Inorganica Chimica Acta, *175* (1990) 105–110

Crystal structure of tetraguanidinium tri(carbonato)oxotitanium(IV) dihydrate, $[C(NH_2)_3]_4[TiO(CO_3)_3]\cdot 2H_2O$

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(Received January 19, 1990; revised March 23, 1990)

Abstract

The title complex has been prepared and characterized by IR spectroscopy and X-ray crystallography. The crystals are monoclinic, space group $P2_1$, with $a = 9.2010(9)$, $b = 13.044(3)$, $c = 9.888(4)$ Å, $\beta = 109.35(2)°$ and $Z = 2$. The structure has been refined to $R_F = 0.038$ for 288 variables and 3385 observed Mo Kα reflections. The crystal consists of an assembly of $[C(NH_2)_3]^+$ cations, $[TiO(CO_3)_3]^{4-}$anions, and water molecules which are interlinked by hydrogen bonds to form a three-dimensional network. The coordination geometry about the titanium atom may be described as a distorted pentagonal bipyramid, the axial positions being occupied by the oxo ligand and an oxygen atom of one of the chelating bidentate carbonato ligands.

Introduction

Relatively few carbonato complexes of titanium(IV) are known. Recently Nabivanets and Omel'chenko reported the equilibrium constant for the formation of $[Ti_2(CO_3)_5(OH)_3]^{5-}$ in aqueous solution [1]. Ammonium titanium carbonate has been used to improve the manufacture of TiO_2 by thermal decomposition [2]. Owing to the high ratio of charge to ionic radius, normal salts of titanium(IV) cannot be prepared from aqueous solutions, which in general yield basic hydrolyzed species. A number of oxotitanium(IV) compounds have been isolated and were originally thought to contain discrete TiO^{2+} ions, but subsequent studies have shown that nearly all of them are polymeric in the solid state. For example, $TiOSO_4\cdot H_2O$ has infinite zigzag –Ti–O–Ti–O– chains [3], $TiO(acac)_2$ is a oxygen-bridged dimer [4], while $(NH_4)_2TiO(C_2O_4)_2\cdot H_2O$ contains cyclic tetrameric anions with a central eight-membered $(\text{–Ti–O–})_4$ ring [5]. On the other hand, Raman and ^{17}O NMR spectra have confirmed that in strong acid the TiO^{2+} ion is in equilibrium with $[Ti(OH)_2]^{2+}$ and $Ti^{4+}(aq)$ [6], and there are rare examples containing Ti=O bonds though they are mostly porphyrins and related complexes [7, 8]. In the present study, we prepared the title complex by the reaction of $TiCl_4$ with guanidinium carbonate in aqueous solution and characterized it via X-ray crystallography.

Experimental

Preparation

Titanium tetrachloride was dissolved in 4 M HCl to give a 1 M solution of titanium tetrachloride. Potassium hydrogen carbonate (4 g) was added to a saturated solution of $KHCO_3$ (50 ml), and 1 M titanium tetrachloride (19 ml) was introduced dropwise with stirring until the solution became clear. Subsequently, guanidinium carbonate (14 g) was dissolved in this solution. The final solution was filtered, and the filtrate at pH 8 was placed in a desiccator charged with silica gel. The crystals of the title complex were obtained from slow evaporation of this aqueous solution. *Anal.* Found: C, 16.18; H, 5.40; N, 31.90; O, 37.17; Ti, 9.14. Calc. for $[C(NH_2)_3]_4[TiO(CO_3)_3]\cdot 2H_2O$: C, 16.16; H, 5.42; N, 32.31; O, 36.90; Ti, 9.20%. IR spectra (nujol mull) were recorded in the region 3600–400 cm^{-1} with a Perkin Elmer-283 spectrophotometer.

X-ray structure analysis

Intensity data were collected on a Nicolet R3m/V diffractometer at room temperature. The unit cell

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and data collection parameters are listed in Table 1. Two standard reflections monitored after every 125 data measurements showed only random fluctuations within 1% of their mean values during data collection. The raw intensities were processed with the learnt-profile procedure [9] and absorption corrections were applied by fitting a pseudo ellipsoid to the ψ-scans of selected reflections over a range of 2θ angles [10].

Patterson superposition yielded the positions of most non-hydrogen atoms. The others and all hydrogen atoms were derived from subsequent difference Fourier syntheses. Non-hydrogen atoms were sujbected to anisotropic refinement, and hydrogen atoms were assigned appropriate isotropic thermal parameters and held fixed. The final cycles of refinement converged to $R_F = 0.038$ and $R_G = 0.048$ for 288 variables and 3385 observed reflections (see Table 1).

Computations were performed on a DEC MicroVAX-II computer with the SHELXTL-PLUS program package [11]. Analytic expressions of neutral atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [12]. The final atomic coordinates and thermal parameters are given in Table 2, and bond distances and angles in Table 3.

