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Synthesis and characterization of new titanium hexanuclear oxo carboxylato alkoxides. Molecular structure of $[Ti_6(\mu_3\text{-}O)_6(\mu\text{-}O_2CC_6H_4OPh)_6(OEt)_6]$

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The reaction between $Ti(OR)_4$ (R = Et or Pr^i) and 2-phenoxybenzoic acid in refluxing toluene led to $[Ti_6(\mu_3\text{-}O)_6(\mu\text{-}O_2CC_6H_4OPh)_6(OR)_6]$; its structure corresponds to an assembly of two staggered triangular units sharing six edges (actually the μ_3-O ligands) and connected *via* the carboxylate ligands.

Substitution of alkoxide ligands by carboxylate ligands was first investigated as a means of stabilizing metal alkoxides such as $Ti(OR)_4$ (R = Et, Pr^i or Bu) in sol–gel processing; acetic acid was commonly used.[1] These reactions were extended to functionalized acids having polymerizable groups such as methacrylic acid for hybrid materials applications[2] or to oleic acid for colloid stabilisation in non-aqueous media.[3] The reactions were carried out at room temperature mostly without any solvent and in the stoichiometry $Ti(OR)_4$–$R'CO_2H$ = 1 : 2. Hexanuclear titanium oxo carboxylato alkoxides were generally isolated and characterized by X-ray diffraction. They display two types of formulations, namely $[Ti_6O_4(R'CO_2)_4(OR)_{12}]$ [R′ = Me, R = Pr^i;[4] R′ = Np (neopentyl), R = Pr^i or H;[5] R′ = $Co_3C(CO)_9$, R = Et or Pr^i[6]] or $[Ti_6O_4(R'CO_2)_8(OR)_8]$ (R′ = Me[7] or $CMeCH_2$,[2a] R = Et; R′ = Me, R = Bu[8]). Recently, tetranuclear clusters with a greater number of oxo groups per metal atom of formulation $[Ti_4O_4(R'CO_2)_4(OR)_4]$ [R′ = $Co_3C(CO)_9$, R = Pr^i, Et or Ph;[6] R′ = Pr^i, R = Bu[5]] were obtained. The generation of the oxo ligands was attributed to hydrolysis reactions as a result of esterification between excess acid and the alcohol generated by the substitution reaction.[8] The difference in the formulation of the three types of clusters was attributed to the nature of the OR and $R'CO_2$ ligands.[6] No mention was made of temperature effects which regulate the kinetics of substitution, esterification, hydrolysis and condensation reactions.

This factor allowed us to obtain and characterize the new hexanuclear titanium oxo carboxylato alkoxide cluster $[Ti_6(\mu_3\text{-}O)_6(\mu\text{-}O_2CC_6H_4OPh)_6(OEt)_6]$ and analogs $[Ti_6(\mu_3\text{-}O)_6(\mu\text{-}O_2CR')_6(OR)_6]$ with R = Pr^i, R′ = C_6H_4OPh or Me and R = Et, R′ = Me. The reaction between titanium tetraethoxide and 2-phenoxybenzoic acid (1 : 2 stoichiometry) in refluxing CH_2Cl_2 for 3 h shows unreacted acid detected by IR spectroscopy [ν(CO_2) 1690 cm^{-1}]. After refluxing for 15 h in toluene free acid is no longer detected. The FT-IR spectrum of the raw product indicates ester formation [ν(CO) 1728 cm^{-1}]. The ^1H NMR spectra show signals characteristic of a heteroleptic titanium species with a OR–$R'CO_2$ integration ratio of 1 : 1 and additional signals due to ester [integration ratio OR(Ti complex)–(ester) = 1 : 1]. This latter value is incompatible with the formation of the known hexanuclear complexes $[Ti_6O_4(OR)_{12}(O_2CR')_4]$ or $[Ti_6O_4(OR)_8(O_2CR')_8]$ which would lead to a ratio OR(complex)–OR(ester) of 3 : 1 or 2 : 1 respectively. It is however consistent with a $[Ti_4O_4(OR)_4(O_2CR')_4]$ tetranuclear species. Crystallisation in CH_2Cl_2 affords a pure titanium species **1** in 64% yield.‡ In the absence of informative ^1H NMR data (one type of ethoxide ligand only), its structure was investigated by single crystal X-ray diffraction.§

