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A titanium salicylate, $Na_4[Ti(C_7H_4O_3)_3]_2 \cdot 11H_2O$

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Key indicators

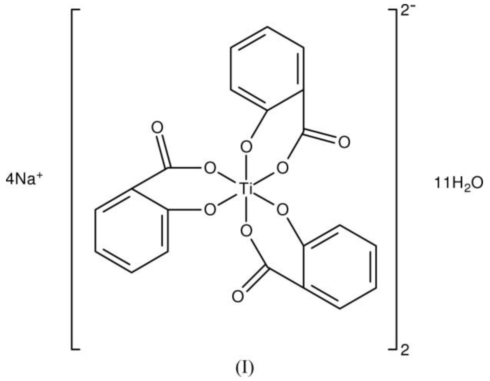
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
H-atom completeness 53%
Disorder in solvent or counterion
R factor = 0.063
wR factor = 0.170
Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, tetrasodium bis[tris(salicylato-titanate(IV)] undecahydrate, $Na_4[Ti(C_7H_4O_3)_3]_2 \cdot 11H_2O$, crystallizes with two titanium salicylate complex ions, four sodium ions and 11 water molecules in the asymmetric unit. One water O atom is disordered over two positions, having 0.74 (5) and 0.26 (5) occupancy. Both Ti atoms and three sodium ions adopt a distorted octahedral coordination by O atoms. The fourth sodium ion has a distorted trigonal–bipyramidal coordination by oxygen, sharing one edge with a sodium coordination octahedron.

Comment

Salicylic acid is prepared commercially by heating sodium phenolate with carbon dioxide under pressure to form sodium salicylate, which is treated with sulfuric acid to liberate salicylic acid. Sodium salicylate is used to a small extent as a food preservative and as an antiseptic agent in mouthwashes and toothpastes. Phenyl salicylate is used in medicine as an antiseptic and antipyretic agent. Salicylic acid has multifunctional properties to help with a variety of skin problems including acne, pimples and blemishes. It is an excellent exfoliant and at the same time has good anti-irritant qualities as well as anti-inflammatory properties (Patterson & Lawrence, 2002). Another positive feature of salicylic acid is that it helps with the treatment of skin ailments because of its antimicrobial properties. Salicylic acid is also known to improve skin thickness, skin barrier functions, collagen production and cell renewal (Pierard *et al.*, 1999). It is well known for its biological activity, which is related to its ability to bind metal ions. Salicylate metal complexes are more effective, as the toxicity problems related to the injection of salicylic acid are diminished. Titanium salicylate as a mixture with titanium dioxide and titanium peroxide, used to form a protective film on the skin against irritation and repeated wetting, is suitable for the prevention of urinary rash and nappy rash in children.



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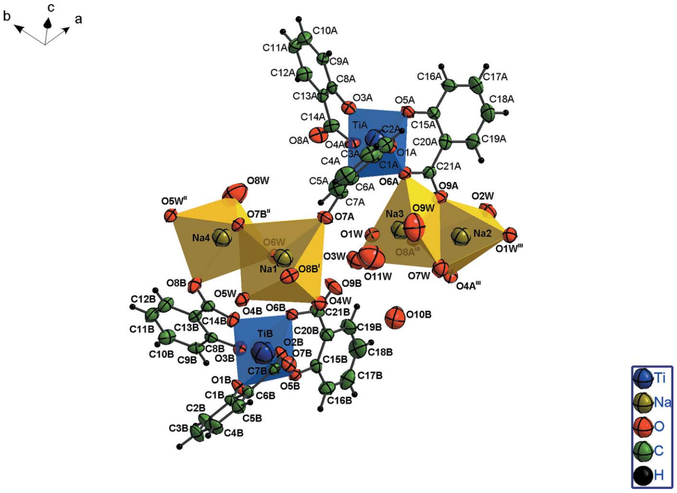

Figure 1
The asymmetric unit, showing displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]

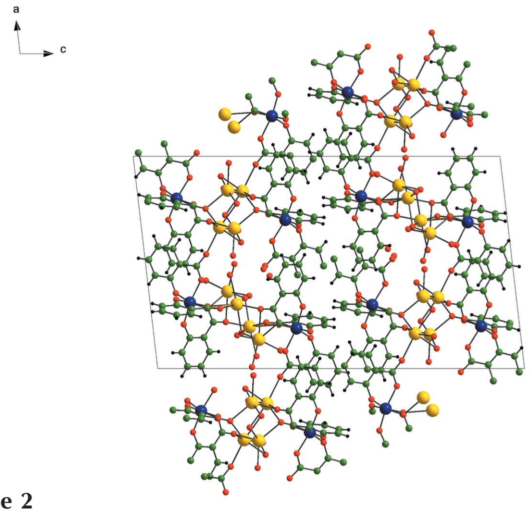

Figure 2
The packing, viewed along the *b* axis.

