Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(dimethylammonium) *mer*-tris(salicylato-κ^2O,O')-titanate(IV)

Yun-Long Fu,[a] Zhi-Wei Xu,[a] Jia-Lin Ren[a] and Seik Weng Ng[b]*

[a]School of Chemistry and Materials Science, Shanxi Normal University, Linfen 041004, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Received 18 July 2005
Accepted 2 August 2005
Online 12 August 2005

In the title compound, $(C_2H_8N)_2[Ti(C_7H_4O_3)_3]$, the Ti^{IV} atom is chelated by three salicylate ligands in a *mer*-octahedral geometry. The cations and complex anions are linked by hydrogen bonds into a layer structure.

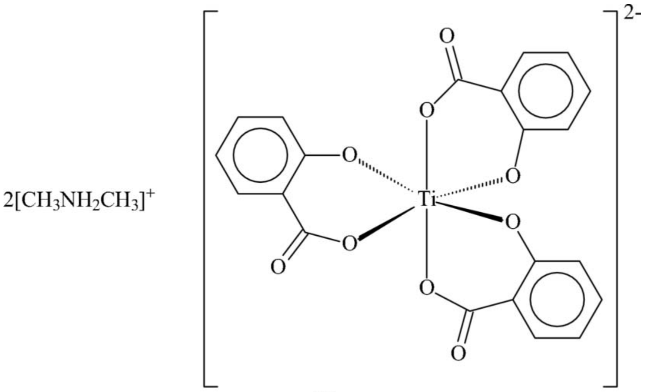
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.055
wR factor = 0.186
Data-to-parameter ratio = 16.9

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

Comment

As the deprotonated anion of salicylic acid can function as a dianionic chelate, two or more salicylate(2−) anions should be able to bind to metal atoms to form $[M(C_7H_4O_3)_n]$ ions. Such anionic salicylate complexes have been authenticated in a small number of salts, as noted from the Cambridge Structural Database (Version 5.26; Allen, 2002). For example, with the Be^{II} complex, the charge is balanced by ammonium cations (Schmidbaur & Kumberger, 1993); the Cu^{II} derivative has as counter-ion the bis(2-amino-2-methyl-1-propanol)copper cation (Muhonen, 1982). Also featuring two salicylate dianions is the dioxomolybdenum complex, which exists as the bis(1-methylimidazolium) (Boutilier *et al.*, 1993), bis(pyridinium) (Edwards *et al.*, 1992) and bis(tetramethylammonium) (Edwards *et al.*, 1993) salts. Both the sodium and the ammonium bis(salicylato)manganate(III) complexes are not simple ionic salts (Kirk *et al.*, 1991), however. With titanium in particular, a neutral tris-chelated octahedral compound, $[Ti(C_7H_4O_3)_2(C_7H_5O_3)]$ is known; the study (Gigant *et al.*, 2001) also describes the possible coordination modes of the titanium derivatives of salicylic acid.



(I)

The tris(salicylato)titanate(IV) dianion was first isolated as its crystalline sodium and ammonium salts (Babko *et al.*, 1961); a spectroscopic study (Faizutdinova *et al.*, 1986) assigned an octahedral geometry to the metal atom in the sodium salt. The title compound, (I), is the first example of a crystallographically authenticated tris-chelated salicylate complex; the Ti atom in the tris(salicylato)titanate(IV) ion is sixcoordinate in a *mer*-octahedral geometry, and its charge is balanced by two dimethylammonium cations (Fig. 1). For each chelate, the Ti—$O_{hydroxy}$ bond is shorter than the Ti—$O_{carboxyl}$ bond. The carbonyl O atoms engage the cations in hydrogen-bonding interactions (Table 2), giving rise to a layer structure. In the following paper, the structure of the piperazium salt of *fac*-tris(salicylato)titanate(IV), (II), is reported (Fu *et al.*, 2005).

Experimental

Tetrabutyl titanate (0.34 ml, 1 mmol) and salicylic acid (0.40 g, 3 mmol) were dissolved in DMF (10 ml). The clear yellow solution was set aside for three months. The red crystals of (I) that separated from solution were isolated in about 90% yield (based on Ti). The dimethylammonium cation probably resulted from the decomposition of DMF in the presence of salicylic acid, which would serve as catalyst. The DMF solvent was not incorporated into the crystal structure of (I), whereas it was incorporated into (II), when piperazine was added.

