

Review

The structural chemistry of titanyl oligomers and polymers

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ABSTRACT

Chain-like and cyclic structures of compounds with a $\cdots\text{Ti}-\text{O}-\text{Ti}-\text{O}\cdots$ backbone are reviewed, that is, compounds in which the coordination octahedra of the titanium atoms share corners by means of μ_2 -O atoms. The charge of the TiO^{2+} unit is balanced by organic or inorganic ligands which additionally complete the coordination sphere of the titanium atoms. Typical substitution patterns are two mono-anionic bidentate ligands, two monodentate anionic plus two neutral ligands, or one tetradentate dianionic ligand. While only few examples of polymeric chain structures, or segments thereof, were structurally characterized, several types of cyclic compounds are known. This includes rings in which the Ti polyhedra are only linked via the μ_2 -O atoms, capped rings, or rings in which the titanium octahedra are additionally bridged by organic ligands.

1. Introduction

The structures of oligo- or poly(dialkylsiloxanes), $(\text{R}_2\text{SiO})_{n/\infty}$, are composed of corner-sharing $[\text{R}_2\text{SiO}_2]$ tetrahedra, where each oxygen atom bridges two silicon atoms (μ_2 -O). Polysiloxane chains (silicones) or cyclic oligomers are formed in this manner. Fig. 1 (left) shows the structure of the cyclic tetramer $(\text{Me}_2\text{SiO})_4$ ("D4") [1] as a typical example.

The Ti(IV) analogue of siloxanes are titanyl compounds, *i.e.*, compounds containing the TiO^{2+} unit. Contrary to silicon, Ti(IV) prefers higher coordination numbers, typically an octahedral coordination. Formation of structures analogous to that of poly- and oligosiloxanes, but with corner-sharing *octahedral* repeat units, thus requires the coordination of groups which balance the charge of the TiO^{2+} unit, but occupy *four* coordination sites. The composition of uncharged compounds is thus $[\text{TiOL}_4]_{n/\infty}$, where the ligands can, for example, be two bidentate monoanions, one mono- plus one tridentate anion, or a tetradentate dianion, as will be discussed in detail in hereafter. The β -diketonate complex $[\text{TiO}(\text{thd})_2]_4$ ($\text{thd} = t\text{BuC}(\text{O})-\text{CH}-\text{C}(\text{O})t\text{Bu}$) [2] (Fig. 1, right), as an example, is thus the structural titanyl analogue to $(\text{Me}_2\text{SiO})_4$. The analogy of R_2SiO and titanyl units with chelating ligands is also supported by ring systems containing both units [3].

In this article, the structures of such chain-like or cyclic titanyl compounds are reviewed, *i.e.*, homometallic compounds with a $\cdots\text{Ti}-\text{O}-\text{Ti}-\text{O}\cdots$ backbone (excluding dimeric compounds with Ti–O–Ti or Ti_2O_2 linkages) and a O:Ti ratio of 1. It complements early reviews where the structural chemistry of such compounds was a partial aspect, such as Ref. [4]. Titanium oxo compounds with μ_3 - or μ_4 -O linkages (titanium oxo clusters) are not subject of the current article. Also excluded are structures in which each titanium atom is bonded to more than two μ_2 -O, *i.e.*, where the O:Ti ratio is > 1 (as in $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]^{8+}$ with a cubic Ti_8O_{12} core [5], a structural analogue to the silsesquioxanes $\text{R}_8\text{Si}_8\text{O}_{12}$).

2. Chains and chain segments

There are only few structurally characterized examples of *polymers* with a $\cdots\text{Ti}-\text{O}-\text{Ti}-\text{O}\cdots$ backbone. This does not mean that they do not exist, but such compounds may be difficult to crystallize.

The leading structure is that of titanyl sulfate hydrate, $\text{TiO}(\text{SO}_4)\cdot\text{H}_2\text{O}$ (Fig. 2), with zigzag chains of corner-sharing $[\text{TiO}_6]$ octahedra [6]. The sulfate groups bridge every first and third Ti atom within the chains and additionally crosslink the TiO chains. Each Ti atom is thus surrounded by two μ_2 -O, one water molecule, and the oxygen atoms of three

Abbreviations: acac, acetylacetonate; BL, bridging ligand; CL, chelating ligand; Cp, η^5 -cyclopentadienyl; Cp*, η^5 -pentamethylcyclopentadienyl; Cp', η^5 -methylcyclopentadienyl; dpta, 2-hydroxypropane-1,3-diamine-*N,N,N',N'*-tetraacetate; H₂acacen, bis(acetylacetonate)ethylenediamine; H₂salen, bis(salicyliden)ethylenediamine; H₂thd, 2,2,6,6-tetramethyl-3,5-heptanedione; H₄calix[4], *t*Bu-calix[4]arene; Ind, η^5 -indenyl; MCy, pentamethylcyclopropyl; Mes, mesityl; TL, tetradentate ligand; Xyl, xylyl.

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bridging sulfate ions. The structure of anhydrous $\text{TiO}(\text{SO}_4)$ is similar.

Several polymorphs of potassium and sodium titanyl phosphate, $\text{M}[\text{TiO}(\text{PO}_4)]$, with a TiO backbone are known [7], where the PO_4^{3-} groups also bridge the titanium atoms within the chains and crosslink the chains, just as the sulfate groups in titanyl sulfate. The polymorphs differ by different crosslinking of the TiO chains. In zwitterionic $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2\text{-TiO}(\text{PO}_4)$ [8], one Ti coordination site is occupied by the nitrogen atom of ethylene diamine instead of a phosphate oxygen, but otherwise the structure is like that of the titanyl phosphates. The crystal structure of $[\text{TiO}(\text{PO}_4)_2]^{4-}$ consists of infinite spirals of $[\text{TiO}_6]$ octahedra, where the $\mu_2\text{-O}$ atoms are either *cis* or *trans* to each other [9]. Two adjacent Ti atoms in the chain are bridged by two PO_4^{3-} groups each, whereby each Ti atom gets octahedrally coordinated. Two oxygen atoms of each PO_4^{3-} group are not coordinated and thus carry the negative charges.

