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Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$

R factor = 0.089

wR factor = 0.191

Data-to-parameter ratio = 13.8

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

catena-Poly[hemi[diacuacopper(II)]- μ -salicylato- $\kappa^3\text{O}:O',O''$ -[(salicylato- $\kappa^2\text{O},O'$)titanate(IV)]- μ -salicylato- $\kappa^3\text{O},O':O''$ -hemi[bis(N,N -dimethylformide- κO)copper(II)]]

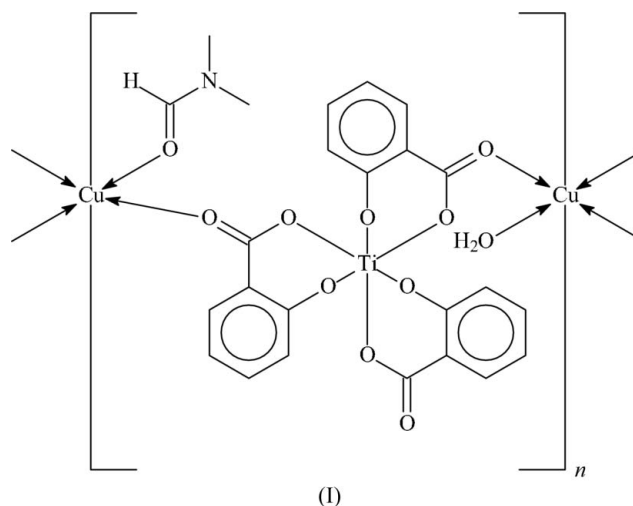
The octahedral tris(salicylato)titanate entity in polymeric $\{[\text{Cu}(\text{C}_3\text{H}_7\text{NO})_2]_{1/2}[\text{Cu}(\text{H}_2\text{O})_2]_{1/2}[\text{Ti}(\text{C}_7\text{H}_4\text{O}_3)_3]\}_n$ links adjacent bis(N,N -dimethylformamide)copper and diaquacopper units through the carboxylate O atoms to form a chain motif. Hydrogen bonds within the chain further consolidate the structure. The two independent Cu atoms lie on different sites of $\bar{1}$ symmetry.

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Comment

The deprotonated salicylic acid dianion chelates to a number of metal ions; with titanium(IV), if three dianions bind simultaneously to the metal, then a six-coordinate tris-salicylatotitanate(IV) dianion would be formed. This expectation is borne out in our study on the bis(dimethylammonium) salt, (Fu *et al.*, 2005). We have extended this study and now have attempted to isolate the titanate dianion as a copper(II) salt. The copper compound that is formed is $[\text{Cu}(\text{C}_3\text{H}_7\text{NO})_2]_{1/2}[\text{Cu}(\text{H}_2\text{O})_2]_{1/2}[\text{Ti}(\text{C}_7\text{H}_4\text{O}_3)_3]$, (I) (Fig. 1), whose Ti atom has bond dimensions similar to those found in the bis(dimethylammonium) salt. The dianion further interacts with two Cu atoms, one of which is coordinated by two DMF molecules and the other by two water molecules, to give rise to a chain structure (Fig. 2); the Cu atoms show square-planar coordination. Hydrogen bonds within the chain (Table 2) further consolidate the structure.



Experimental

Tetrabutyl titanate (0.60 g, 1.8 mmol) and salicylic acid (0.76 g, 5.5 mmol) were dissolved in DMF (8 ml), and to the solution was added copper carbonate hydrate (0.32 g, 1.4 mmol). The mixture was

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stirred until the carbonate dissolved completely. The solution was set aside for several days for the crystals to separate; these were obtained in about 50% yield.

Crystal data

[CuTi(C₇H₄O₃)₃(C₃H₇NO)(H₂O)]
M_r = 610.86
 Triclinic, *P* $\bar{1}$
a = 9.629 (1) Å
b = 9.915 (1) Å
c = 14.558 (2) Å
 α = 70.783 (2)°
 β = 85.346 (2)°
 γ = 69.579 (2)°

V = 1229.1 (2) Å³
Z = 2
D_x = 1.651 Mg m⁻³
 Mo *K*α radiation
 μ = 1.25 mm⁻¹
T = 295 (2) K
 Block, yellow-green
 0.16 × 0.08 × 0.07 mm

