

The first structural examples of tricitratotitanate $[\text{Ti}(\text{H}_2\text{cit})_3]^{2-}$ dianions †

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The crystal structures of the mixed-cation compounds $\text{KMg}_{1/2}[\text{Ti}(\text{H}_2\text{cit})_3] \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)\text{Mg}_{1/2}[\text{Ti}(\text{H}_2\text{cit})_3] \cdot 6\text{H}_2\text{O}$ (H_4cit = citric acid), which were synthesized by a modified Pechini process, feature three bidentate $[(\text{HO}_2\text{CCH}_2)_2\text{C}(\text{CO}_2^-)\text{O}^-]$ citrato groups that chelate to the titanium atom through their negatively-charged α -alkoxyl and α -carboxyl oxygen atoms; the other two β -carboxylic acid groups are free.

The Pechini method for the preparation of ceramic oxides such as the multicomponent MTiO_3 ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$) and $\text{Ln}_2\text{Ti}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nb}, \text{Y}$) oxides in large quantities centers on the use of a mixed citrate precursor that yields the product in an extremely pure form after calcination,^{1,2} and of particular interest are the composition and the structure of the precursor citrato titanate anion. As the crystal structure of the anion has not been reported, the bonding of the citrato group to the titanium atom in citrato titanates has been deduced from spectroscopic measurements.^{3–8} However, the formulation has not even been satisfactorily resolved. A recent proposed model suggests that the titanium atom is tris-chelated by the citrato units through the α -alkoxyl and β -carboxylic acid oxygen atoms; and the α -carboxyl groups remain free.⁷ Another model requires the involvement of all three α -alkoxyl groups, one α -carboxyl group, and two β -carboxylic acid groups.⁸

In our hands, a modification of the Pechini method by replacement of cationic entities afforded four tricitratotitanates $\text{MM}'[\text{Ti}(\text{H}_2\text{cit})_3] \cdot n\text{H}_2\text{O}$ (**1** $M = M' = \text{K}$, $n = 4$; **2** $M = \text{K}$, $M' = \text{Mg}_{1/2}$, $n = 6$; **3** $M = \text{NH}_4$, $M' = \text{Mg}_{1/2}$, $n = 6$; and **4** $\text{MM}' = \text{Ba}$, $n = 4$) in fairly good yields. ‡ Attempts to procure a crystalline specimen of barium tricitratotitanate **4** (BTC) proved unsuccessful. The recrystallization of **2** and **3** from water resulted in the isolation of needle-shaped crystals, which upon crystal-structure analysis proved to consist of the yet-undocumented $[\text{Ti}(\text{H}_2\text{cit})_3]^{2-}$ entity, which has three-fold symmetry. § Fig. 1 and Fig. 2 are the ORTEP plots of the dianions of **2** and **3**.

The solution ^{13}C -NMR spectra show the existence of an equilibrium between the tricitratotitanate and (organic) citrato anions. The downfield shifts (*ca.* 18 ppm for carbon atom bearing the α -alkoxyl oxygen atom and *ca.* 11 ppm for the α -carboxyl carbon atom) relative to the monopotassium salt of citric acid corroborate the coordination mode of the α -alkoxyl and α -carboxyl groups. In contrast, the two β -carboxylic acid groups show only a small shift (*ca.* 3 ppm), which argues against the coordination of two β -carboxylic acid groups.^{7,8}

The crystal structures of both **2** and **3** comprise a hexa-aquamagnesium cation, a potassium or ammonium cation, lattice water molecules and the tricitratotitanate anion. The titanium atom is six-coordinated in an octahedral environment; this geometry differs from that found for titanium in