Tetradentate dianionic organic ligands would be well suited for the formation of coordination polymers with a TiO backbone. Porphyrins, however, as an example for such ligands, only form monomeric $\text{TiO}(\text{porphyrin})$ complexes with 5-coordinate Ti. A tetradentate ligand with a more adaptable geometry is the dianion of bis(salicylidene)ethylenediamine (salen) and related compounds. No coordination polymers have been documented, but segments thereof. In the compounds $[\text{Ti}_n\text{O}_{n-1}(\text{salen} \text{ or } \text{acacen})_n\text{L}_2]^{2+}$ ($n = 3$ or 4 , acacen = dianion of bis(acetyl-acetone)ethylenediamine) the tetradentate dianions coordinate to the equatorial positions of the TiO_4N_2 octahedron with the $\mu_2\text{-O}$ perpendicular to this plane. This results in linear chain fragments of corner-sharing octahedra, which are terminated by two uncharged Lewis base molecules (L) [10]. The structure of $[\text{Ti}_4\text{O}_3(\text{acacen})_4(\text{THF})_2]^{2+}$ is shown in Fig. 3 as an example. In $[\text{Ti}_4\text{O}_3(\text{salen})_4(\text{H}_2\text{O})(\text{OSO}_2\text{OEt})]^+$ one end of the chain is terminated by an aqua ligand and the other by an anionic sulfonate group [11].

In $\text{Ti}_4\text{O}_3\text{Cl}_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O})_4$, a Ti_4O_3 segment is terminated by Cl atoms [12]. The Ti atoms are pairwise coordinated by the cyclopentadienylsilanolate ligands in a way that each Ti atom is bonded to a $\eta^5\text{-C}_5\text{R}_5$ ring and the neighboring Ti atom to a silanolate oxygen. A special case is $\text{Ti}_4\text{O}_3\text{Se}_2\text{Cp}_6$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). The backbone is a Ti_4O_3 chain, but the outer two Ti–O–Ti groups are additionally bridged by a $\mu_2\text{-Se}$ each [13]. The terminal Ti atoms of the Ti_4O_3 unit are coordinated by two Cp ligands, and the inner Ti atoms by just one.

A Ti_3O_2 segment is stabilized by organic ligands in the compound $\text{Ti}_3\text{O}_2(\text{NMe}_2)_3[4,5\text{-}(\text{Ph}_2\text{SeP})_2\text{C}_2\text{N}_3]_5$ ($\text{H}_3\text{C}_2\text{N}_3 = \text{triazole}$) [14]. The triazolyl groups coordinate unsymmetrically in a rather complex manner as mono-, di and tridentate (bridging and terminal) ligands. Each Ti atom is also coordinated by a dimethylamide ligand. The $\mu_2\text{-O}$ are *cis* to

each other at the central Ti atom, *i.e.*, the Ti_3O_2 unit is bent.

A section of the titanyl phosphate structures is found in $[\text{Ti}_3\text{O}_2(\text{HPO}_4)_2(\text{PO}_4)_2]^{2-}$ [15,16]. The HPO_4^{2-} and PO_4^{3-} ions in this compound bridge the Ti atoms of the Ti_3O_2 string (Ti–O–Ti–O–Ti unit) and connect the Ti_3O_2 units with each other.

3. Rings

It is well known from polysiloxane chemistry that rings are thermodynamically more stable than chains, because of less steric interaction of the organic substituents. It is therefore not surprising that more ring than chain structures were also found for titanyl compounds, with 3, 4, 6 or 8 $\mu_2\text{-O}$ -bridged polyhedra forming the rings.

3.1. Rings without additional organic bridges

The structurally simplest case are cyclic compounds in which the Ti polyhedra are only connected by the $\mu_2\text{-O}$ (as in the example in Fig. 1, right). There are several possibilities, how the four remaining coordination sites of octahedrally coordinated Ti atoms can be occupied.

The longest known and best investigated examples are the compounds $[\text{TiO}(\text{C}_5\text{R}_5\text{X})_n]$ with various cyclopentadienyl ligands (C_5R_5) and monodentate anionic groups X, which are mainly derived from partial hydrolysis of $(\text{C}_5\text{R}_5)\text{TiX}_3$ (an $\eta^5\text{-cyclopentadienyl}$ ring formally occupies three coordination sites). Structurally characterized examples of six-membered rings (three corner-sharing octahedra) are $\text{Ti}_3\text{O}_3\text{Cp}^*\text{X}_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{X} = \text{Cl}$ [17], Br [18], Me [19], $\text{CH}_2\text{CH}=\text{CH}_2$ [20]) and $\text{Ti}_3\text{O}_3(1,3\text{-}t\text{Bu}_2\text{C}_5\text{H}_3)_3\text{Cl}_3$ [21]. Two groups X are on one side of the approximately planar Ti_3O_3 ring, and the third on the opposite side.