Compound **1** corresponds to a hexanuclear cluster of formula $[Ti_6(\mu_3\text{-}O)_6(OEt)_6(\mu\text{-}O_2CC_6H_4OPh)_6]$ (Fig. 1). Each titanium center is surrounded by three μ_3-O, two μ-carboxylate and one alkoxide ligand in a distorted octahedron [O–Ti–O angles 77.3(2)–179.0(2)°]. The structure is symmetric and compact. It can be viewed as an assembly of two staggered triangular units built by sharing vertices of the octahedra [average Ti···Ti distances of 3.111(2) Å] which are joined by six common edges (Fig. 2). All μ_3-oxo ligands are trigonal (average Σ = 333.8°) and belong to the shared edges, the alkoxide ligands are in apical positions and the six carboxylate ligands are connecting the two triangular units. This arrangement makes enough room for the aromatic rings which are oriented toward the outside like an equatorial crown. The Ti–O bond lengths are in the range 1.751(5)–2.154(4) Å. The Ti–μ_3-O distances within the triangular units [1.878(4)–1.912(4) Å] are significantly shorter than those of the interunits [2.150(5)–2.154(4) Å] and the Ti–μ-O (carboxylate) distances [2.026(5)–2.081(5) Å] are longer than the Ti–OR [1.751(5)–1.770(5) Å]. The Ti–O–C angles related to the alkoxide ligands are quite large [149.0(8)–167.9(11)°] as commonly observed for early transition metals. These values are in agreement with those reported in the literature.[8,9] The alkoxide ligands and carboxylate ligands are both equivalent on the NMR timescale, the ^1H NMR spectrum shows only one signal per ligand type indicating that the solid-state structure is retained upon

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‡ All manipulations were routinely performed under nitrogen using Schlenk and vacuum-line techniques. 2-Phenoxybenzoic and acetic acid (Aldrich) were used as received, $Ti(OEt)_4$ and $Ti(OPr^i)_4$ (Aldrich) were distilled before use. A solution of 2-phenoxybenzoic acid (2.789 g, 13.08 mmol) in toluene (50 ml) was added to $Ti(OEt)_4$ (1.49 g, 6.54 mmol) in toluene (20 ml). After refluxing for 15 h, the solvent was removed under vacuum and cluster **1** was obtained at 0 °C from a CH_2Cl_2 solution (1.35 g, 64%) (Found C, 54.87; H, 4.06. Calc. for $C_{90}H_{84}O_{30}Ti_6$: C, 55.92; H, 4.35%). Similar synthetic procedures were applied for $[Ti_6O_6(OPr^i)_6(O_2CC_6H_4OPh)_6]$ **2**, $[Ti_6O_6(OR)_6(OAc)_6]$ (R = Pr^i **3** and R = Et **4**).

§ *Crystal data* for **1**: $C_{90}H_{84}O_{30}Ti_6\cdot 4C_6H_5CH_3$, *M* = 2301.6, triclinic, space group $P\bar{1}$, *a* = 13.162(6), *b* = 14.977(6), *c* = 17.110(2) Å, α = 102.97(2), β = 103.48(3), γ = 112.15(3)°, *U* = 2849(2) Å³, *Z* = 1, μ(Mo-Kα) = 4.68 cm^{-1}, 10 493 data of which 10 018 were unique were collected at room temperature, *R* = 0.0617, *R′* = 0.0735 for 626 parameters. CCDC reference number 186/1036. See http://www.rsc.org/suppdata/dt/1998/2285/ for crystallographic files in .cif format.

Table 1 Characterization of the different titanium oxo carboxylato alkoxides

	1	2	3	4	5
IR/cm^{-1}					
ν(CO_2)	1604s, 1584s, 1538s	1608s, 1591s, 1538s	1603s, 1548s	1594s, 1543s	1595s, 1571s, 1555s
ν(M–O–M)	734s	733s	726s	738s	785s–772s
ν(M–OR), ν(M–O_2CR')	659s, 623m, 503m, 480m	660s, 627m, 502m, 480m	659s, 629m, 605m, 487m	659s, 631m, 610m, 477m	689m–655s, 625s, 590m–543m, 510m–456m
^1H NMR ($CDCl_3$, ppm)					
OR	1.10 (t, 8 Hz, Me), 4.35 (q, CH_2)	1.22 (d, 7 Hz, Me), 4.92 (sept, CH)	1.35 (d, 7 Hz, Me), 5.15 (q, CH)	1.39 (t, 7 Hz, Me), 4.82 (q, CH_2)	1.25 (t, 7 Hz, Me), 4.35, 4.55, 4.90 (m, 3:4:1, CH_2)
$R'CO_2$	7.97 (d, 7 Hz, aromatic C–H α to CO_2)	8.05 (d, 7 Hz, aromatic C–H α to CO_2)	2.04 (s, Me)	2.10 (s, Me)	2.20 (s, Me)
OR–O_2CR' ratio	1:1	1:1	1:1	1:1	1:1