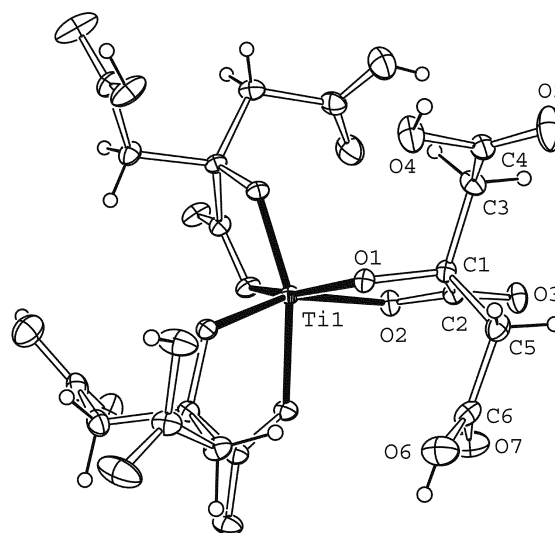


Fig. 1 ORTEP plot of the anion for $\text{KMg}_{1/2}[\text{Ti}(\text{H}_2\text{cit})_3] \cdot 6\text{H}_2\text{O}$ at the 30% probability level. Selected bond lengths and angles: $\text{Ti1-O1} = 1.865(1)$, $\text{Ti1-O2} = 2.045(1)$, $\text{O4} \cdots \text{O3}^i = 2.634(2)$, $\text{O6} \cdots \text{O7}^{ii} = 2.654(2)$, Å; $\text{O1-Ti1-O1}^{iii} = 95.23(4)$, $\text{O1-Ti1-O2} = 79.99(4)$, $\text{O1-Ti1-O2}^{iii} = 107.89(5)$, $\text{O1-Ti1-O2}^{iv} = 156.52(5)$, $\text{O2-Ti1-O2}^{iii} = 81.19(4)^\circ$. Symmetry transformations: $i = x, y, -1 + z$; $ii = -1 - x, -1 - y, 1 - z$; $iii = 1 - y, x - y, z$; $iv = 1 - x + y, 1 - x, z$.

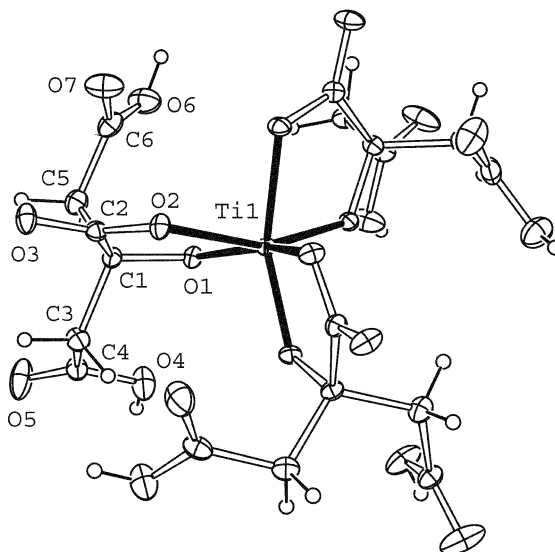


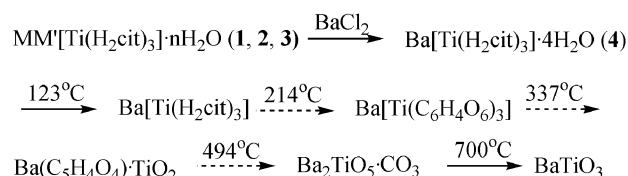
Fig. 2 ORTEP plot of the anion for $(\text{NH}_4)\text{Mg}_{1/2}[\text{Ti}(\text{H}_2\text{cit})_3] \cdot 6\text{H}_2\text{O}$ at the 30% probability level. Selected bond lengths and angles: $\text{Ti1-O1} = 1.866(2)$, $\text{Ti1-O2} = 2.049(2)$, $\text{O4} \cdots \text{O3}^i = 2.638(3)$, $\text{O6} \cdots \text{O7}^{ii} = 2.659(4)$, Å; $\text{O1-Ti1-O1}^{iii} = 95.85(9)$, $\text{O1-Ti1-O2} = 78.58(8)$, $\text{O1-Ti1-O2}^{iii} = 107.78(9)$, $\text{O1-Ti1-O2}^{iv} = 156.10(9)$, $\text{O2-Ti1-O2}^{iii} = 81.05(9)^\circ$. Symmetry transformations: $i = x, y, 1 + z$; $ii = 3 - x, 3 - y, 1 - z$; $iii = 1 - y, x - y, z$; $iv = 1 - x + y, 1 - x, z$.