A great variety of eight-membered ring structures (four corner-sharing octahedra) of $[\text{TiO}(\text{C}_5\text{R}_5\text{X})_4]$ is known, with the groups X alternately above and below the plane of the roughly planar Ti_4O_4 ring (up-down-up-down), as shown in Fig. 4, left, as a typical example:

- $\text{Ti}_4\text{O}_4(\text{Cp})_4\text{X}_4$: $\text{X} = \text{Cl}$ [22], $\text{O}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ [23],
- $\text{Ti}_4\text{O}_4(\text{Cp}')_4\text{X}_4$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$): $\text{X} = \text{Cl}$ [24], I [25],
- $\text{Ti}_4\text{O}_4(\text{C}_5\text{HMe}_4)_4\text{Br}_4$ [18],
- $\text{Ti}_4\text{O}_4\text{Cp}^*_4\text{X}_4$ ($\text{X} = \text{F}$ [26] (Fig. 4, left), Br [27]),
- $\text{Ti}_4\text{O}_4(\text{C}_5\text{H}_4\text{Y})_4\text{X}_4$ ($\text{Y} = \text{SiMe}_3$, $\text{X} = \text{NCS}$ [17]; $\text{Y} = \text{CH}_2\text{CH}_2\text{Br}$, $\text{X} = \text{Br}$ [28]).
- $\text{Ti}_4\text{O}_4(\text{Ind})_4\text{Cl}_4$ ($\text{Ind} = \eta^5\text{-indenyl}$) [29,30].

The up-down-up-down positioning of the X ligands changes to up-up-

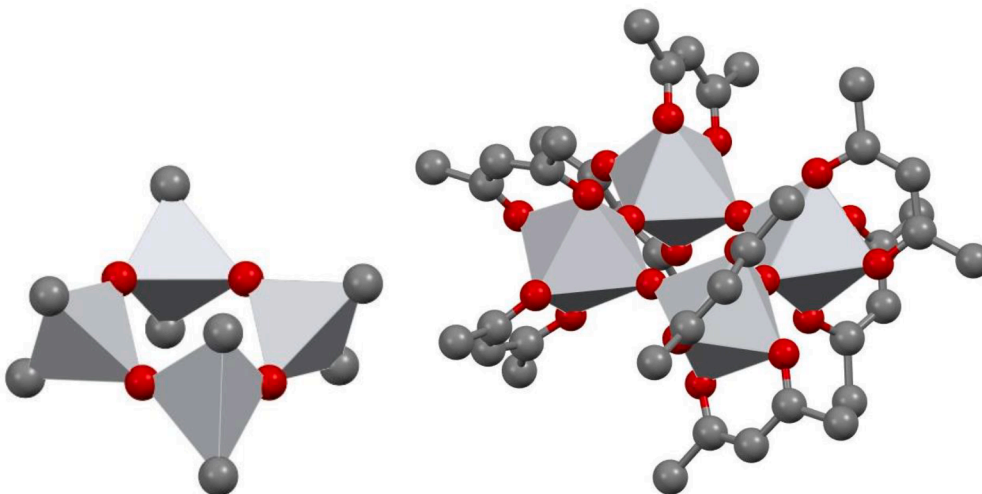


Fig. 1. Left: structure of $(\text{Me}_2\text{SiO})_4$ without hydrogen atoms; right: structure of $[\text{TiO}(\text{thd})_2]_4$ without CH_3 groups (red: O; grey: C; the Si or Ti atoms are in the center of the polyhedra).

down-down, when two adjacent Cp rings are connected with each other, as in $\text{Ti}_4\text{O}_4\text{Cl}_4(\text{C}_5\text{H}_4\text{-SiMe}_2\text{-C}_5\text{H}_4)_2$ (Fig. 4, right) [31] or $\text{Ti}_4\text{O}_4\text{Cl}_4[\text{C}_5\text{H}_3(\text{SiMe}_2)_2\text{C}_5\text{H}_3]_2$ [32].

When the positive charges of the TiO^{2+} unit are compensated by two anionic monodentate groups X, two uncharged donor atoms must additionally be coordinated to reach an octahedral coordination of the Ti atoms, *i.e.*, the rings must have the composition $[\text{TiOL}_2\text{X}_2]_x$ (L = uncharged ligand). There are only few examples of this structure type, with $\text{Ti}_3\text{O}_3\text{Cl}_6(\text{THF})_6$ as a prototypical case (Fig. 5) [33,34]. Two Cl substituents are in the ring plane, two above and two below the plane, rendering the substitution pattern of the Ti_3O_3 ring unsymmetrical. The two THF ligands coordinated to each Ti atom are *cis*. In $[\text{Ti}_3\text{O}_3\text{Cl}_8(\text{H}_2\text{O})_4]^{2-}$ [35], two neutral ligands are replaced by additional chloride ligands. In the resulting anionic heterocycle, six Cl are above and below the ring plane and the other two Cl share the in-plane positions with the four aqua ligands. In the analogous compound $\text{Ti}_4\text{O}_4\text{Cl}_8(\text{MeCN})_8$, four Cl^- are in the Ti_4O_4 plane and the other four alternately above and below the ring plane [36].

Each Ti atom in the two compounds $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}'_4(\text{iPrOH})_4$ (L' = 4-bromo-2-(chloromethyl)-6-methoxyphenolate) [37] and $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}''_4$ (L'' = $\text{Et}_2\text{N-C}_2\text{H}_4\text{-NH-CMe-CH-CMe-O}^-$) [38] is substituted by only one chloride each. The second negatively charged group is the oxygen atom of the bi- or tridentate organic ligand. A coordinated alcohol molecule and the OMe group complete the Ti coordination octahedron in $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}'_4(\text{iPrOH})_4$, and the NH and NET_2 groups in $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}''_4$. The chlorine atoms in $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}'_4(\text{iPrOH})_4$ are alternately arranged above and below the Ti_4O_4 ring plane as in the $\text{Ti}_4\text{O}_4\text{Cp}_4\text{X}_4$ derivatives. In $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}''_4$, this position is taken by the oxygen atoms of L'', due to the meridional coordination of L''. The chelating phenolate ligands in $\text{Ti}_4\text{O}_4\text{Cl}_4\text{L}'_4(\text{iPrOH})_4$ are approximately coplanar with the Ti_4O_4 ring.

