

Active peroxy titanium complexes: syntheses, characterization and their potential in the photooxidation of 2-propanol†

Markus Rohe and Klaus Merz*

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Two novel peroxy titanium complexes, $\text{Li}_2(\text{NH}_4)_4[\text{Ti}_2(\text{O}_2)_2\text{(cit)(Hcit)}]_2 \cdot 5\text{H}_2\text{O}$ and $\text{Zn}(\text{NH}_4)_4[\text{Ti}_4(\text{O}_2)_4\text{(Hcit)}_2\text{(cit)}_2] \cdot 12\text{H}_2\text{O}$ (cit = citrate), show encouraging results in the photochemical oxidation of 2-propanol.

Interest in the use of heterogeneous photocatalysis with titania to degrade a variety of environmental pollutants is intense and increasing.^{1–3} Active species are generated at the TiO_2 surface under UV irradiation, and various substances in solution are decomposed, mainly *via* oxidation reactions.⁴ Molecular-adsorbed oxygen and the radicals OH^{\bullet} and $\text{O}_2^{\bullet-}$ have been observed during the photoadsorption of oxygen on the anatase modification of TiO_2 .⁵ The reduction of molecular oxygen is an essential part of the photocatalytic processes taking place on TiO_2 particles. On a molecular basis, however, little is known about the mechanism that takes place on the surface of supported catalysts. In the case of the photochemical oxidation of 2-propanol, products like acetone, CO_2 or propene are reported in different yields, depending on the modified titania.⁶ In many cases, these modified TiO_2 catalysts are produced by the hydrolysis of a TiO_2 -precursor by additional treatment during the one-pot production, for example with metal salts, to reduce the band gap energy of the resulting photocatalyst. The result of such syntheses are inhomogeneous powders of titania incorporated with side products of the hydrolysis procedure.⁷

To investigate the role of reduced oxygen in the photochemical oxidation of 2-propanol, we transfer the situation from the catalyst surface on a molecular level. By following a model catalyst approach, we have synthesized well-defined titanium oxo-complexes modified by peroxy units and additional metal ions.

In this work, we present two well-defined peroxy-rich molecular TiO complexes, $\text{Li}_2(\text{NH}_4)_4[\text{Ti}_2(\text{O}_2)_2\text{(cit)(Hcit)}]_2 \cdot 5\text{H}_2\text{O}$ (**1**) and $\text{Zn}(\text{NH}_4)_4[\text{Ti}_4(\text{O}_2)_4\text{(Hcit)}_2\text{(cit)}_2] \cdot 12\text{H}_2\text{O}$ (**2**) (cit = citrate), and show their activity in the oxidation of 2-propanol under UV light.

Water soluble peroxy titanium complexes are accessible by the hydrolysis of TiCl_4 in the presence of H_2O_2 , NH_3 and citric

acid. The incorporation of metal centres in these complexes can be achieved by treatment with appropriate metal salts. Thus, the addition of lithium carbonate during the hydrolysis of TiCl_4 leads to the novel lithium peroxy titanium complex $\text{Li}_2(\text{NH}_4)_4[\text{Ti}_2(\text{O}_2)_2\text{(cit)(Hcit)}]_2 \cdot 5\text{H}_2\text{O}$ (**1**) with two independent discrete $[\text{Ti}_2(\text{O}_2)_2\text{(cit)(Hcit)}]^{6-}$ anions, which lie about independent inversion centers; one of these anions is shown in Fig. 1.†

In the unit cell of **1**, the complex anions are isolated from each other and do not form polymer chains. The peroxy titanium complex anion consists of two binuclear fragments interlinked through the bridging carboxylate group of one citrate ligand.

The O–O (1.464(7)–1.475(7) Å) and Ti–O (1.864(5)–2.136(5) Å) bond lengths are comparable with metal-free peroxy titanium complexes.⁸ In **1**, the counterions ammonium and lithium, as well as the lattice water, are situated in the channels of a three dimensional network. The ⁷Li MAS-NMR spectrum of **1** shows a signal at 1.1 ppm that is consistent with the hydrated lithium cations described in the literature.⁹

The determined structure of this compound is in harmony with the corresponding Raman spectrum. Sharp bands at 894 cm^{-1} for $\nu_{\text{O-O}}$ and 636 cm^{-1} for $\nu_{\text{Ti-O}_2}$ are assigned to non-bridging η^2 -peroxy ligands.¹⁰ The zinc peroxy titanium complex $\text{Zn}(\text{NH}_4)_4[\text{Ti}_4(\text{O}_2)_4\text{(Hcit)}_2\text{(cit)}_2] \cdot 12\text{H}_2\text{O}$ (**2**) was obtained by the addition of zinc carbonate during the

