

Fig. 2. The twelve-membered 'water cage'.

Table 2. Relevant data on the geometry of $\text{CaCu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$

Bond distances (Å)			
Cu—O(1)	1.969 (1)	Ca—W(2)	2.343 (2)
Cu—O(2)	2.289 (2)	C(1)—O(1)	1.227 (3)
		C(1)—O(2)	1.499 (3)

Bond angles (°)			
O(1)—Cu—O(1 ^b)	168.1 (1)	O(2)—Ca—W(2)	91.3 (1)
O(1)—Cu—O(1 ^b)	90.6 (1)	O(1)—C(1)—O(2)	122.0 (2)
O(2)—Ca—O(2 ^b)	82.7 (1)	O(1)—C(1)—C(2)	117.5 (2)
O(2)—Ca—O(2 ^b)	97.3 (1)	O(2)—C(1)—C(2)	120.4 (2)

Hydrogen bonds (Å, °)							
	O...O	O—H	H...O	∠O—H...O	∠H...O—X	X	
W(1)—H(4)...	O(1 ^b)	2.751 (2)	0.77 (3)	1.98 (3)	178 (4)	121 (1)	C(1 ^b)
W(1)—H(5)...	W(1 ^b)	2.780 (3)	0.69 (4)	2.11 (4)	168 (4)	121 (3)	H(4 ^b)
						102 (3)	H(5 ^b)
W(2)—H(6)...	W(1)	2.774 (2)	0.85 (3)	1.93 (3)	175 (3)	104 (3)	H(4)
						104 (3)	H(5)

Symmetry code: (i) $1-x, -y, z$; (ii) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, y, 1-z$; (iv) $y, 1-x, z$.

The bond distances and angles from this analysis are in good agreement with the values reported by Langs & Hare (1967). The acetato-bridged Cu...Ca distance [4.060 (1) Å] is much longer than the corresponding distance in $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]_2$ with Cu—Cu = 2.616 (1) Å (de Meester, Fletcher & Skapski, 1973). The coordination sphere of Cu consists of the eight oxygen atoms of four acetate ligands; four O atoms coordinated in an approximate square-planar configuration with a short Cu—O distance of 1.969 (1) Å and four O atoms coordinated tetrahedrally with a

much longer Cu...O distance of 2.788 (2) Å. The Ca atoms are octahedrally surrounded by four oxygen atoms of four acetato ligands and two oxygen atoms of water molecules. The water molecules in the structure are arranged on the corners of decahedrons with exact $4/m$ symmetry, the centres of which are at sites (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Sixteen hydrogen atoms of this water cluster form hydrogen bridges which are directed along the edges of the decahedron. The eight remaining hydrogen atoms are directed outward from the cage and are hydrogen bonded to the acetate O(1) atoms. The decahedron shares four O atoms with the Ca octahedra which are part of the four surrounding chains. There is a void with a diameter of about 3 Å within the water cage.

The crystals were grown and kindly supplied by P. van der Sluis and E. van der Donk.

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Acta Cryst. (1983). **C39**, 1344–1346

Dimer of (2, 2', 2''-Nitrilotriethanolato)(2-propanolato)titanium(IV), [Ti₂(C₆H₁₂NO₃)₂(C₃H₇O)₂]

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(Received 25 March 1983; accepted 27 June 1983)

Abstract. $M_r = 506.31$, monoclinic, $C2/c$, $a = 91.65$ (1) Å, $V = 2356$ Å³, $Z = 4$, $D_x = 1.427$ g cm⁻³, 12.240 (1), $b = 13.379$ (2), $c = 14.394$ (1) Å, $\beta = 90.0$ (1)°, $\lambda = 0.71069$ Å, $\mu = 7.5$ cm⁻¹, $F(000) = 1072$,

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173 K, $R = 0.028$ for 2088 reflections with $I > 3\sigma(I)$. Situated across a crystallographic center of inversion at $\frac{1}{4}, \frac{1}{4}, 0$, each half of the dimer contains one titanium, one 2, 2', 2''-nitrilotriethanolate ligand, and one 2-propanolate group; the dimer is formed and octahedral coordination is achieved when an oxygen atom on one arm of the nitrilotriethanolate chelate serves as a bridging group.

Introduction. A reaction between a tetra(alkoxy)-titanium(IV) and any tetradentate ligand will often yield a number of products. One factor is the variability in the coordination number of titanium(IV) which is commonly found to be either 6 or 7, although 5-coordinate complexes are also known (Olmstead, Power & Viggiano, 1983). The tendency to form dimers, trimers, etc. is a second factor. A third problem is the ready formation of oxo bridges (Ti—O—Ti) if a small amount of H₂O, OH⁻, or O₂ is present in the reaction mixture. When tetrakis(2-propanolato)-titanium(IV), one of Du Pont's TYZOR[®] family of organic titanates [Du Pont name: tetra(isopropoxy)-titanium(IV)], is reacted with 2,2',2''-nitrilotriethanol (more commonly known as triethanolamine), at least two products, identified by X-ray single-crystal diffraction techniques, are formed. The simplest of these is presented here.