Another possibility for compensating the positive charges of the TiO^{2+} unit and, all at once, filling all coordination sites of Ti are two anionic bidentate chelating ligands (CL), as in the titanyl β -diketonate in Fig. 1, right. The rings then have the composition $[\text{TiO}(\text{CL})_2]_3$ or 4. For Ti_3O_3 rings, such structures have been found with CL = phenylhydroxamate (ON-CPh-O) [39], diphenylacetamidinate (PhN-CMe-NPh) [40], bis(ferrocenyldiketonate) [41] and N-phenylsalicylideneimine (OC₆H₄CH = NPh) [42] ligands. CL ligands in $[\text{TiO}(\text{CL})_2]_4$ compounds are oxalate ("titanyl oxalate" $[\text{Ti}_4\text{O}_4(\text{C}_2\text{O}_4)_8]^{8-}$, where one oxygen atom per COO group is coordinated [43]), β -diketonates OC(R)-CH-C(R)O (R = *t*Bu [2], Fig. 1, right; Ph/CF₃ [44]), *o*-methoxyphenolate [45], 1-phenyl-3-methyl-4-benzoylpyrazol-5-onate [46] and a combination of 5-sulfosalicylate and 1,10-phenanthroline [47].

A hybrid between the $[\text{TiOL}_2\text{X}_2]_4$ and $[\text{TiO}(\text{CL})_2]_4$ structures is $[\text{Ti}_4\text{O}_4(\text{OMe})_2(\text{acac})_4\text{L}_2]^{2+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), where the titanium atoms are alternately substituted either by two acac ligands or by an OMe and L ligand [48].

A final possibility is the coordination of one dianionic tetradentate ligand, $\text{TiO}(\text{TL})$. *Trans* position of the two coordination sites left blank by the TL ligand results in chain structures, as discussed in Section 2; they must be *cis* for ring formation. An illustrative example is $[\text{Ti}_4\text{O}_4(\text{nitrilotriacetate})_4]^{4-}$ (Fig. 6) [49]. $[\text{Ti}_4\text{O}_4(\text{dpta})_2]_2^{4-}$ (dpta = 2-hydroxypropane-1,3-diamine-N,N,N',N'-tetraacetate) has the same structure, where, however, the dpta ligands additionally connect two Ti_4O_4 rings [50]. Other TL ligands in Ti_4O_4 rings are (pyridin-2-ylmethyl)amino diacetate [51] and cyclohexyldiaminobis(phenolate) [52]. Tetradentate ligands in Ti_3O_3 rings are salen [53,54], Schiff base [55], piperidine [56] or semi-crown derivatives [57] with complex compositions.

A special case is a $\text{Ti}_4\text{O}_4\text{L}_4$ ring with tridentate dianionic ligands [$\text{S-C}_6\text{H}_4\text{-N=CH-(Me-*t*Bu-C}_4\text{H}_4\text{-O)}_2$]²⁻ [58], resulting in the rare case of a structure with 5-coordinate Ti(IV).

3.2. Capped rings

The monodentate anionic substituents X in the approximately planar Ti_3O_3 and Ti_4O_4 ring systems discussed in Section 3.1 are located above or below the ring plane, with more or less parallel Ti-X axes. This allows pairwise replacement of two neighboring X groups by bridging dianionic groups (Section 3.3) or, if all X are located at the same side of the ring, by appropriately charged tri- or tetradentate ligands. The rings are then capped by the multidentate ligands. Retention of the basic ring structure is possible, if the distance between the donor atoms in the multidentate ligands is approximately the same as the X-X distance in Ti_nO_n rings. There is some flexibility, however, because the corner-sharing Ti octahedra can be tilted relative to each other to some degree, *i.e.*, the rings can adopt a chair conformation.

Two cases have been found for Ti_3O_3 rings. The first is that the Ti_3 unit is capped by a single atom, *viz.* derivatives of the type $\text{Ti}_3\text{O}_3(\text{C}_5\text{R}_5)_3(\mu_3\text{-X})$. A prototypical example is $\text{Ti}_3\text{O}_3\text{Cp}^*_3(\mu_3\text{-N})$ shown in Fig. 7, left [59]. Note that the Ti_3O_3 ring is no longer planar, *i.e.*, the Ti octahedra share O...X edges. Other examples for such structures are $\text{Ti}_3\text{O}_3\text{Cp}^*_3(\mu_3\text{-X})$ with X = CH [60] or CMe [61].

An alternative possibility for capping a Ti_3O_3 ring is by means of a three-legged ligand, as the phosphate group in $\text{Ti}_3\text{O}_3(\text{tripod})_3(\text{PO}_4)$ [62] (Fig. 7, right). Since the Kläui tripod ligand, $\text{CpCo}[\text{PO}(\text{OEt})_2]_3$, is

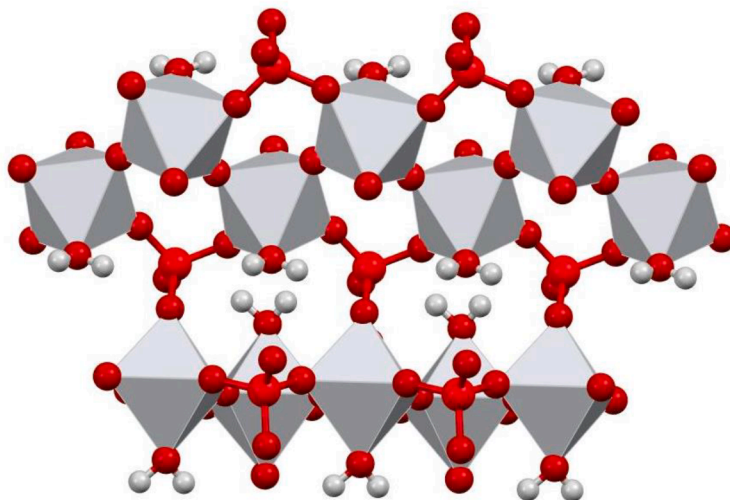


Fig. 2. Section from the crystal structure of $\text{TiO}(\text{SO}_4)\cdot\text{H}_2\text{O}$ (bright red: S).