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.825, *T_{max}* = 0.917

8739 measured reflections
 4291 independent reflections
 2943 reflections with *I* > 2σ(*I*)
R_{int} = 0.056
 θ_{max} = 25.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.089
wR (*F*²) = 0.191
S = 1.13
 4291 reflections
 310 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 1.6052P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ti1—O1	1.865 (5)	Ti1—O8	1.986 (5)
Ti1—O2	2.054 (5)	Cu1—O3	1.929 (4)
Ti1—O4	1.853 (5)	Cu1—O1 <i>w</i>	1.907 (5)
Ti1—O5	2.043 (5)	Cu2—O6	1.990 (5)
Ti1—O7	1.857 (5)	Cu2—O10	1.949 (5)
O1—Ti1—O2	83.2 (2)	O4—Ti1—O7	99.7 (2)
O1—Ti1—O4	92.0 (2)	O4—Ti1—O8	100.3 (2)
O1—Ti1—O5	94.2 (2)	O5—Ti1—O7	167.5 (2)
O1—Ti1—O7	97.4 (2)	O5—Ti1—O8	82.3 (2)
O1—Ti1—O8	166.8 (2)	O7—Ti1—O8	85.4 (2)
O2—Ti1—O4	165.4 (2)	O3—Cu1—O1 <i>w</i>	94.3 (2)
O2—Ti1—O5	82.1 (2)	O3—Cu1—O1 <i>w</i> ⁱ	85.7 (2)
O2—Ti1—O7	94.5 (2)	O6—Cu2—O10	91.2 (2)
O2—Ti1—O8	83.7 (2)	O6—Cu2—O10 ⁱⁱ	88.8 (2)
O4—Ti1—O5	84.5 (2)		

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1 <i>w</i> —H1 <i>w</i> 1...O9 ⁱⁱⁱ	0.85	1.77	2.536 (7)	148
O1 <i>w</i> —H1 <i>w</i> 2...O2	0.85	1.86	2.586 (7)	143

Symmetry code: (iii) $-x, -y + 2, -z + 1$.

The crystal in the diffraction study did not diffract strongly, and as the proportion of *I* > 2σ(*I*) reflections was not high, the aromatic rings were refined as rigid hexagons with bond lengths of 1.39 Å. This gave a reflections:parameters ratio of nearly ten. All H atoms were posi-

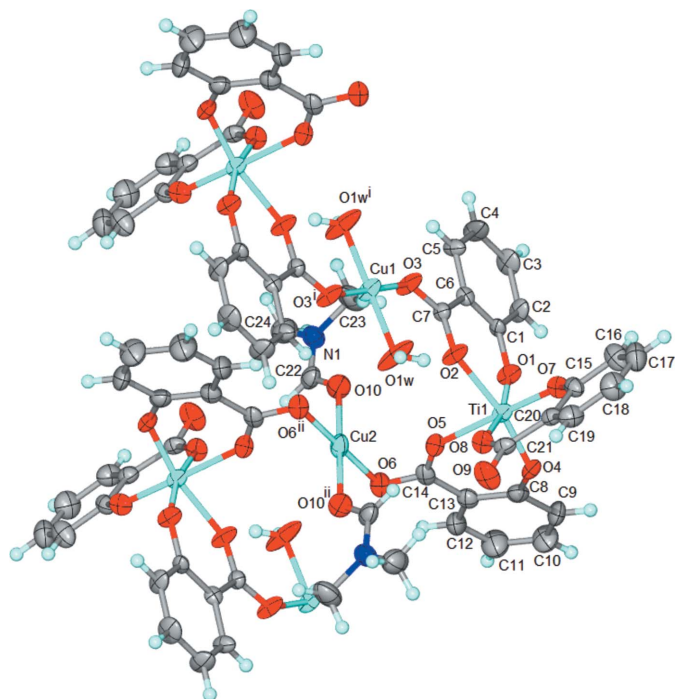


Figure 1

ORTEP plot illustrating the coordination geometry of the Cu and Ti atoms. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.]

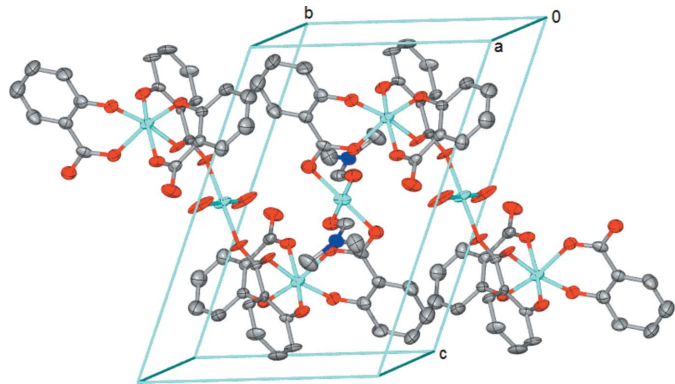


Figure 2

ORTEP plot of the chain structure. H atoms have been omitted.

tioned geometrically (C—H = 0.93 Å for *Csp*² and 0.96 Å for methyl H atoms, and O—H = 0.85 Å). The displacement parameters were set to 1.2 or 1.5 times *U_{eq}* of the parent atoms. The methyl groups and water molecules were rotated to fit the electron density.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics X-SEED (Barbour, 2001); software used to prepare material for publication: SHELXL97.

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