lithium and titanium atoms, while the μ_2-oxo groups bridge two titanium atoms.



Scheme 1. The cluster core of $Li_4Ti_2O_2(O^iPr)_6$ (**1**). The four terminal O^iPr ligands (one per Ti atom) and the ^iPr substituents of the bridging O^iPr ligands were omitted for clarity. The oxo ligands are drawn in bold letters.

In this article we describe the synthesis and structures of bis-imide derivatives of this cluster, where the two μ_2-oxo groups are replaced by μ_2-NR groups.

Results and Discussion

We obtained the bis-imide derivatives by two different synthesis protocols. In the first, benzylamine or cyclohexylamine solutions in *n*-heptane were reacted with one molar equivalent of lithium di-*iso*-propylamide or butyllithium at −60 °C. One molar equivalent of $Ti(O^iPr)_4$ was then added to this solution resulting in a color change to dark yellow (with benzylamine) or dark red (with cyclohexylamine). The solutions were concentrated and stored at r. t. (cyclohexylamine reaction) or at 4 °C (benzylamine reaction). After a few days mixtures of crystal were obtained which consisted of colorless $Li_2Ti_2(O^iPr)_{10}$ [2] as the main product and yellow $Li_4Ti_4O_2(O^iPr)_{12}(NR)_2$ (**2a**: R = $CH_2C_6H_5$; **2b**: R = C_6H_{11}) as a by-product. $Li_2Ti_2(O^iPr)_{10}$ was identified by single crystal X-ray diffraction. The crystals of **2a** and **2b** were separated manually.

In the second route, equimolar amounts of butylamine and $Ti(O^iPr)_4$ were first reacted in *n*-heptane at −60 °C. This resulted in the precipitation of the colorless amine adduct $Ti_2(O^iPr)_8(H_2NC_4H_9)_2$, as previously described [3]. When a solution of one molar equivalent of lithium di-*iso*-propylamide or butyllithium was slowly added, the color of the solution again changed to yellow. The solution was concentrated and stored at 4 °C. After three days, dark yellow crystals of $Li_4Ti_4O_2(O^iPr)_{12}(NBu)_2$ (**2c**) in a matrix of $Li_2Ti_2(O^iPr)_{10}$ [2] were obtained.

The structures of the bis-imide derivatives **2a – c** were determined by single crystal X-ray diffraction. The centrosymmetric clusters have the same overall

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Table 1. Selected bond lengths (pm) and angles (deg) in **2a** (atoms with an asterisk denote inversion-related atoms).

Ti(2)–O(1)	201.1(1)	O(1)–Ti(2)–O(1)*	76.55(5)
Ti(2)–O(1)*	214.5(1)	O(3)–Ti(2)–O(5)	165.71(5)
Ti(2)–N(1)	195.5(2)	O(1)–Ti(2)–O(2)	178.54(5)
Ti(2)–O(2)	180.3(1)	N(1)–Ti(2)–O(2)	98.72(7)
Ti(2)–O(3)	201.9(1)	N(1)–Ti(2)–O(1)	79.82(6)
Ti(2)–O(5)	203.9(1)	N(1)–Ti(2)–O(1)*	156.26(7)
Ti(1)–O(1)	200.3(1)	N(1)–Ti(1)–O(1)	81.29(6)
Ti(1)–N(1)	190.2(2)	N(1)–Ti(1)–O(4)	100.34(7)
Ti(1)–O(4)	181.4(1)	O(1)–Ti(1)–O(4)	178.15(6)
Ti(1)–O(7)	194.3(1)	O(7)–Ti(1)–O(6)	132.58(6)
Ti(1)–O(6)	192.8(1)	N(1)–Ti(1)–O(6)	110.92(6)
Li(1)–O(3)*	191.1(3)	N(1)–Ti(1)–O(7)	112.61(6)
Li(1)–O(5)	200.8(3)	Ti(1)–N(1)–Ti(2)	102.12(7)
Li(1)–O(6)	192.4(3)	Ti(2)–O(1)–Ti(1)	96.74(5)
Li(1)–O(1)	204.7(3)	O(3)*–Li(1)–O(1)	89.1(1)
Li(2)–O(5)	190.8(3)	O(5)–Li(1)–O(1)	87.0(1)
Li(2)–O(3)*	200.3(3)	O(6)–Li(1)–O(1)	83.8(1)
Li(2)–O(7)*	191.4(3)	O(5)–Li(2)–O(1)*	88.7(1)
Li(2)–O(1)*	203.5(3)	O(3)*–Li(2)–O(1)*	86.6(1)
		O(7)*–Li(2)–O(1)*	83.8(1)