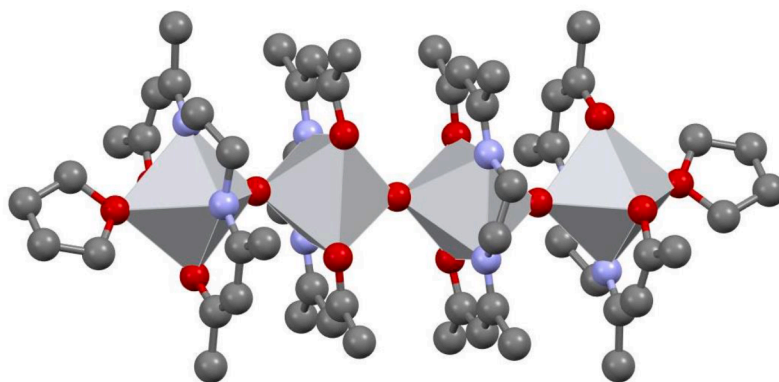


Fig. 3. The molecular structure of $[\text{Ti}_4\text{O}_3(\text{acacen})_4(\text{THF})_2]^{2+}$ (blue: N).

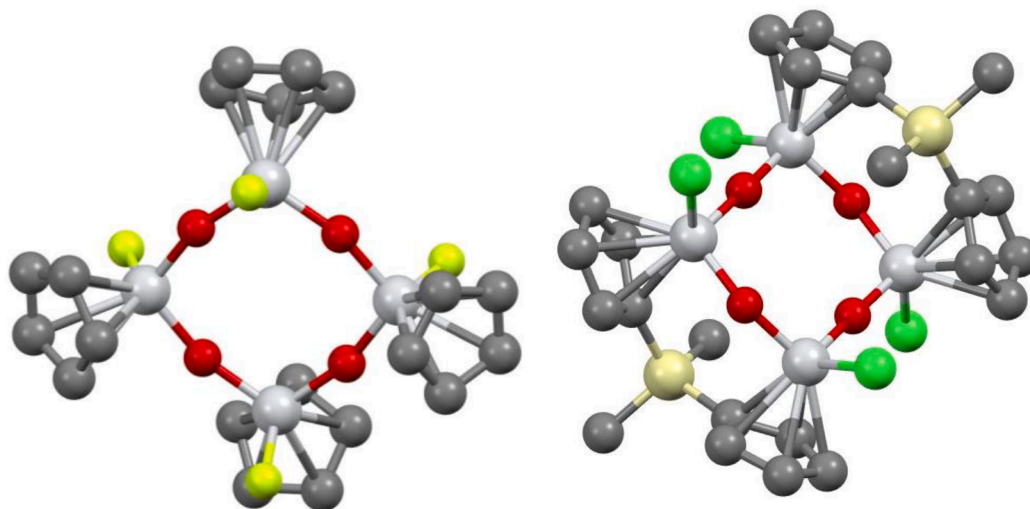


Fig. 4. Left: Structure of $\text{Ti}_4\text{O}_4\text{Cp}^*_4\text{F}_4$ (the CH_3 substituents of the Cp ring were not drawn for clarity; yellow: F). Right: Structure of $\text{Ti}_4\text{O}_4\text{Cl}_4(\text{C}_5\text{H}_4\text{-SiMe}_2\text{-C}_5\text{H}_4)_2$ (green: Cl).

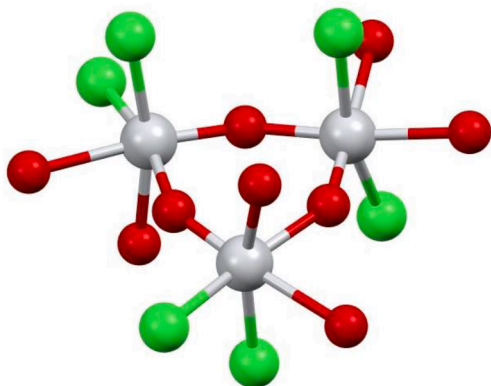


Fig. 5. Structure of $\text{Ti}_3\text{O}_3\text{Cl}_6(\text{THF})_6$ (only the coordinated oxygen atoms [red] of the THF molecules are drawn for clarity).

equivalent to an $\eta^5\text{-C}_5\text{R}_5^-$ ligand from a coordination point of view, $\text{Ti}_3\text{O}_3\text{Cp}^*_3(\text{O}_3\text{SiR})$ has the same structure, with a RSiO_3 group ($\text{R} = t\text{Bu}$ [63], $\text{N}(\text{SiMe}_3)\text{-C}_6\text{H}_3i\text{Pr}_2$ [64]) symmetrically capping the $\text{Ti}_3\text{O}_3\text{Cp}^*_3$ ring system. The Ti_3O_3 ring in both compounds is slightly puckered to adjust to the three-legged capping ligand. Tridentate ligands unsymmetrically capping $\text{Ti}_3\text{O}_3\text{Cp}^*_3$ ring systems are $[\text{MesN-C-CMe-C-NMes}]^{3-}$ (each NC unit is coordinated to one Ti, and the central allyl

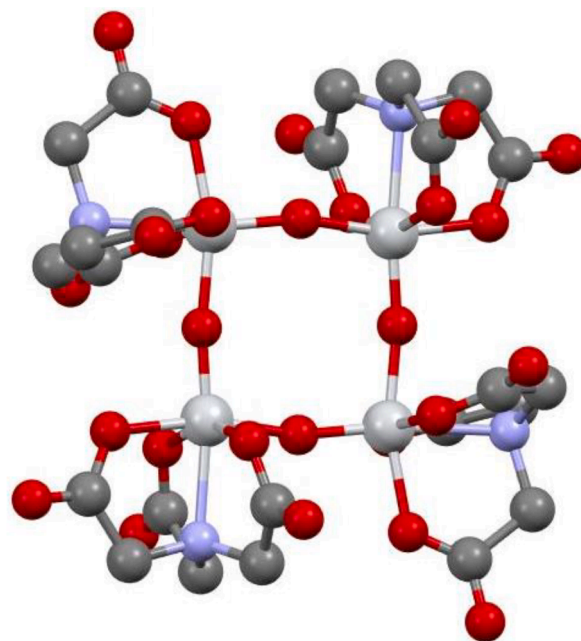


Fig. 6. The molecular structure of $[\text{Ti}_4\text{O}_4(\text{nitrilotriacetate})_4]^{4-}$.