Crystal data

$(C_2H_8N)_2[Ti(C_7H_4O_3)_3]$
$M_r = 548.39$
Monoclinic, $P2_1/n$
$a = 11.589$ (1) Å
$b = 14.270$ (1) Å
$c = 15.463$ (1) Å
$\beta = 92.259$ (1)°
$V = 2555.1$ (3) Å^3
$Z = 4$
$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3721 reflections
$\theta = 2.2$–25.2°
$\mu = 0.39$ mm^{-1}
$T = 295$ (2) K
Block, red
0.35 × 0.22 × 0.20 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 1996)
$T_{min} = 0.784$, $T_{max} = 0.926$
14492 measured reflections
5654 independent reflections
4430 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 15$
$k = -18 \rightarrow 13$
$l = -19 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.186$
$S = 1.07$
5654 reflections
334 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1131P)^2 + 0.5921P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ti1—O1	1.872 (2)	Ti1—O4	1.906 (2)
Ti1—O2	1.973 (2)	Ti1—O7	1.891 (2)
Ti1—O5	2.063 (2)	Ti1—O8	1.958 (2)
O1—Ti1—O2	86.35 (8)	O2—Ti1—O8	176.31 (8)
O1—Ti1—O4	94.11 (8)	O4—Ti1—O5	83.49 (8)
O1—Ti1—O5	175.11 (8)	O4—Ti1—O7	168.03 (8)
O1—Ti1—O8	96.46 (8)	O4—Ti1—O8	89.23 (9)
O1—Ti1—O7	97.50 (9)	O5—Ti1—O7	85.14 (8)
O2—Ti1—O4	92.97 (9)	O5—Ti1—O8	87.79 (8)
O2—Ti1—O5	89.51 (8)	O7—Ti1—O8	86.60 (8)
O2—Ti1—O7	90.66 (8)		

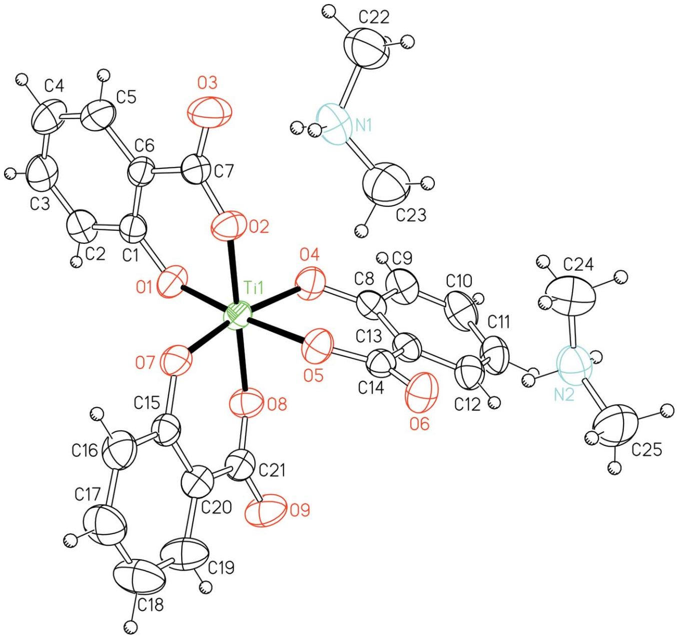


Figure 1
ORTEPII plot (Johnson, 1976), showing the atom-numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*a*···O3	0.90	1.92	2.793 (3)	163
N1—H1*b*···O6^{i}	0.90	1.89	2.775 (3)	169
N2—H2*a*···O6	0.90	1.98	2.859 (3)	165
N2—H2*b*···O9^{ii}	0.90	1.81	2.714 (3)	177

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

The carbon-bound H atoms were positioned geometrically [C—H = 0.93 Å for the aromatic H atoms and C—H = 0.96 Å for the methyl H atoms; $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic H atoms and $1.5U_{eq}(C)$ for the methyl H atoms]. Although the nitrogen-bound H atoms could be located in difference Fourier maps, they could not be satisfactorily refined, even with an N—H distance restraint. These atoms were also positioned geometrically [N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(N)$]. All H atoms were included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the Natural Scientific Foundation Committee of Shanxi Province (No. 20041031) and the University of Malaya for generously supporting this study.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Babko, A. K., Volkova, O. I. & Get'man, T. E. (1961). *Zh. Neorg. Khim.* **6**, 354–359. (In Russian.)

Acta Cryst. (2005). E**61**, m1730–m1732 Fu *et al.* • $(C_2H_8N)_2[Ti(C_7H_4O_3)_3]$ **m1731**

Boutilier, K., MacGillivray, L. F., Subramanian, S. & Zaworotko, M. J. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 773–778.

Bruker (2002). *SAINT* and *SMART*. Versions 6.3A. Bruker AXS Inc., Madison, Wisconsin, USA.

Edwards, C. F., Griffith, W. P., White, A. J. P. & Williams, D. J. (1992). *Polyhedron*, **11**, 2711–2712.

Edwards, C. F., Griffith, W. P., White, A. J. P. & Williams, D. J. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3813–3819.

Faizutdinova, Z. Sh., Khakimova, K. S. & Medvedskaya, N. Ya. (1986). *Uzb. Khim. Zh.* pp. 7–10. (In Russian.)

Fu, Y.-L., Xu, Z.-W., Ren, J.-L. & Ng, S. W. (2005). *Acta Cryst.* E**61**, m1733–m11734.

Gigant, K., Rammal, A. & Henry, M. (2001). *J. Am. Chem. Soc.* **123**, 11632–11637.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kirk, M. L., Myoung, S. H., Raptopoulou, C., Kessissoglou, D. P., Hatfield, W. E. & Pecoraro, V. L. (1991). *Inorg. Chem.* **30**, 3900–3907.

Muhonen, H. (1982). *Acta Cryst.* B**38**, 2041–2043.

Schmidbaur, H. & Kumberger, O. (1993). *Chem. Ber.* **126**, 3–9.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

m1732 Fu *et al.* • $(C_2H_8N)_2[Ti(C_7H_4O_3)_3]$ *Acta Cryst.* (2005). E**61**, m1730–m1732