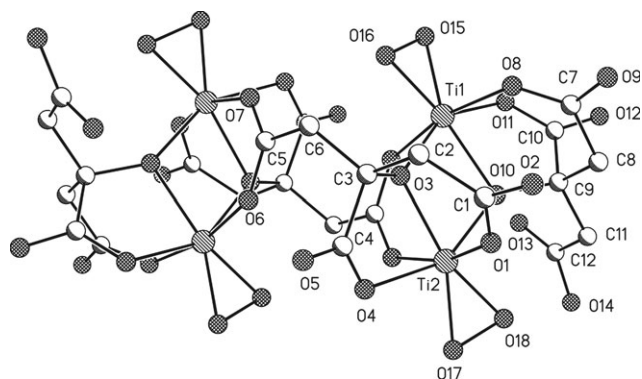


Fig. 1 Molecular structure of $\text{Li}_2(\text{NH}_4)_4[\text{Ti}_2(\text{O}_2)_2\text{(cit)(Hcit)}]_2 \cdot 5\text{H}_2\text{O}$ (**1**). Hydrogen, water molecules and NH_4 cations are omitted for clarity. Selected distances (Å) and angles ($^\circ$): Ti(1)–O(16) 1.855(4), Ti(1)–O(15) 1.859(4), Ti(1)–O(6) 2.014(4), Ti(1)–O(3) 2.016(4), Ti(1)–O(8) 2.019(4), Ti(1)–O(10) 2.057(4), Ti(1)–O(11) 2.092(4), O(17)–O(18) 1.448(7), O(15)–O(16) 1.450(6); O(16)–Ti(1)–O(15) 45.96(18), O(6)–Ti(1)–O(3) 83.08(16), O(16)–Ti(1)–O(8) 93.03(18), O(15)–Ti(1)–O(8) 92.54(18), O(6)–Ti(1)–O(8) 166.90(16), O(3)–Ti(1)–O(8) 94.67(17).

Anorganische Chemie I, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany. E-mail: Klaus.Merz@rub.de; Fax: +49 234 32 14378; Tel: +49 234 32 24187

† Electronic supplementary information (ESI) available: Molecular structure and selected distances (Å) and angles ($^\circ$) of **2** and **3**; formation of acetone during the irradiation of 2-propanol with **2**; formation of CO_2 during the irradiation of **1**. See DOI: 10.1039/b716199a

hydrolysis of TiCl_4 . In contrast to the citrato peroxy precursor of BaTiO_5 ,¹¹ the metal cation of **2**, which lies about an inversion centre, does not coordinate and block any active peroxy groups (Fig. S1, ESI†).‡ The hydrated cations in the crystal packing of **2** are placed in the channels between the chains, meaning that all the peroxy units in **2** are available for oxidation processes. The Raman spectrum shows bands of $\nu_{\text{O-O}}$ at 894 cm^{-1} and $\nu_{\text{Ti-O}}$ at 636 cm^{-1} , which are in the same region as the peroxy groups in **1**.

To investigate the influence of the peroxy groups and the promoting effect of lithium ions on the photochemical activity of titanium complexes, we synthesized the peroxy-free complex $\text{Li}_2\text{Ti}(\text{H}_2\text{cit})_3 \cdot 4\text{H}_2\text{O}$ (**3**). The hydrolysis of TiCl_4 in the presence of lithium hydroxide leads to the formation of complex **3** (Fig. S2, ESI†). The X-ray analysis of the complex shows that each Ti^{4+} atom is coordinated by three H_2cit ligands.‡ Two H_2cit ligands of the $\text{Ti}[(\text{H}_2\text{cit})_3]^{2-}$ anions are coordinated to a bridging lithium atom, forming polymeric chains. The Ti–O bond lengths and angles are in same region as those observed for citratotitanates.¹² The tetrahedral geometry of the bridging lithium atom is completed by two water molecules.

In order to study the photochemical activity of the metal peroxy titanium complexes **1** and **2**, and the peroxy free complex **3**, samples of a 2-propanol solution were irradiated with UV light in the presence of the titanium complexes. The oxidation of 2-propanol was monitored by ^1H and ^{13}C NMR spectroscopy.

Peroxy titanium complexes **1** and **2** showed a significant activity in the photochemical oxidation of 2-propanol at room temperature.

As an example of the activity of the peroxy titanium complexes, the variation in conversion yield of 2-propanol to acetone in the presence of **1** with elapsed time is shown in Fig. 2. Similar results were obtained using the zinc peroxy titanium complex **2** (Fig. S3, ESI†).

The NMR spectra of the samples with complexes **1** and **2** indicate that the peroxy complexes oxidized 2-propanol to acetone without any oxidation side products being detectable by NMR.