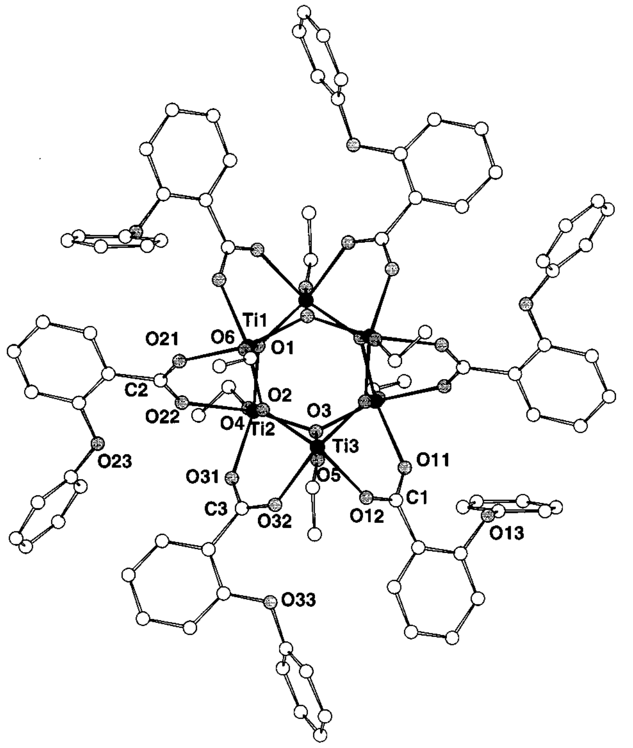


Fig. 1 Ball and stick drawing of the [$Ti_6(\mu_3\text{-}O)_6(OEt)_6(\mu\text{-}O_2CC_6H_4OPh)_6$] cluster showing the atom numbering scheme. Selected average bond lengths (Å): Ti–μ_3-O 1.980, Ti–OR 1.761, Ti–μ-O_2CR' 2.056

dissolution. Cluster **1** represents the first hexanuclear titanium oxo carboxylato alkoxide having the formula [$Ti_6O_6(OR)_6(O_2CR')_6$].

Refluxing $Ti(OPr^i)_4$ and 2-phenoxybenzoic acid in toluene leads to analogous crystalline material (yield 30%) identified by FT-IR and ^1H NMR spectroscopy as [$Ti_6O_6(OPr^i)_6(O_2CC_6H_4OPh)_6$] **2** (Table 1). Application of the same procedure to $Ti(OR)_4$ and acetic acid afforded [$Ti_6O_6(OR)_6(OAc)_6$] (R = Pr^i **3** or Et **4**) in 60 and 33% yields respectively indicating that the formation of compounds of type **1** does not depend on the nature of R [equation (1)].

$$6Ti(OR)_4 + 12R'CO_2H \xrightarrow{\text{heat,toluene}} [Ti_6O_6(OR)_6(R'CO_2)_6] + 6R'CO_2R + 12ROH \quad (1)$$