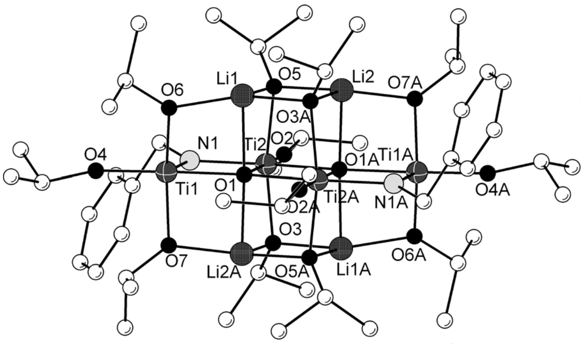

Fig. 1. Molecular structure of $Ti_4Li_4O_2(O^iPr)_{12}(NCH_2\text{-}C_6H_5)_2$ (**2a**).

structure as the parent compound $Li_4Ti_2O_2(O^iPr)_6$ (**1**) (Scheme 1); only the μ_2-oxo groups are replaced by μ_2-NR groups. The structure of **2a** is shown in Fig. 1, that of **2b** and **2c** are very similar. Selected bond lengths and angles are given in Table 1.

Replacement of the μ_2-oxo by μ_2-NR groups results in only a slight distortion of the structure, because the Ti–N distances are somewhat longer than the corresponding Ti–O distances in **1**. Thus, the Ti–N distances in **2a** are 195.5(2) pm for Ti(2)–N(1) and 190.2(2) pm for Ti(1)–N(1), and the corresponding distances in **2b** and **2c** are 194.9(2)/193.6(2) pm and 190.7(2)/193.6(2) pm, while the corresponding Ti–O distances in **1** are 189.0(2) and 179.9(2) pm. The longer distances correspond to the 6-coordinate Ti atoms and the shorter ones to the 5-coordinate. The smaller Ti–N–Ti angles in **2a – c** (102.12(7), 101.33(9) and 102.21(11)°), compared to the Ti–O–Ti angles in **1** (107.0(1)°), compensate to some extent the structural influence of the longer Ti–N bonds.

The geometry of the clusters results in an unusual (distorted) trigonal pyramidal coordination of the lithium atoms, with the μ_5-O(1) in the apical position. The Li–μ_5-O distances in **2a – c** are in the range 201.3(4) – 204.7(3) pm, compared to 201.7(3) – 203.5(3) pm in **1**. The Ti–O^iPr distances in **2a – c** and **1** do not differ significantly.

The Ti_2O_2 ring in the center of the clusters is formed by the octahedrally coordinated Ti atoms (Ti(2) in **2a**) and the μ_5-oxo groups (O(1) in **2a**). The pronounced asymmetry of the Ti–O distances in this ring of 197.6(2) – 201.1(1) *vs.* 214.2(2) – 220.3(2) pm in **2a – c** (compared with 200.1(2) *vs.* 205.0(2) pm in **1**) is probably a consequence of the imide substituent, which is *trans* to the longer Ti–O bond. The coordination octahedra of the central titanium atoms are completed by one terminal and two μ_3-O^iPr ligands. The corresponding Ti–O distances in **1** and **2a – c** are nearly the same.

The outer titanium atoms are only 5-coordinate. The axial positions of the (distorted) trigonal bipyramid are occupied by the μ_5-O atom and the terminal O^iPr group. The Ti–μ_5-O distances of **2a – c** (200.3(1) – 201.8(2) pm) are shorter than the corresponding distance in **1** (206.3(1) pm). Since the nitrogen atom is located in the trigonal plane, the difference in bond lengths is less pronounced than for the octahedral Ti atoms. The bond angles at the Ti atoms in **1** and **2a – c** are very similar.