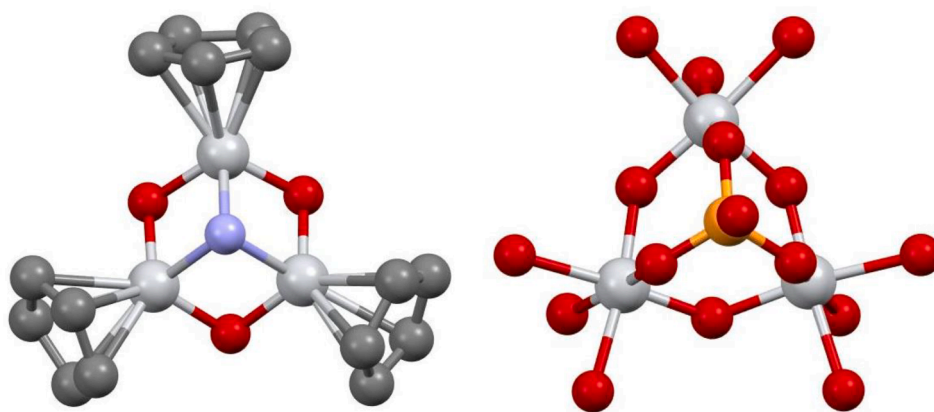


Fig. 7. Capped Ti_3O_3 rings. Left: $\text{Ti}_3\text{O}_3\text{Cp}^*_3(\mu_3\text{-N})^{3-}$ (the CH_3 substituents of the Cp^* ring are not drawn for clarity). Right: $\text{Ti}_3\text{O}_3(\text{tripod})_3(\text{PO}_4)$ (only the three coordinating oxygen atoms of the tripod ligands are drawn) (orange red: P).

unit coordinated to the 3rd) and $[\text{C}=\text{CMe-NMe}_3]^{3-}$ (C is bridging two Ti atoms and N coordinated to the third) [65].

Analogous capping of a Ti_4O_4 ring requires more extended ligands. Deprotonation of *t*Bu-calix[4]arene provides a suitable tetra-anionic and tetradentate ligand, where all phenoxy groups of each cone-shaped ligand coordinate to the same titanium atom. Since the calixarene group in $\text{Ti}_4\text{O}_4\text{Cp}_4(\text{calix}[4])$ [66] completely caps one side of the Ti_4O_4 ring, all Cp ligands must be on the other side (*i.e.*, the conformation of the $\text{Ti}_4\text{O}_4\text{Cp}_4$ unit is inherently different to that in the $\text{Ti}_4\text{O}_4\text{Cp}_4\text{X}_4$ derivatives, where the Cp ligands are alternately above and below the ring plane).

3.3. Rings with bridging ligands

The largest ring structures of corner-sharing $[\text{TiO}_6]$ octahedra with bridging ligands (BL) are the titanyl carboxylates $\text{Ti}_8\text{O}_8(\text{O}_2\text{CR})_{16}$ ($=[\text{TiO}(\text{O}_2\text{CR})_2]_8$) (R = *t*Bu [67,68], CH_2tBu [69], $\text{CMe}=\text{CH}_2$ [70,71], Ph [68,72], C_6F_5 [73], NEt_2 [74]) (Fig. 8). Approximately planar rings of eight corner-sharing $[\text{TiO}_6]$ octahedra are formed, where each titanium is linked to both neighboring $\text{TiO}(\text{O}_2\text{CR}')_2$ units by means of a $\mu_2\text{-O}$ and two carboxylate bridges each. Each titanium atom is thus coordinated by

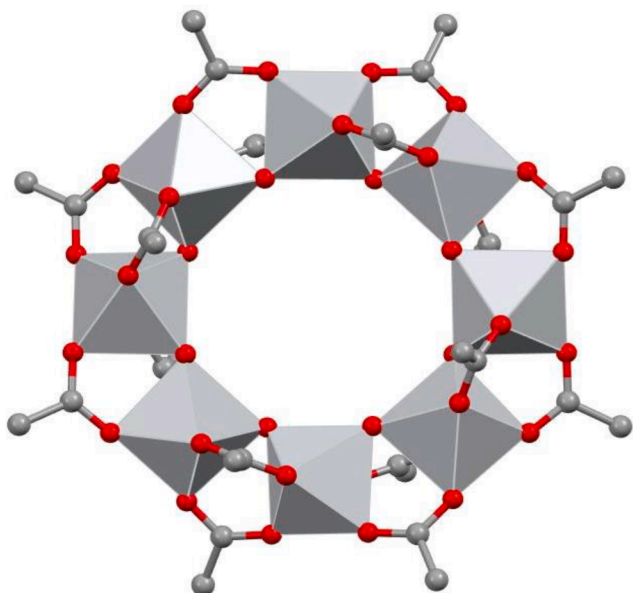


Fig. 8. Polyhedral representation of the structures of $\text{Ti}_8\text{O}_8(\text{O}_2\text{CR}')_{16}$ (only the $\alpha\text{-C}$ atoms of the carboxylate groups are drawn for clarity).

two $\mu_2\text{-O}$ in *cis* position and four carboxylate oxygen atoms. Eight carboxylate ligands are approximately coplanar with the Ti_8O_8 ring, and the other eight alternately above and below the Ti_8O_8 plane. $[\text{Ti}_8\text{O}_8(\text{SO}_4)_{16}]^{8-}$ [72,75,76] has the same ring structure, with the sulfate ions in place of the carboxylate groups. In undistorted rings of eight $[\text{TiO}_6]$ units, the $\text{O}\cdots\text{O}$ distance in the ring plane between two neighboring octahedra is in the range 220–230 pm. This distance would be larger in rings with a smaller number of $[\text{TiO}_6]$ units and can no longer be spanned by carboxylate ligands. The geometry of the BL thus determines the ring size.