In the title compound three salicylate ligands coordinate to each Ti^{4+} ion, through their carboxylic and phenolic O atoms. The conformations of the two independent complex anions contained in the asymmetric unit are similar. The coordination of Ti by O may be described as distorted octahedral. Fig. 1 represents a three-dimensional view of the entire asymmetric unit with the atom numbering scheme. The Ti—O distances (Table 1) range between 1.846 (4) and 2.077 (4) Å in complex *A*, and between 1.847 (4) and 2.042 (4) Å in complex *B*. Similar Ti—O distances are found in many recently determined crystal structures of titanium complexes (Honda *et al.*, 2003; Thurston *et al.*, 2004). The bite angles of the ligands (Table 1) range between 84.3 (2) and 85.1 (2)°. The C—O distances are similar to those in salicylic acid itself (Sundaralingam & Jensen, 1965; Cochran, 1953). The average value of the angles made by the carboxylic group at the C atom of the benzene ring is 119.4° for both anions. Corresponding angles with values of 117° (Cochran, 1953) and 116° (Sundaralingam & Jensen, 1965) are found in salicylic acid. The dihedral angles among the three mean planes passing through titanium and the three carboxylic and phenolic groups attached to the three aromatic rings vary from 66.9 (2) to 88.7 (2)°. As in the optimized geometry of salicylic acid adsorbed on titanium oxide surfaces, here also an aromatic plane lies above the Ti atom and prevents interaction between titanium and one of the H atoms of the aromatic ring. The dihedral angles among the three aromatic rings of the salicylate ligands range from 56.6 (3) to 82.9 (3)°.

In addition to the two titanium salicylate anionic complexes, the asymmetric unit contains four sodium ions and 11 water molecules, one of which is disordered over two positions. The Na atoms also have distorted octahedral coordination by O atoms, with the exception of atom Na4, which is coordinated by five O atoms, sharing one edge of its trigonal bipyramid with the octahedron around Na1. The octahedron around Na2 also shares one edge with the octahedron around Na3. The packing, with stacking of aromatic rings, is shown in Fig. 2, where a layered structure of sodium ions parallel to the *ab* plane is revealed.

Experimental

A chemically pure sample of titanium perchlorate was obtained from the Chemistry Laboratory of the University College of Science, Calcutta. To a well stirred mixture of titanium(IV) perchlorate (2.23 g, 0.005 mol) and salicylic acid (2.28 g, 0.0165 mol) in water (20 ml), a dilute solution of sodium hydroxide (1.32 g, 0.033 mol) in water (30 ml) was added dropwise with stirring over a period of 1.5 h. When the pH was about 4.5 the solution assumed a yellow colour. This solution was then allowed to evaporate slowly on a warm water bath to yield small orange–yellow crystals. Recrystallization from water by very slow evaporation at room temperature gave crystals suitable for X-ray analysis.

Crystal data

$Na_4[Ti(C_7H_4O_3)_3]_2\cdot 11H_2O$
$M_r = 1180.37$
Monoclinic, $P2_1/n$
$a = 17.572\ (3)$ Å
$b = 9.588\ (5)$ Å
$c = 30.126\ (3)$ Å
$\beta = 96.60\ (2)°$
$V = 5042\ (3)$ Å^3
$Z = 4$
$D_x = 1.555$ Mg m^{-3}
$D_m = 1.60$ Mg m^{-3}
D_m measured by flotation in benzene/bromoform
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.2–25.0°$
$\mu = 0.45$ mm^{-1}
$T = 293\ (2)$ K
Rhomb, yellow
0.25 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
9046 measured reflections
8865 independent reflections
4399 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.0°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 35$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.170$
$S = 0.93$
8865 reflections
706 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.083P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.85$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.38$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Ti*A*—O1*A*	1.846 (4)	O1*A*—C1*A*	1.353 (6)
Ti*A*—O3*A*	1.869 (4)	O2*A*—C7*A*	1.288 (6)
Ti*A*—O5*A*	1.875 (4)	O4*A*—C14*A*	1.297 (7)
Ti*A*—O6*A*	2.011 (4)	O3*A*—C8*A*	1.358 (6)
Ti*A*—O4*A*	2.032 (4)	O6*A*—C21*A*	1.302 (6)
Ti*A*—O2*A*	2.077 (4)	O5*A*—C15*A*	1.349 (6)
Ti*B*—O5*B*	1.847 (4)	O2*B*—C7*B*	1.293 (6)
Ti*B*—O3*B*	1.864 (4)	O1*B*—C1*B*	1.345 (6)
Ti*B*—O1*B*	1.875 (3)	O3*B*—C8*B*	1.340 (6)
Ti*B*—O4*B*	2.029 (4)	O4*B*—C14*B*	1.296 (7)
Ti*B*—O6*B*	2.042 (3)	O5*B*—C15*B*	1.352 (6)
Ti*B*—O2*B*	2.042 (4)	O6*B*—C21*B*	1.290 (6)

O5*A*—Ti*A*—O6*A*	84.29 (16)	O2*A*—C7*A*—C6*A*	119.5 (5)
O3*A*—Ti*A*—O4*A*	84.52 (16)	O4*A*—C14*A*—C13*A*	119.2 (5)
O1*A*—Ti*A*—O2*A*	84.32 (16)	O6*A*—C21*A*—C20*A*	119.2 (5)
O3*B*—Ti*B*—O4*B*	85.12 (16)	O2*B*—C7*B*—C6*B*	119.2 (5)
O5*B*—Ti*B*—O6*B*	85.14 (15)	O4*B*—C14*B*—C13*B*	119.4 (5)
O1*B*—Ti*B*—O2*B*	84.63 (15)	O6*B*—C21*B*—C20*B*	119.7 (5)

All aromatic H atoms were included in a riding-model approximation, with a C—H distance of 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Most water H atoms were located in a difference Fourier synthesis but, as refinement of their positions was unstable, they were removed from the final model.

Data collection: *XDS* (Kabsch, 1988); cell refinement: *XDS; data* reduction: *XDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *PLATON* (Spek, 2003).

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