Experimental. Sample supplied by C. S. Rondestvedt Jr and G. Teufer; crystal approximately 0.25 × 0.25 × 0.25 mm, Syntex P3 diffractometer; low-temperature apparatus cooled crystal to 173 K; unit-cell parameters refined from Bragg angles of 49 reflections, 2θ 20–25°; 2711 reflections measured, ω scan (1° scan, 4–10° min⁻¹, $4 < 2\theta < 55^\circ$); four standard reflections every 200 reflections, only statistical variations noted; empirical absorption correction based on ψ scans, transmission coefficients 0.958–1.000. Structure solved by direct methods, refined by full-matrix least squares on F ; positions of hydrogen atoms initially idealized, later allowed to refine; all calculations with local modifications of the Enraf–Nonius SDP package of programs on a PDP-11/55 computer (Frenz, 1978); other computation and mathematical details (weighting scheme, atomic scattering factors, etc.) can be found elsewhere (Nugent & Harlow, 1979); 2088 reflections with $I > 3\sigma(I)$, 212 variables refined (Ti, O, N, and C anisotropic, H isotropic), $R_w = 0.033$, $S = 1.66$; * $\Delta\rho$ excursions $\leq 0.34 \text{ e } \text{\AA}^{-3}$ in final difference Fourier, the largest positive peaks were near the Ti atom.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38689 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Positional parameters are given in Table 1 and bond lengths and angles in Table 2.


As Fig. 1 clearly shows, the reaction product is a centrosymmetric dimer having a Ti:2-propanolate:nitrilotriethanolate ratio of 1:1:1. The titanium atoms have achieved a coordination number of 6 via an unsymmetrical Ti  Ti bridge. Considering the four oxygen atoms of the ethoxy arms as forming the base of an octahedron, the axial sites are occupied by the nitrogen atom and by the oxygen atom of the 2-propanolate group. Notably, these two axial bonds include the longest and shortest metal–ligand bond lengths in the structure; the Ti–N bond is 0.5 Å longer than the *trans* Ti–O(1) bond.

Table 1. Positional parameters and their e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)*
Ti	0.17018 (3)	0.15839 (3)	0.03974 (2)	1.176 (5)
O(1)	0.2656 (1)	0.0874 (1)	0.1148 (1)	1.89 (3)
O(11)	0.1967 (1)	0.3057 (1)	0.04375 (9)	1.28 (2)
O(12)	0.0711 (1)	0.1582 (1)	0.13638 (9)	1.65 (2)
O(13)	0.1236 (1)	0.0644 (1)	−0.0476 (1)	1.67 (3)
N	0.0121 (1)	0.2289 (1)	−0.0267 (1)	1.33 (3)
C(1)	0.2551 (2)	0.0360 (2)	0.2005 (1)	1.77 (4)
C(2)	0.3127 (2)	0.0940 (2)	0.2778 (2)	2.76 (5)
C(3)	0.2998 (2)	−0.0693 (2)	0.1912 (2)	3.09 (5)
C(11)	0.0183 (2)	0.3396 (2)	−0.0204 (1)	1.63 (3)
C(12)	0.1039 (2)	0.3688 (2)	0.0539 (1)	1.64 (4)
C(13)	−0.0772 (2)	0.1861 (2)	0.0284 (2)	1.74 (4)
C(14)	−0.0404 (2)	0.1860 (2)	0.1305 (1)	1.92 (4)
C(15)	0.0118 (2)	0.1902 (2)	−0.1228 (1)	1.89 (4)
C(16)	0.0428 (2)	0.0797 (2)	−0.1187 (2)	2.02 (4)

* Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$\frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}\cos\gamma + ac\beta_{13}\cos\beta + bc\beta_{23}\cos\alpha).$$