Cyclic structures may also be formed with one di-anionic tetradentate ligand (L) instead of two bidentate, mono-anionic ligands, *i.e.*, if the composition is $[\text{TiOL}]_n$. This is the case for the cyclopentadienylsilanolate ligand in $\text{Ti}_6\text{O}_6(\text{C}_5\text{Me}_4\text{SiMe}_2\text{O})_6$ [12] forming a ring of six Ti polyhedra. The C_5R_5 moiety coordinates to one Ti atom and the silanolate oxygen atom to the neighboring titanium atom round the ring. Each titanium atom is thus coordinated by a Cp ring and three oxygen atoms (two $\mu_2\text{-O}$ and the silanolate oxygen). In $\text{Ti}_6\text{O}_6[(\text{OCH}_2\text{CH}_2\text{NMe})_2]_6$, coordination of the dianion of *N*-methyldiethanolamine results in a similar ring system with C_6 -symmetry. The diethoxomethylamino ligand occupies four coordination sites because one oxygen is chelating-bridging. Two neighboring titanium atoms are thus bridged by a $\mu_2\text{-O}$ and one oxygen atom of the diethoxomethylamino group [77]. A Ti_6O_6 heterocycle is also the central structural unit in $[\text{Ti}_6\text{O}_6\{\text{SiW}_{10}\text{O}_{34}(\text{OH})_3\}_3]^{9-}$, where two titanium atoms are pairwise part of each polyoxometallate unit [78].

Bridging of an edge by typical bidentate ligands is no longer possible in rings of four titanium polyhedra (Ti_4O_4) for geometric reasons, the BL are instead positioned perpendicular to the ring plane. The most symmetrical case of BL-substituted Ti_4O_4 rings is that every Ti-O-Ti is bridged by a bidentate dianionic ligand. Chain structures of titanyl sulfate, $\text{TiO}(\text{SO}_4)$ were discussed in Section 2; the structure of $\text{Ti}_4\text{O}_4(\text{SO}_4)_4(\text{H}_2\text{O})_8$ [35] is a cyclic variety, with the bridging SO_4^{2-} groups alternately above and below the plane of the puckered Ti_4O_4 ring (Fig. 9). $[\text{Ti}_4\text{O}_4\text{Cl}_2(\text{SO}_4)_4(\text{H}_2\text{O})_6]^{2-}$ has the same structure, with two aqua ligands replaced by Cl^- [35]. The same substitution pattern was found in $\text{Ti}_4\text{O}_4(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{O})_4$ [79], with the cyclopentadienylsilanolate as the dianionic bridging ligand.

A Ti_4O_4 ring can also be identified in the structure of $[\text{P}_2\text{W}_{20}\text{Ti}_4\text{O}_{78}]^{10-}$ where two Keggin-type heteropolyanions $[\text{PW}_{10}\text{Ti}_2\text{O}_{39}]^{5-}$ are dimerized through two Ti-O-Ti units [80]. Two Ti_4O_4 rings as well as two additional Ti-O-Ti units are also part of the complex $[(\text{K}_2\text{Na})@\text{Ti}_{12}\text{O}_{10}(\text{GeW}_9\text{O}_{36})_4]^{25-}$ structure [81].

In the $\text{Ti}_3\text{O}_3(\text{C}_5\text{R}_5)_3\text{X}_3$ derivatives discussed in Section 3.1, two groups X are above the Ti_3O_3 ring plane, and the third below. The overall geometry of the compounds, esp. the ring conformation, thus should essentially be the same, if the two groups X located above the ring plane

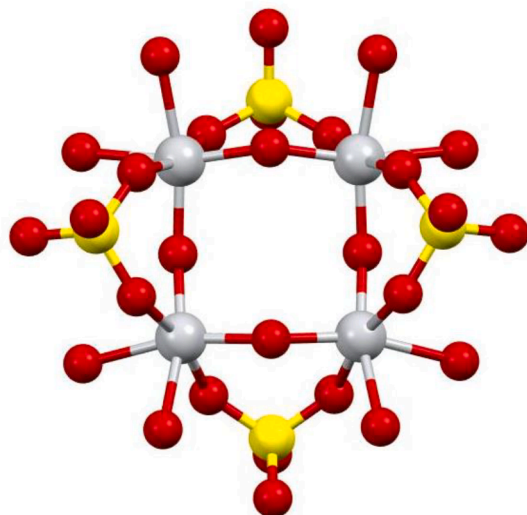


Fig. 9. Molecular structure of $\text{Ti}_4\text{O}_4(\text{SO}_4)_4(\text{H}_2\text{O})_8$ (yellow: S).

