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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C)$ = 0.006 Å
 Disorder in solvent or counterion
 R factor = 0.050
 wR factor = 0.124
 Data-to-parameter ratio = 15.7

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

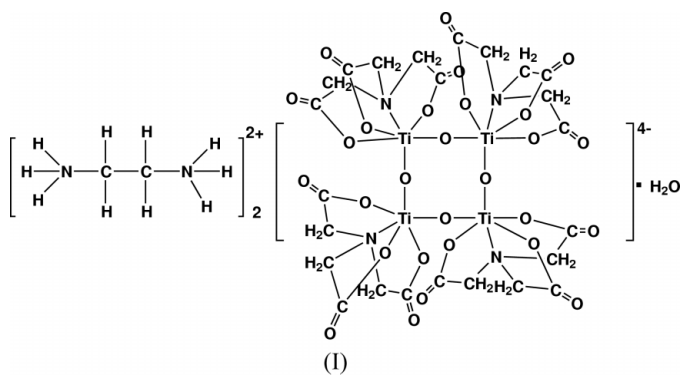
Bis(ethylenediammonium) tetra- μ -oxo-tetrakis[(nitrilotriacetato)titanate(IV)] monohydrate

The asymmetric unit of the title compound, $(C_2H_{10}N_2)_2[Ti_4O_4(C_6H_6NO_6)_4]$, consists of halves of two centrosymmetric tetrameric $[Ti_4O_4\{N(CH_2COO)_3\}_4]^{4-}$ anions, two $[H_3N(CH_2)_2NH_3]^{2+}$ cations and a disordered molecule of water of crystallization. In the $[Ti_4O_4\{N(CH_2COO)_3\}_4]^{4-}$ tetramer, each Ti atom is coordinated by one nitrilotriacetate ligand and two μ -oxo ligands, so that four titanium and four μ -O atoms form an eight-membered ring. The tetramers are connected by hydrogen bonds with $[H_3N(CH_2)_2NH_3]^{2+}$ cations and with water molecules, leading to an intricate three-dimensional network.

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Comment

Titanium nitrilotriacetate complexes are considered to be a precursor of Schwarzenbach's peroxo complexes (Wieghardt *et al.*, 1980), but the synthesis of these complexes has not been highly developed as a result, in large part, of the strong tendency of group 4 complexes toward hydrolysis and polymerization reactions even in strong acid media (Cotton & Wilkinson, 1988; Intorre & Martell, 1960). The existence of titanium nitrilotriacetate complexes has been documented, but relatively few complexes of this type have been characterized (Wieghardt *et al.*, 1980; Schwarchzenbach & Girgis, 1975). All contain a tetrameric titanate anion and an inorganic cation, and this is the first time that the crystal structure of such a complex with a diprotonated organic amine cation has been reported.



The asymmetric unit of the title compound, (I), consists of halves of two centrosymmetric $[Ti_4O_4\{N(CH_2COO)_3\}_4]^{4-}$ anions, two $[H_3N(CH_2)_2NH_3]^{2+}$ cations and a disordered molecule of water of crystallization. The tetrameric unit, $[Ti_4O_4\{N(CH_2COO)_3\}_4]^{4-}$ (Fig. 1) is very similar to that reported for $Cs_4[TiO(NTA)]_4 \cdot 6H_2O$ (Wieghardt *et al.*, 1980). Each tetrameric anion lies on a center of symmetry. The titanium(IV) centers are six-coordinate, with two *cis*- μ -oxo

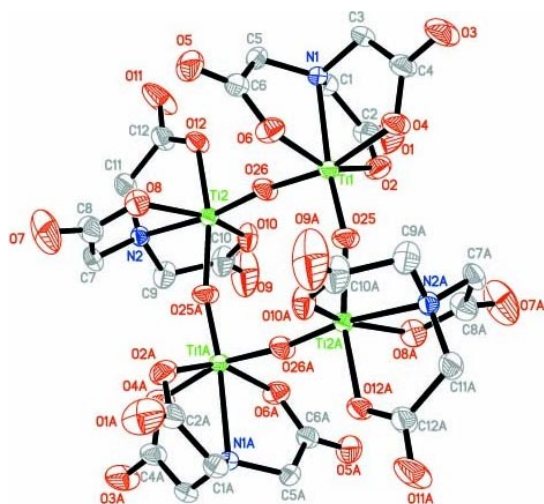


Figure 1
A perspective view of one anion of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (A) $1 - x, 1 - y, 2 - z$]

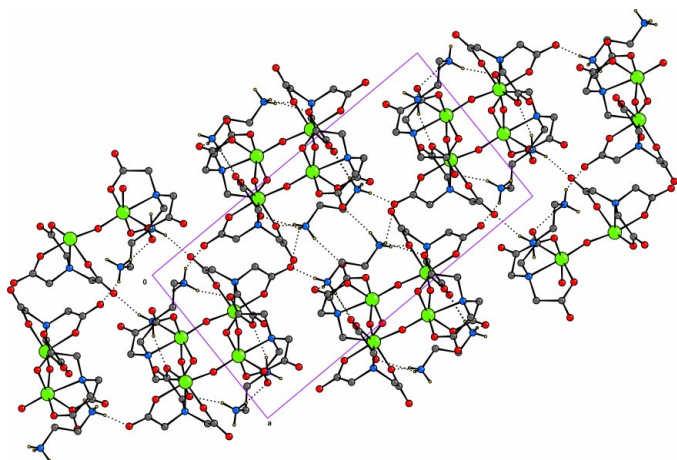


Figure 2
Strong hydrogen bonds between cations and anions.

bridging atoms; the Ti and μ -O atoms form a puckered eight-membered ring with dimensions 3.905×4.150 Å. The μ -oxo bridges are not symmetrical. A short Ti—O bond (average bond distance ~ 1.75 Å) and a longer bond (~ 1.89 Å) alternate. The Ti—O—Ti bond angles are in the range 160 – 175° . The short Ti—O bonds of the bridging O atoms indicate considerable double-bond character (Ti=O). The nitrilotriacetate ligand is bonded in a conventional fashion to the titanium(IV) center as a tetradentate ligand.