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s

Ti—O(1)	1.833 (1)	O(11)—C(12)	1.427 (2)
Ti—O(11)	1.998 (1)	O(12)—C(14)	1.414 (2)
Ti—O(11')	2.108 (1)	O(13)—C(16)	1.417 (2)
Ti—O(12)	1.872 (1)		
Ti—O(13)	1.856 (1)	N—C(11)	1.486 (2)
Ti—N	2.333 (1)	N—C(13)	1.483 (2)
		N—C(15)	1.477 (2)
Ti...Ti'	3.356 (1)		
		C(11)—C(12)	1.526 (2)
O(1)—C(1)	1.422 (2)	C(13)—C(14)	1.524 (2)
C(1)—C(2)	1.514 (3)	C(15)—C(16)	1.526 (3)
C(1)—C(3)	1.518 (3)		
O(1) Ti O(11)	113.20 (5)	Ti O(11) Ti'	109.66 (5)
O(1) Ti O(11')	87.95 (5)	Ti O(11) C(12)	117.2 (1)
O(1) Ti O(12)	88.69 (5)	Ti' O(11) C(12)	123.7 (1)
O(1) Ti O(13)	103.05 (5)	Ti O(12) C(14)	126.8 (1)
O(1) Ti N	163.33 (5)	Ti O(13) C(16)	125.8 (1)
O(11) Ti O(11')	70.34 (5)	Ti N C(11)	109.8 (1)
O(11) Ti O(12)	95.05 (5)	Ti N C(13)	103.9 (1)
O(11) Ti O(13)	137.26 (5)	Ti N C(15)	102.8 (1)
O(11) Ti N	75.23 (4)	O(11) C(12) C(11)	108.1 (1)
O(11') Ti O(12)	162.19 (5)	O(12) C(14) C(13)	108.4 (1)
O(11') Ti O(13)	89.87 (5)	O(13) C(16) C(15)	109.6 (1)
O(11') Ti N	108.65 (4)	N C(11) C(12)	109.3 (1)
O(12) Ti O(13)	108.02 (5)	N C(13) C(14)	108.3 (1)
O(12) Ti N	75.95 (4)	N C(15) C(16)	108.0 (1)
O(13) Ti N	76.20 (5)		
Ti O(1) C(1)	133.6 (1)		
O(1) C(1) C(2)	109.7 (1)		
O(1) C(1) C(3)	109.3 (2)		
C(2) C(1) C(3)	112.3 (2)		

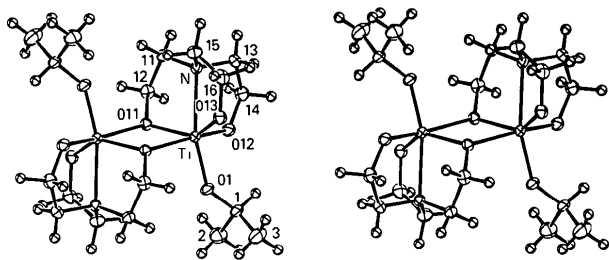


Fig. 1. Stereodrawing of $\{\text{Ti}[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3][(\text{CH}_2)_2\text{CHO}]\}_2$. The hydrogen atoms have been assigned arbitrary radii.

No other structures containing a (2,2',2''-nitriloethanolato)titanium(IV) moiety have been reported. Titanium complexes with nitrilotriacetate, a similar tetradentate with a central nitrogen atom and three oxygen atoms, have much longer Ti—O(non-bridging) bonds, 1.96–2.08 Å (Wieghardt, Quilitzsch, Weiss & Nuber, 1980; Schwarzenbach & Girgis, 1975); the ethanolate group, $-\text{CH}_2\text{CH}_2\text{O}^-$, clearly forms a stronger bond because the negative charge on the oxygen atom is not diluted by resonance as it is within the acetate group, $-\text{CH}_2\text{COO}^-$. The higher charge density placed on the Ti atom by the ethanolate groups produces a longer Ti—N bond in the present structure than in the

nitrilotriacetate complexes: 2.33 Å compared with a range of 2.27–2.31 Å.

The large difference in the Ti—O(non-bridging) and Ti—N bond lengths, 1.87 vs 2.33 Å, in the (nitrilotriethanolato)titanium moiety does not seem unusual when compared with similar bonds in nitrilotriethanolato complexes of other metals. $\text{Ge}(\text{C}_2\text{H}_5)_3[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]$ (Atovmyan, Bleidelis, Kemme & Shibaeva, 1970) and $\text{Si}(\text{C}_6\text{H}_5)_2[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]$ (Turley & Boer, 1968), for example, have bond lengths with even larger $M\text{—O}$ and $M\text{—N}$ differences: Ge—O, 1.75, Ge—N, 2.24; and Si—O, 1.66; Si—N, 2.19 Å.

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Acta Cryst. (1983). C**39**, 1346–1349

Structures Cristallines du [2.2.2]Paracyclophane (I) ($\text{C}_{24}\text{H}_{24}$) et de son Complexe avec le Perchlorate d'Argent (II) ($\text{C}_{24}\text{H}_{24}\cdot\text{AgClO}_4$)

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Abstract. (I): $M_r = 312.45$, Cc , $a = 18.700$ (8), $b = 6.332$ (6), $c = 18.456$ (8) Å, $\beta = 123.9$ (1)°, $V = 1813.9$ Å³, $Z = 4$, $D_x = 1.14$ Mg m⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.487$ mm⁻¹, $T = 153$ K, $F(000) = 672$; (II): $M_r = 519.77$, $P2_12_12_1$, $a = 11.507$ (7), $b = 18.069$ (8), $c = 10.435$ (7) Å, $V = 2169.6$ Å³, $Z = 4$, $D_x = 1.59$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.058$ mm⁻¹, $T = 293$ K, $F(000) = 1056$. The struc-

tures were refined to R values of 0.076 (I) and 0.062 (II) for 1245 and 1495 intensities respectively. In both cases, the conformations of the paracyclophane molecules are similar with respect to the orientation of the three aromatic rings around a threefold pseudo-axis of symmetry, the rings being parallel to that axis. In the complex, the Ag^+ ion lies on the threefold pseudo-axis, slightly off the cavity formed by the three rings.