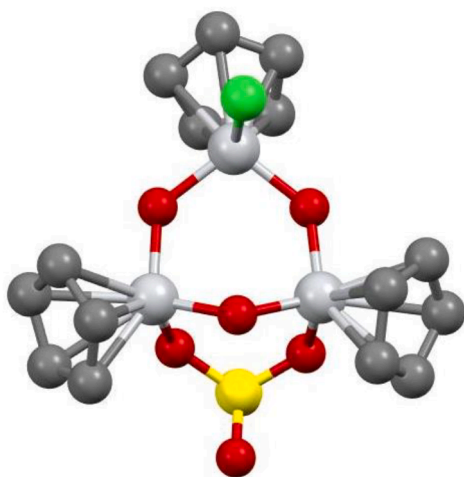


Fig. 10. Molecular structure of $\text{Ti}_3\text{O}_3\text{Cp}^*_3\text{Cl}(\text{SO}_4)$ (the CH_3 substituents of the Cp ring were not drawn for clarity) (yellow: S; green: Cl).

are replaced by a bridging dianionic ligand, as in $\text{Ti}_3\text{O}_3\text{Cp}^*_3\text{Cl}(\text{SO}_4)$ as an example (Fig. 10) [82]. In the related compound $[\text{Ti}_3\text{O}_3\text{Cp}^*_3\text{Cl}(\text{P}_3\text{O}_9)]^-$, a bridging trimetaphosphate anion is in place of the sulfate anion [83]. Other structurally characterized compounds of the composition $\text{Ti}_3\text{O}_3\text{Cp}^*_3\text{X}(\text{BL})$ are:

- BL = CH_2 , X = OCPh_2R (R = Me, Ph) [84],
- BL = CHMe , X = OiPr [84], OtBu [84,85], OSiPr_3 [63], NPh_2 [86],
- BL = $\text{O}_2\text{SiRR}'$ (R = OH, R' = $t\text{Bu}$; R, R' = $i\text{Pr}$), X = Et [63],
- BL = NPh , X = $\text{CH}=\text{CHPh}$ [87],
- BL = $\text{Xyl-N-C}=\text{C}=\text{N-Xyl}$, X = $\text{N}=\text{C}=\text{N-Xyl}$ (Xyl = $\text{C}_6\text{H}_3\text{Me}_2$) [88],
- BL = Xyl-N-C-N-Xyl , X = CN [88],

as well as $\text{Ti}_3\text{O}_3(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_3(\text{OMe})(\text{OC}_3\text{H}_4)$ (C_3H_4 = cyclobutenyl) [89].

4. Conclusions

Bridging the metal atoms in polymetallic titanium oxo compounds by $\mu_3\text{-O}$ or combinations of $\mu_2\text{-O}$ and $\mu_3\text{-O}$, sometimes even $\mu_4\text{-O}$, results in clusters in which all or part of the titanium polyhedra share edges.

Subject of this review article are compounds with only $\mu_2\text{-O}$ and a O:Ti ratio of 1. The Ti polyhedra in such “titanyl” compounds exclusively share corners, resulting in the formation of chains (or fragments thereof) or rings. The stabilizing ligands therefore must not only compensate the two positive charges of each TiO unit but also fill the four coordination sites per Ti atom left vacant by the $\mu_2\text{-O}$ to achieve an octahedral coordination of the titanium atoms.

The most obvious case is tetradentate, dianionic ligands, with which formation of clusters with $\mu_3\text{-O}$ is not possible. Depending on the ligand geometry, the unoccupied coordination sites can be *cis* or *trans*, resulting in cyclic or chain-like structures, respectively. However, such ligands, with a suitable arrangement of the four donor atoms for coordination to Ti(IV), are rare.

In compounds of the composition $[\text{TiO}(\text{BL}/\text{CL})_2]_n$ the oxygen atoms also cannot become μ_3 . Rings with or without bridged edges are therefore formed, depending on the geometry and adaptability of the (mono-anionic) bidentate ligands. Typical examples are, as discussed before, $[\text{TiO}(\beta\text{-diketonate})_2]_4$ (Fig. 1, right) and $[\text{TiO}(\text{carboxylate})_2]_4$ (Fig. 8); in Ti(IV) compounds, β -diketonates are almost always chelating and carboxylates bridging. Chain structures would also be possible with mono-anionic bidentate ligands, but crystalline compounds have not been obtained until present (only with di-anionic BL, see Section 2).

A frequent substitution pattern of titanyl compounds is one negatively charged tridentate ligand, such as C_5R_5 derivatives, plus one mono-anionic, monodentate ligand X. Again, formation of $\mu_3\text{-O}$ is not possible with this combination of ligands. Two neighboring groups X may be replaced by a single di-anionic bridging ligand, such as SO_4^{2-} , or three neighboring groups X by a tri-anionic capping ligand, such as PO_4^{3-} or RSiO_3^{3-} .

Only few examples are known, where two monodentate anionic ligands X are combined with two neutral ligands L, *i.e.*, compounds $[\text{Ti}(\mu_2\text{-O})\text{X}_2\text{L}_2]_n$. Instead of coordinating two neutral ligands, conversion of a $\mu_2\text{-O}$ into a $\mu_3\text{-O}$, is conceivable. However, compounds of the composition $[\text{Ti}(\mu_3\text{-O})\text{X}_2\text{L}]_n$ were not observed so far. The conclusion that coordination of a second “external” ligand L was more favorable than converting a $\mu_2\text{-O}$ into a $\mu_3\text{-O}$ is nevertheless premature. If the combination of an X and a L ligand is replaced by a mono-anionic bidentate ligand (BL or CL), cyclic compounds of the composition $[\text{Ti}(\mu_2\text{-O})(\text{BL}/\text{CL})\text{XL}]_n$ are not formed, but instead $[\text{Ti}(\mu_3\text{-O})(\text{BL}/\text{CL})\text{X}]_n$ clusters. For example, a great number of carboxylate-substituted titanium oxo clusters $[\text{Ti}(\mu_3\text{-O})(\text{OOCR}')(\text{OR})]_4$ or $_6$ is known, with carboxylates as bridging and alkoxides as terminal ligands [90]. Another example is $\text{Ti}_6\text{O}_6(\text{oximate})_6(\text{OR})_6$ [91].

In conclusion, in addition to other parameters, the ligand set has a great influence on the composition and structure of titanium oxo compounds.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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