Ethylenediamine plays the role of counter-ion in the structure. One of the amines exhibits a *cis* configuration, and the other displays a *trans* configuration. The anions are connected by hydrogen bonds to $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^{2+}$, leading to an intricate three-dimensional network, as shown in Fig. 2. The disordered water molecules are also involved in hydrogen bonding with O atoms of the tetramer units (Table 1).

Experimental

$\text{Ti}(\text{SO}_4)_2$ (0.4 g, 1.67 mmol), nitrilotriacetic acid (1.0 g, 5.22 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3 ml, 0.15 mol l^{-1}) and H_2O (5 ml) were mixed, and $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ was added carefully to give a pH of 4.5. After stirring, the reaction mixture was sealed in a 20 ml Teflon-lined stainless steel vessel and heated at 373 K for 2 d under autogeneous pressure. After the reaction was complete, the vessel was cooled slowly to room temperature and colorless crystals were obtained.

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{Ti}_4\text{O}_4(\text{C}_6\text{H}_6\text{NO}_6)_4] \cdot \text{H}_2\text{O}$
 $M_r = 1150.33$
 Triclinic, $P\bar{1}$
 $a = 10.8082$ (10) Å
 $b = 10.9099$ (11) Å
 $c = 19.6832$ (15) Å
 $\alpha = 91.483$ (5) $^\circ$
 $\beta = 90.796$ (3) $^\circ$
 $\gamma = 104.374$ (5) $^\circ$
 $V = 2247.1$ (4) Å 3

$Z = 2$
 $D_x = 1.697 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12$ – 18°
 $\mu = 0.79 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Block, colorless
 $0.46 \times 0.42 \times 0.40 \text{ mm}$

Data collection

Rigaku Weissenberg IP diffractometer
 ω – 2θ scans
 20 995 measured reflections
 10 124 independent reflections
 7090 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -14 \rightarrow 13$
 $k = 0 \rightarrow 14$
 $l = -25 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.124$
 $S = 1.01$
 10 124 reflections
 644 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 2.7799P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, $^\circ$).

D —H \cdots A	D —H	H \cdots A	$D\cdots A$	D —H \cdots A
N5—H5A \cdots O100	0.89	2.13	2.942 (13)	151
N5—H5A \cdots O11 ⁱ	0.89	2.35	2.875 (5)	117
N5—H5A \cdots O17 ⁱⁱ	0.89	2.51	3.172 (6)	132
N5—H5B \cdots O20 ⁱⁱ	0.89	1.96	2.827 (5)	163
N5—H5C \cdots O15 ⁱⁱⁱ	0.89	2.19	3.016 (7)	155
N6—H6A \cdots O21 ^{iv}	0.89	2.00	2.891 (5)	176
N6—H6A \cdots O22 ^{iv}	0.89	2.50	3.080 (4)	124
N6—H6B \cdots O11 ^v	0.89	1.90	2.781 (4)	172
N6—H6C \cdots O13 ^{iv}	0.89	1.91	2.778 (5)	166
N7—H7A \cdots O7 ^{vi}	0.89	1.93	2.733 (4)	150
N7—H7B \cdots O10 ^v	0.89	2.03	2.872 (4)	157
N7—H7C \cdots O3 ^{vii}	0.89	2.04	2.889 (5)	159
N8—H8A \cdots O5 ^v	0.89	1.90	2.762 (4)	163
N8—H8B \cdots O23 ^{viii}	0.89	2.00	2.795 (4)	148
N8—H8C \cdots O3 ^{vii}	0.89	1.87	2.743 (4)	167
O100—H10A \cdots O15	0.84	2.16	2.781 (10)	130
O100—H10A \cdots O16	0.84	2.53	3.329 (10)	158
O200—H20A \cdots O14 ^{iv}	0.87	2.18	2.755 (10)	124
O200—H20B \cdots O16 ⁱⁱⁱ	0.86	2.27	3.087 (11)	160
O200—H20B \cdots O15 ⁱⁱⁱ	0.86	2.45	3.187 (12)	145
O300—H30A \cdots O4 ^{ix}	0.88	2.14	2.917 (15)	147
O300—H30A \cdots O3 ^{ix}	0.88	2.19	2.767 (14)	123
O300—H30B \cdots O6	0.85	1.86	2.647 (13)	153
O300—H30B \cdots O5	0.85	2.58	3.314 (15)	145

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, y - 1, z$; (v) $1 - x, 1 - y, 2 - z$; (vi) $-x, 1 - y, 2 - z$; (vii) $x, 1 + y, z$; (viii) $-x, 2 - y, 2 - z$; (ix) $1 - x, -y, 2 - z$.

All H atoms of the cations and anions were positioned geometrically [$C-H = 0.97 \text{ \AA}$, $N-H = 0.89 \text{ \AA}$, and $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(N)$] and treated as riding. The H atoms of the molecule of water of crystallization were placed in calculated positions ($O-H = 0.8440-0.8808 \text{ \AA}$) (Nardelli, 1999) and were not further refined [$U_{iso}(H) = 0.05 \text{ \AA}^3$].

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXL97*.

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