$$R = Et \text{ or } Pr^i \qquad R' = PhOC_6H_4 \text{ or } Me$$

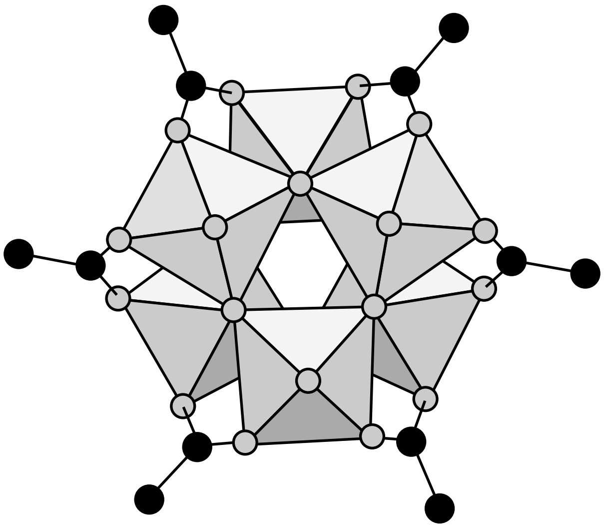


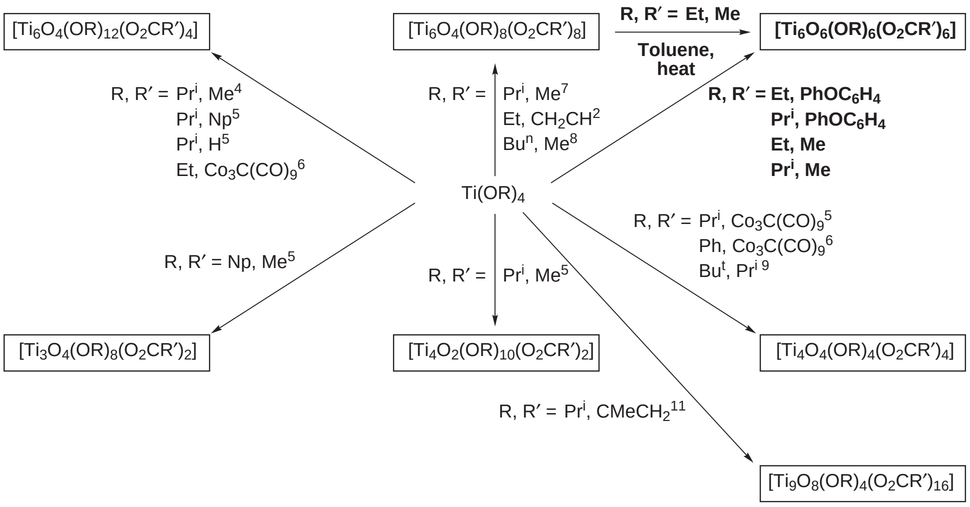
Fig. 2 The assembly of the co-ordination polyhedra in [$Ti_6(\mu\text{-}O)_6(OEt)_6(\mu\text{-}O_2CR)_6$]

The formation of **3** is quite easy to explain since temperature favors higher incorporation of carboxylato or oxo ligands into the metal co-ordination sphere. A similar oxocluster, [$Sn_6O_6(OBu^t)_6(OAc)_6$], was obtained by non-hydrolytic condensation between $Sn(OAc)_4$ and $Sn(OBu^t)_4$ in refluxing toluene.[10] Such a reaction was envisioned as a means to convert [$Ti_6O_4(OR)_8(O_2CR')_8$] into a complex with a greater number of oxo groups. The cluster [$Ti_6O_4(OEt)_8(OAc)_8$] **5** was thus prepared according to the literature.[7] Cluster **4** was obtained in 40% yield after refluxing **5** in toluene for 15 h and crystallisation from CH_2Cl_2 solution. Its formation can only be explained by elimination of the ester during heating. Cluster **4** can thus be obtained by two routes: substitution reactions between metal alkoxides and carboxylic acids [equation (1)] or by elimination of the ester from [$Ti_6O_4(OR)_8(O_2CR')_8$] [equation (2)]. Condensation with

$$[Ti_6O_6(OR)_8(R'CO_2)_8] \xrightarrow{\text{heat,toluene}} [Ti_6O_6(OR)_6(R'CO_2)_6] + 2R'CO_2R \quad (2)$$

$$R = Et \text{ or } Pr^i \qquad R' = Me$$

elimination of ester promoted by heating was observed for systems involving the metal alkoxides (Pb–Ti or Pb–Nb systems) and carboxylates.[9] Table 1 shows the differences between **5** and **4**. These new hexanuclear clusters can be distinguished from each other using FT-IR and ^1H NMR spectroscopy. Cluster **4**



Scheme 1 Reactions between titanium alkoxides and various carboxylic acids (bold = present work)

has a strong ν(Ti–O) absorption band around 740 cm^{-1} in its FT-IR spectrum, whereas more complex spectra are observed for compounds of type **5**. Only one sharp ^1H NMR signal is observed for the OR ligands in **4** in contrast to three signals for the magnetically non-equivalent alkoxides of $[Ti_6(\mu\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OR)_2(OR)_6(\mu\text{-}O_2CR')_8]$ clusters of type **5**.

Scheme 1 summarises the various titanium oxo carboxylato alkoxides known. The temperature plays an important role and is a factor which must be taken into account in the build-up of an already rich series of titanium oxo carboxylato alkoxide species. The recent report of the formation of the $[Ti_9(\mu\text{-}O)_6(\mu_3\text{-}O)_2(OPr^i)_4(O_2CCMeCH_2)_{16}]$ species obtained by reacting $Ti(OPr^i)_4$ and excess methacrylic acid illustrates the structural diversity.[11]

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