† Electronic supplementary information (ESI) available: ^{13}C NMR spectra, thermogravimetric analysis and powder X-ray diagram. See <http://www.rsc.org/suppdata/dt/b3/b304358d/>

the oxalatotitanates $[\text{TiO}(\text{C}_2\text{O}_4)_2]_4^{8-} \cdot \{\text{Ba}[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}, (\text{NH}_4)_8[\text{TiO}(\text{C}_2\text{O}_4)_4] \cdot 4\text{H}_2\text{O}, \text{K}_2[\text{TiO}(\text{C}_2\text{O}_4)_4] \cdot 10\text{H}_2\text{O}\}^9$ and in $\text{Cs}_4[\text{Ti}_4\text{O}_4(\text{C}_6\text{H}_6\text{NO}_6)_4] \cdot 6\text{H}_2\text{O},^{10} [(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{TiOCl}]_4^{11}$ and $(\text{NH}_4)_8[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)(\text{O}_2)]_4 \cdot 8\text{H}_2\text{O}.^{12}$

The titanium atom lies on a three-fold axis. The citrato group binds through the α -alkoxyl and α -carboxyl groups; the other two uncoordinated terminal carboxylic acid groups are protonated, and they participate in hydrogen bonding interactions. Such bidentate coordination of citrato group through its α -alkoxyl group and α -carboxyl group is not common; typically, as in $(\text{NH}_4)_3[\text{Ga}(\text{Hcit})_2] \cdot 4\text{H}_2\text{O},^{13} (\text{NH}_4)_4[\text{M}(\text{Hcit})_2] \cdot x\text{H}_2\text{O}$ [M = Mn(II), Co(II), x = 0; M = Ni(II), x = 2]¹⁴ and $(\text{NH}_4)_5[\text{M}(\text{cit})_2] \cdot 2\text{H}_2\text{O}$ (M = Mn(III), Fe and Al),^{14,15} it uses α -hydroxyl or α -alkoxyl, α - and β -carboxyl groups to interact with the metal atom. Some examples of bidentate chelation are found for $[\text{Sb}(\text{H}_2\text{cit})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (M = Li, Na),¹⁶ $\text{Na}_2[\text{MO}_2(\text{H}_2\text{cit})_2] \cdot 3\text{H}_2\text{O}$ (M = Mo, W),¹⁷ $\text{K}_2[\text{VO}_2(\text{H}_2\text{cit})_2] \cdot 4\text{H}_2\text{O},^{18}$ $[\text{Si}(\text{H}_2\text{cit})_2\text{CH}_2\text{NH}(\text{CH}_3)_2] \cdot \text{H}_2\text{O}$ and $[\text{M}(\text{H}_2\text{cit})_2\text{CH}_2\text{NH}(\text{C}_4\text{H}_8\text{O})] \cdot \text{H}_2\text{O}$ (M = Si and Ge).¹⁹ The Ti–O _{α -alkoxyl} bond distances in **2** [1.865(1) Å] and **3** [1.866(2) Å] are similar to those found in related complexes having an α -alkoxyl group,²⁰ but are much shorter than that [2.085(1) Å] found in $(\text{NH}_4)_8[\text{Ti}(\text{O}_2)(\text{cit})_4] \cdot 8\text{H}_2\text{O}.^{12}$ The Ti–O _{α -carboxyl} distances in **2** [2.045(1) Å] and **3** [2.049(2) Å] are normal, the distances being similar to those in other systems.^{12,20}