NMR spectroscopic investigations in solution were only performed with **2a**, because the solubility of **2b** and **2c** was not high enough to obtain meaningful spectra. However, the NMR data fully corresponded to the solid state structure. Four sets of signals were observed for the O^iPr groups according to the molecular symmetry. The ratio of the signal intensities was 2 : 2 : 1 : 1 for four μ_3-O^iPr, four μ_2-O^iPr and 2 × 2 chemically different terminal O^iPr groups. The C*H* signal of the μ_3-O^iPr units appears at lowest field at 4.87 (^{13}C 72.5) ppm, and the C*H* signal at highest field (at 4.24 ppm; ^{13}C 67.8 ppm) can be assigned to the μ_2-O^iPr groups.

Conclusions

The structures of the three $Li_4Ti_4O_2(NR')_2(O^iPr)_{12}$ derivatives (**2**) with different NR ligands reported in

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this work are very similar to that of $Li_4Ti_4O_4(O^iPr)_{12}$ (**1**) [1]. The two μ_2-O groups of **1** were replaced by μ_2-NR ligands. This modification of the cluster has only little consequences on the structural and geometric parameters.

The imide-substituted clusters were reproducibly obtained as by-products when the amine adduct $Ti_2(O^iPr)_8(H_2NC_4H_9)_2$ was reacted with a strong base (LiN^iPr_2 or LiBu), or when benzylamine or cyclohexylamine were first reacted with the base and then with $Ti(O^iPr)_4$. The main product in each case was $Li_2Ti_2(O^iPr)_{10}$ [2]. This leads to the conclusion that the reaction sequence is probably rather complex, and one can only speculate about potential intermediates in the formation of **2**.

$Li_4Ti_4O_4(O^iPr)_{12}$ was obtained by controlled hydrolysis of $Li_2Ti_2(O^iPr)_{10}$ [1]. The source of the oxo groups in **2** is less obvious. Unintentional hydrolysis can be ruled out for several reasons. First, the imide derivatives were reproducibly obtained in several runs. Second, if water would be present, the strong bases lithium di-*iso*-propylamide or butyllithium would preferentially react with water and would thus remove water from the system. It is very unlikely that imide groups would be formed in the presence of water. Third, **2** was obtained independent of whether $Ti(O^iPr)_4$ was added before or after addition of the base. Thus, the only reasonable source of the oxo groups are the OR groups. Possible routes would be the abstraction of an ^iPr group from an O^iPr ligand (being activated by coordination to one or more Ti atoms) with concomitant formation of tri-*iso*-propylamine, or the elimination of di-*iso*-propylether. Non-hydrolytic sol-gel processes (*i. e.* the formation of oxo groups from metal alkoxides in the absence of water) are well known [4].

Experimental Section

All operations were carried out in a moisture- and oxygen-free argon atmosphere using the Schlenk technique. All solvents were dried by standard methods. $Ti(O^iPr)_4$ (Aldrich, 97 %) was used as received.

*Synthesis of $Li_4Ti_4O_2O\,^iPr_{12}(NCH_2C_6H_5)_2$ (**2a**)*

An amount of 196 mg (1.83 mmol) of benzylamine (Aldrich 99 %, used as received) was dissolved in 5 mL of *n*-heptane and cooled to −40 °C. Then 1.14 mL (2.01 mmol) of lithium di-*iso*-propylamide (1.8 M solution in THF/heptane/ethylbenzene) was slowly added with stirring, followed by the addition of 519 mg (1.83 mmol) of $Ti(O^iPr)_4$. The pale brown solution was allowed to reach r. t. within 1 h and was then concentrated to half its volume. Colorless crystals of $Li_2Ti_2(O^iPr)_{10}$ [2] and yellow crystals of **2a** were obtained after 6 d at 4 °C. The crystals of **2a** were separated manually. – ^1H NMR (CD_2Cl_2, 21 °C) δ = 7.62 – 7.16 (m, C_6H_5), 5.83 (s, NCH_2Ph), 4.87, 4.72, 4.32, 4.24 (m, $OCHMe_2$), 1.27, 1.22, 1.17, 1.08 ppm (d, J = 6.1 Hz, $OCH(CH_3)_2$). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C) δ = 127.4, 127.1, 124.9 (C_6H_5), 74.0, 73.9, 72.5, 67.8 ($OCHMe_2$), 28.4, 27.6, 27.0, 26.1 ($OCH(CH_3)_2$) ppm. – ^7Li-NMR (CD_2Cl_2, 21 °C) δ = 0.5 ppm.