It is known that acetone is finally oxidized to CO_2 in the presence of TiO_2 under aerobic conditions if the reaction is allowed to continue for a long period of time.¹³ In such systems, the photochemical oxidation of 2-propanol proceeds through chemisorbed species, leading to a fast and direct oxidation to CO_2 .¹⁴ In contrast to these studies on the catalyst surface of TiO_2 , the anaerobic photochemical reaction of 2-propanol with **1** shows acetone to be the main product after a long period of time, with only a small amount finally being oxidized further to CO_2 . The additional monitoring of the reaction with a CO_2 IR detector showed the formation of CO_2 , depending on irradiation time. During the irradiation, an amount of 2.1% CO_2 (0.021 mmol) was formed (Fig. 2). This reaction runs almost parallel to the formation of acetone. Considering the small amount of CO_2 from the decomposition of **1** (Fig. S4, ESI†), the total yield of the conversion of 2-propanol to acetone is 40%, from which a small amount is further oxidized to the final oxidation product, CO_2 .

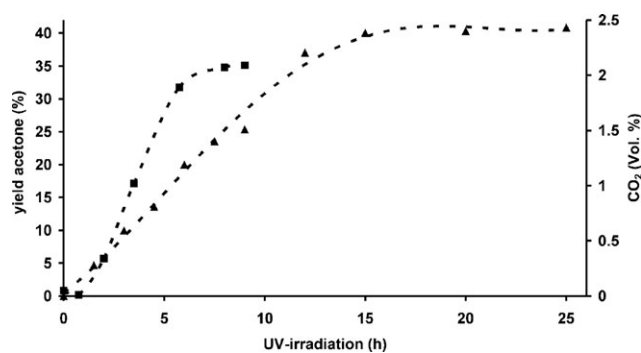


Fig. 2 Acetone (\blacktriangle) and CO_2 (\blacksquare) formation during the photochemical oxidation of 2-propanol in the presence of the lithium peroxy titanium complex **1**.

The Raman and IR spectra show the degradation of the bands for peroxy units and formation of bands for water units, depending to the irradiation time. Simultaneously, we detected the formation of superoxide as a further reduced oxygen species by using Nitroblue tetrazolium (NBT).

The presence of the reduced oxygen species in the titanium complex is absolutely necessary. A comparable irradiation experiment with 2-propanol solution in the presence of the peroxy-free complex **3** did not show any conversion of the alcohol.

We have shown that the controlled anaerobic photochemical oxidation of 2-propanol using novel metal peroxy titanium complexes **1** and **2** stopped with the formation of acetone. These complexes seem to be molecular models for investigating the role of reduced oxygen species in the conversion of alcohols under UV light irradiation. In contrast to the insufficient conversion of 2-propanol under thermal conditions, complexes **1** and **2** show a significant activity under UV light irradiation. The lithium-containing peroxy titanium complex **1** converts 2-propanol to acetone as the main product, and only of a small amount of CO_2 is formed as the side product. On the basis of these metal peroxy titanium complexes, further investigations using additional spectroscopic methods will give deeper insights into the photochemical oxidation processes of alcohols.

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UV irradiation: Photocatalytic experiments were carried out in a quartz glass NMR tube (5 mm) containing **1** (0.18 mmol), **2** (0.05 mmol), 2-propanol (45 μl , 0.59 mmol) and deuterium oxide (800 μl). To dissolve the complex in D_2O before irradiation, it was necessary to heat the mixture to $90\text{ }^\circ\text{C}$. The solution was then irradiated with a 150 W medium pressure mercury lamp (Heraeus, TQ 150). The lamp generated light in the 300 to 500 nm range, with a maximum wavelength intensity at 366 nm. The distance between the NMR tube and the Hg lamp was 5 cm in a water bath in all cases.

CO_2 detection: The CO_2 developed during UV irradiation was analysed by an IR detector from Leybold-Heraeus (Binos 1.2). Before quantitative analyses, the detector was calibrated with argon and a mixture of 4% CO_2 in air.

Li₂(NH₄)₄[Ti₂(O₂)₂(cit)(Hcit)]₂·5H₂O (1) and Zn(NH₄)₄[Ti₄(O₂)₄(Hcit)₂(cit)]₂·12H₂O (2): Titanium(IV) chloride (2.2 ml, 20 mmol) was added dropwise to 30 ml of distilled water, cooled in an ice bath. After hydrolysis, hydrogen peroxide (20 ml, 0.65 mol) and citric acid monohydrate (4.2 g, 20 mmol) were added. After being allowed to warm to room temperature, the solution was treated with 10 mmol of metal carbonate. Afterwards, the pH value was adjusted to 2 by the addition of ammonia (33%). The desired product crystallized in the form of red-orange needles after several days at 4 °C from a water/THF mixture. Yield: **1** 6.1 g (86.4%); **2** 13.5 g (94.6%).