The dipotassium, potassium hemimagnesium and ammonium hemimagnesium salts synthesized in the present study disproportionated barium chloride to afford barium tricitratotitanate as a tetrahydrate **4**. Thermogravimetric and differential thermal analyses on **4** (from the reaction of **2** with BaCl₂) are consistent with the loss of water at 123 °C; and then decomposes as shown in Scheme 1. A weight loss of ca. 70% between 25 °C and 700 °C corresponds to the theoretical weight lost by **4** to yield barium titanate. The mode of decomposition of BTC·nH₂O as documented in a number of studies,^{3–8,21–23} involves three principal stages: an initial dehydration, a decomposition of the dehydrated BTC to intermediate phases such as BaCO₃, TiO₂, and Ba₂Ti₂O₅·CO₃, and the formation of BaTiO₃. The X-ray powder diffractogram of the thermal product of **4** in 700 °C for 2 h in air is that expected for a low-temperature phase of barium titanate.



Scheme 1

Acknowledgements

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Notes and references

‡ The pH of an aqueous solution of titanium tetrachloride (1.90 g, 10 mmol) and citric acid monohydrate (6.30 g, 30 mmol) was adjusted to about 2 by the slow addition of aqueous KOH. The microcrystalline material **1** that separated was collected and recrystallized from hot water; the yield was 80%. CH elemental analysis for C₁₈H₂₆O₂₅K₂Ti: Found (Calc.): C 28.0 (28.1); H 3.0% (3.4%). IR (KBr plate): $\nu(\text{CO}_2\text{H})$, 1729_{vs}, 1705_{vs}, $\nu_{\text{as}}(\text{CO}_2)$, 1634_s, 1590_s, $\nu_s(\text{CO}_2)$, 1430_m, 1373_s, 1333_s, $\nu(\text{Ti}-\text{O})$, 662_s, 631_m, 561_s. ¹H-NMR (500 MHz, D₂O) δ_{H} : 2.76 (d, J = 4.0 Hz, CH₂), 3.01 (d, J = 14.0 Hz, CH₂) ppm; ¹³C-NMR (300 MHz, D₂O)

δ_{C} : 189.0, (CO₂)_α, 176.9 (CO₂)_β, 91.4 (≡CO), 46.6, 46.0, 46.4 (=CH₂) ppm.

Magnesium oxide (0.20 g, 5 mmol) was suspended in an aqueous solution of titanium tetrachloride (1.90 g, 10 mmol) and citric acid monohydrate (6.30 g, 30 mmol). The pH was raised to 2 with KOH. The mixture was filtered to give a colorless solution, which was then cooled. The solid that separated was collected and recrystallized from water to give colorless crystals of **2** in 70% yield. CH elemental analysis for C₁₈H₃₀O₂₇Mg_{1/2}KTi: Found (Calc.): C 28.7 (28.4); H 4.0% (3.8%). IR (KBr plate): $\nu(\text{CO}_2\text{H})$, 1712_{vs}, $\nu_{\text{as}}(\text{CO}_2)$, 1624_{vs}, 1601_{vs}, $\nu_s(\text{CO}_2)$, 1385_s, 1319_s, $\nu(\text{Ti}-\text{O})$, 666_m, 564_s. ¹H-NMR (500 MHz, D₂O) δ_{H} : 2.74 (d, J = 14.5 Hz, CH₂), 3.00 (d, J = 14.5 Hz, CH₂); ¹³C-NMR (300 MHz, D₂O) δ_{C} : 189.0 (CO₂)_α, 177.1 (CO₂)_β, 91.4 (≡CO), 46.4, 46.0 (=CH₂) ppm. The use of ammonia in place of KOH gave **3** in 65% yield. CH elemental analysis for C₁₈H₃₄O₂₇Mg_{1/2}NTi: Found (Calc.): C 28.3 (28.6); H 4.5% (4.5%). IR (KBr plate): $\nu(\text{CO}_2\text{H})$, 1712_{vs}, $\nu_{\text{as}}(\text{CO}_2)$, 1673_m, 1625_{vs}, 1597_{vs}, $\nu_s(\text{CO}_2)$, 1446_m, 1385_s, $\nu(\text{Ti}-\text{O})$, 666_m, 563_s. ¹H-NMR (500 MHz, D₂O) δ_{H} : 2.73 (d, J = 14.5 Hz, CH₂), 2.99 (d, J = 14.5 Hz, CH₂); ¹³C-NMR (300 MHz, D₂O) δ_{C} : 188.9 (CO₂)_α, 177.0 (CO₂)_β, 91.3 (≡CO), 46.4, 45.9 (=CH₂) ppm.