*Synthesis of $Li_4Ti_4O_2(O\,^iPr)_{12}(NC_6H_{11})_2$ (**2b**)*

An amount of 264 mg (2.66 mmol) of cyclohexylamine (Aldrich 99 %, used as received) was dissolved in 10 mL of *n*-heptane and cooled to −60 °C. Then 1.48 mL (2.61 mmol) of lithium di-*iso*-propylamide (1.8 M solution in THF/heptane/ethylbenzene) was added slowly with stirring, followed by the addition of 761 mg (2.67 mmol) of $Ti(O^iPr)_4$. The dark red solution was allowed to reach r. t. within 1 h and was then concentrated to half its volume. Colorless crystals of $Li_2Ti_2(O^iPr)_{10}$ [2] and yellow prismatic crystals of **2a** were obtained after 3 d at 4 °C. The crystals of **2b** were separated manually.

*Synthesis of $Li_4Ti_4O_2(O\,^iPr)_{12}(NC_4H_9)_2$ (**2c**)*

An amount of 131 mg (1.79 mmol) of 1-butylamine (Aldrich 99.5 %, used as received) was added to a solution of 485 mg (1.71 mmol) of $Ti(O^iPr)_4$ in 6 mL of *n*-heptane at r. t. with stirring. Cooling of the reaction solution to −40 °C led to the precipitation of a white solid. Then 0.95 mL (1.67 mmol) of lithium di-*iso*-propylamide (1.8 M solution in THF/heptane/ethylbenzene) was added slowly through a rubber septum under stirring. The solution was allowed to reach r. t. within 1 h and was then concentrated to half its volume. Colorless crystals of $Li_2Ti_2(O^iPr)_{10}$ [2] and yellow plate-like crystals of **2c** were obtained after 3 d at 4 °C. The crystals of **2c** were separated manually.

X-Ray structure analyses

Data collection (Table 2): The crystals were mounted on a Siemens SMART diffractometer (area detector) and measured in a nitrogen cryo-stream. MoK_α radiation (λ = 71.069 pm, graphite monochromator) was used for all measurements. The data collection at 173 K covered a hemisphere of the reciprocal space, by a combination of three or four sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The crystal-to-detector distance was 5 cm. The data were corrected for polarization and Lorentz effects, and an empirical

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Table 2. Crystallographic data of **2a – 2c**.

	2a	**2b**	**2c**
Empirical formula	$Ti_4Li_4O_2(O^iPr)_{12}(NCH_2C_6H_5)_2$	$Ti_4Li_4O_2(O^iPr)_{12}(NC_6H_{11})_2$	$Ti_4Li_4O_2(O^iPr)_{12}(NC_4H_9)_2$
Formula weight	1170.7	1154.7	1102.5
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [pm]	1143.24(8)	1143.27(7)	2183.4(1)
b [pm]	1222.82(8)	1205.37(7)	1132.29(6)
c [pm]	1355.48(9)	1383.74(8)	2668.3(1)
α [deg]	65.686(1)	66.457(1)	90
β [deg]	89.888(1)	89.002(1)	112.612(1)
γ [deg]	66.839(1)	63.157(1)	90
V [pm$^3 \cdot 10^6$]	1558.5(2)	1528.5(2)	6089.5(6)
Z	1	1	4
Calcd. density [g cm^{-3}]	1.247	1.254	1.203
Abs. coeff. μ [mm^{-1}]	0.551	0.560	0.559
θ Range [deg]	2.13 – 25.00	2.02 – 25.00	2.02 – 25.00
Crystal size [mm]	0.08 × 0.05 × 0.05	0.12 × 0.07 × 0.05	0.09 × 0.04 × 0.03
Refl. coll. / unique	16111 / 5459	13508 / 5377	16065 / 5306
Data / parameters	5459 / 334	5377 / 325	5306 / 302
$R(I \geq 2s(I))$	0.033	0.038	0.049
$wR2(I \geq 2s(I))$	0.090	0.063	0.125
GOF	1.051	0.902	0.977
$\Delta\rho$ max / min [e Å^{-3}]	0.408 / −0.328	0.704 / −0.363	0.509 / −0.777

absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections.

The structures were solved by the Patterson method (SHELXS-97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL-97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. In **2c** one O^{i}Pr group was strongly disordered and was therefore refined using geometric restraints (DFIX, DANG).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 619579 (**2a**), CCDC 619580 (**2b**) and CCDC 619581 (**2c**)). Copies of the data can be obtained *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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