1: mp > 200 °C (dec.); ¹H NMR (250 MHz, D₂O): δ 2.3–3.6 (CH₂); ¹³C MAS NMR (400 MHz): δ 183.4, 180.1 (cit, COO), 177.6 (Hcit, COO), 88.7 (cit, C–O), 83.2 (Hcit, C–O), 45.8 (cit, CH₂) and 41.8 (Hcit, CH₂); ⁷Li NMR (250 MHz, D₂O): δ –0.15; ⁷Li MAS NMR (400 MHz): δ 1.1; Raman (cm⁻¹): 2933 (ν_{C–H}), 894 (ν_{O–O}) and 636 (ν_{Ti–O₂}); C₂₄H₄₄Li₂N₄O₄₁Ti₄ (1250.0) requires C, 23.1; H, 3.6; N, 4.5; Li, 1.1; found C, 23.6; H, 3.5; N, 4.3; Li, 1.0%.

2: mp. > 200 °C (dec.); ¹H NMR (250 MHz, D₂O): δ 2.3–3.6 (CH₂); ¹³C MAS NMR (400 MHz): δ 186.2, 185 (cit, COO), 180.6, 179.3 (Hcit, COO), 87.8 (cit, C–O), 86.1 (Hcit, C–O), 45.0 (cit, CH₂) and 42.8 (Hcit, CH₂); Raman (cm⁻¹): 2933 (ν_{C–H}), 894 (ν_{O–O}) and 634 (ν_{Ti–O₂}). ZnTi₄N₄C₂₄H₅₈O₄₈ (1427.6) requires C, 20.2; H, 4.1; N, 3.9; found C, 20.0; H, 3.8; N, 3.8%.

Li₂Ti(H₂cit)₃·4H₂O (3): Titanium(IV)chloride (5.5 ml, 50 mmol) was added to 100 ml of distilled water placed in an ice bath. At room temperature, the solution was treated with citric acid monohydrate (28 g, 133 mmol) and the pH value adjusted to 2 with lithium hydroxide. Colourless crystals were isolated at room temperature after several days. Yield: 33 g (93.7%).

¹H NMR (250 MHz, D₂O): δ 2.7, 2.5 and 2.4; ¹³C NMR (250 MHz, D₂O): δ 179.8, 176.5 (H₂cit, COO), 76.0 (H₂cit, C–O) and 45.5 (H₂cit, CH₂); ⁷Li NMR (250 MHz, D₂O): δ –0.52; ⁷Li MAS NMR (400 MHz): δ 1.6; Li₂TiC₁₈H₂₆O₂₅ (704.2) requires C, 30.7; H, 3.7; Li, 2.0; found: C, 29.9; H, 3.7; Li, 2.4%.

Notes and references

‡ *Crystallographic data:* **1:** C₂₄H₁₆Li₂N₄O₄₁Ti₄, *M* = 1221.89, triclinic, space group *P*-1, *a* = 13.123(6), *b* = 15.486(7), *c* = 15.608(8) Å, *α* = 84.250(12), *β* = 82.297(11), *γ* = 66.054(11)°, *V* = 2869(2) Å³, *Z* = 2, 2θ_{max} = 50.00°, 13687 measured reflections, 9616 independent reflections, 676 parameters, *μ* = 0.637 mm⁻¹, *R*1 = 0.0770 for 5838

observed reflections (*I* > 2σ(*I*)), *wR*2 = 0.2023 for all reflections. CCDC 664369.

2: C₂₄H₁₆N₄O₄₈Ti₄Zn, *M* = 1385.38 triclinic, space group *P*-1, *a* = 10.108(4), *b* = 10.851(5), *c* = 12.690(5) Å, *α* = 65.087(8), *β* = 87.377(10), *γ* = 79.355(9)°, *V* = 1239.8(9) Å³, *Z* = 1, 2θ_{max} = 50.18°, 5674 measured reflections, 4077 independent reflections, 368 parameters, *μ* = 1.228 mm⁻¹, *R*1 = 0.0639 for 3264 observed reflections (*I* > 2σ(*I*)), *wR*2 = 0.1946 for all reflections. CCDC 664367.

3: C₁₈H₂₃Li₂O₂₅Ti, *M* = 701.14, monoclinic, space group *P*2₁/*c*, *a* = 13.731(7), *b* = 14.940(9), *c* = 14.911(9) Å, *β* = 115.474(14)°, *V* = 2762(3) Å³, *Z* = 4, 2θ_{max} = 50.20°, 15219 measured reflections, 4836 independent reflections, 460 parameters, *μ* = 0.420 mm⁻¹, *R*1 = 0.0521 for 3126 observed reflections (*I* > 2σ(*I*)), *wR*2 = 0.1395 for all reflections. CCDC 664368.

Bruker-AXS-SMART 1000 CCD. Structures solved by direct methods (SHELXS-97) and refined against *F*² with all measured reflections (SHELXL-97,¹⁵ Platon/Squeeze¹⁶). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716199a

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