KMg_{1/2}[Ti(H₂cit)₃]·6H₂O (7.78 g, 10 mmol) was dissolved in water and the pH was altered to 2 by 2 M HCl. Barium chloride dihydrate (2.44 g, 10 mmol) was added; the pH was kept at 2. The water was partially removed by evaporation to produce a solid material **4** that was recrystallized twice from water in 65% yield. CH elemental analysis for C₁₈H₂₆O₂₅BaTi: Found (Calc.): C 25.8 (26.1); H 3.4% (3.3%). IR (KBr plate): $\nu(\text{CO}_2\text{H})$, 1716_{vs}, $\nu_{\text{as}}(\text{CO}_2)$, 1629_{vs}, 1588_s, $\nu_s(\text{CO}_2)$, 1374_s, $\nu(\text{Ti}-\text{O})$, 651_m, 625_m, 564_s. ¹H-NMR (500 MHz, D₂O) δ_{H} : 2.73 (d, J = 13.5 Hz, CH₂), 2.97 (d, J = 13.5 Hz, CH₂); ¹³C-NMR (300 MHz, D₂O) δ_{C} : 189.2 (CO₂)_α, 177.1 (CO₂)_β, 91.1 (≡CO), 46.1, 46.5 (=CH₂) ppm. The use of **1** and **3** in place of **2** gave **4** in about 70% yield.

§ The room-temperature diffraction measurements for the two crystal specimens were recorded on a Bruker APEX diffractometer fitted with Mo-K α radiation. *Crystal data for 2*: C₁₈H₃₀O₂₇Mg_{1/2}KTi₁, M = 777.58, trigonal, space group P-3, a = 15.5178(8), c = 7.6670(4) Å, V = 1598.9(3) Å³, D_c = 1.615 g cm⁻³, Z = 2, R = 0.047. The structure was solved by direct methods and refined by full-matrix least-squares procedures²⁴ with anisotropic thermal parameters for all the non-hydrogen atoms. Based on all of the data (4022 independent reflections) and 408 refined parameters, R₁ = 0.061, wR₂ = 0.133, and the goodness of fit on F² was 0.89. The maximum and minimum peaks were 0.68 and -0.46 e Å⁻³. *Crystal data for 3*: C₁₈H₃₄O₂₇Mg_{1/2}NTi₁, M = 756.52, trigonal, space group P-3, a = 15.566(1), c = 7.6963(7) Å, V = 1614.9(2) Å³, D_c = 1.556 g cm⁻³, Z = 2, R = 0.060. Based on all of the data (2130 independent reflections) and 166 refined parameters, R₁ = 0.091, wR₂ = 0.124, and the goodness of fit on F² is 1.06. The maximum and minimum peaks were 0.53 and -0.58 e Å⁻³. CCDC reference numbers 199259 and 208894. See <http://www.rsc.org/suppdata/dt/b3/b304358d/> for crystallographic data in CIF or other electronic format.

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