Discussion

Crystal structure

The title complex consists of discrete guanidinium cations, $[TiO(CO_3)_3]^{4-}$ anions and water molecules which are interlinked by hydrogen bonds to form a three-dimensional network (Fig. 1). The structure of the $[TiO(CO_3)_3]^{4-}$ complex and its hydrogen bonding interactions with neighboring groups are shown in Fig. 2. In this anion, the coordination geometry about the titanium(IV) atom may be described as a distorted pentagonal bipyramid, with the

TABLE 1. Data collection and processing parameters

Molecular formula	$[C(NH_2)_3]_4[TiO(CO_3)_3]\cdot 2H_2O$
Molecular weight	520.37
Color and habit	yellow plate
Unit cell parameters	
a (Å)	9.2010(9)
b (Å)	13.044(3)
c (Å)	9.888(4)
β (°)	109.35(2)
V (Å^3)	1119.7(5)
Z	2
$F(000)$	544
Density (exp.) (g/cm^3)	1.548
Density (calc.) (g/cm^3)	1.543
Space group	$P2_1$ (No. 4)
Radiation	graphite-monochromatized Mo Kα, $\lambda = 0.71073$ Å
Standard reflections	$(32\bar{1})$, $(42\bar{2})$
Intensity variation (%)	± 1
R_{int} (from merging of equiv. reflections)	0.015
Absorption coefficient (cm^{-1})	4.15
Crystal size (mm)	$0.60 \times 0.50 \times 0.26$
Mean μr	0.088
Transmission factors	0.748 to 0.817
Scan type; scan rate (° min^{-1})	ω–2θ; 2.49–15.63
Scan range (°)	0.70° below Kα_1 to 0.70° above Kα_2
Background counting	stationary counts for 0.4 times of scan time at each end of scan range
Collection range	h, k, $\pm l$; $2\theta_{max} = 65°$
Unique data measured	4214
Observed data with $\lvert F_o\rvert \geqslant 6\sigma(\lvert F_o\rvert)$, n	3385
No. variables, p	288
$R_F = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma\lvert F_o\rvert$	0.038
Weighting scheme	$w = [\sigma^2(F_o) + 0.0012\lvert F_o\rvert^2]^{-1}$
$R_G = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w\lvert F_o\rvert^2]^{1/2}$	0.048
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / (n-p)]^{1/2}$	1.077
Residual extrema in final difference map	+0.25 to −0.76 e Å^{-3}

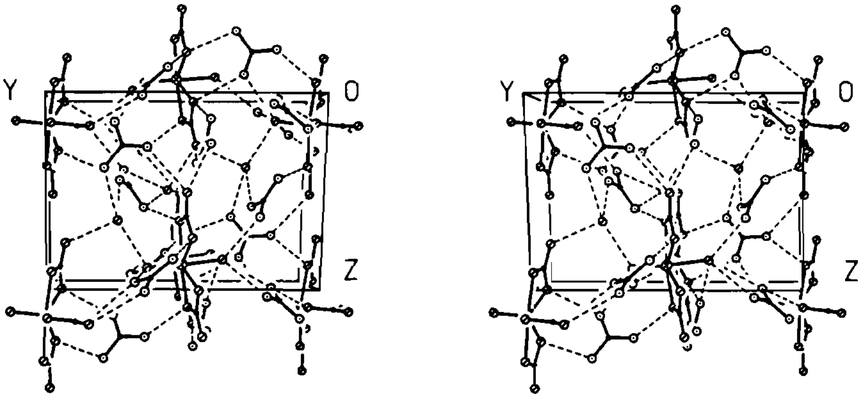

Fig. 1. Stereoview of the crystal structure of the title complex. The origin of the unit cell lies at the upper right corner, with *a* pointing towards the reader, *b* from right to left, and *c* downwards. Hydrogen bonds are indicated by broken lines.

TABLE 2. Atomic coordinates ($\times 10^5$ for Ti; $\times 10^4$ for other atoms) and equivalent isotropic temperature factors[a] ($Å^2 \times 10^4$ for Ti; $\times 10^3$ for other atoms)

Atom	*x*	*y*	*z*	U_{eq}
Ti	16179(4)	0	12588(4)	240(1)
O(1)	1315(3)	1271(2)	1090(2)	38(1)
C(1)	1639(3)	−141(2)	3825(3)	31(1)
O(2)	2865(2)	59(2)	3530(2)	37(1)
O(3)	451(2)	−335(2)	2686(2)	33(1)
O(4)	1551(3)	−153(2)	5056(2)	48(1)
C(2)	−174(3)	−513(2)	−1188(3)	32(1)
O(5)	1231(2)	−237(2)	−973(2)	35(1)
O(6)	−512(2)	−577(2)	−17(2)	35(1)
O(7)	−1139(3)	−699(2)	−2395(2)	47(1)
C(3)	3972(3)	−1091(2)	1413(3)	30(1)
O(8)	3867(2)	−101(2)	1267(2)	35(1)
O(9)	2736(2)	−1536(2)	1482(2)	32(1)
O(10)	5161(2)	−1575(2)	1464(3)	47(1)
C(4)	6909(3)	1223(2)	749(3)	33(1)
N(1)	7994(3)	1766(2)	480(3)	48(1)
N(2)	5436(3)	1460(3)	115(3)	49(1)
N(3)	7273(3)	459(2)	1679(3)	40(1)
C(5)	1299(3)	2236(2)	−2576(3)	32(1)
N(4)	1911(3)	1329(2)	−2646(3)	40(1)
N(5)	1015(3)	2516(2)	−1409(3)	43(1)
N(6)	992(4)	2875(3)	−3691(3)	48(1)
C(6)	5013(4)	−921(3)	7719(3)	40(1)
N(7)	6103(3)	−1124(3)	8951(3)	51(1)
N(8)	3548(3)	−1041(3)	7583(3)	51(1)
N(9)	5385(4)	−613(3)	6596(3)	56(1)
C(7)	5807(4)	1902(3)	5396(3)	42(1)
N(10)	7206(4)	2089(3)	6247(4)	62(1)
N(11)	4614(3)	2269(3)	5704(3)	51(1)
N(12)	5592(3)	1345(3)	4226(3)	55(1)
O(11)	1552(3)	2370(2)	3587(3)	52(1)
O(12)	−1368(3)	355(3)	−4838(3)	67(1)

[a] U_{eq} defined as one third of the trace of the orthogonalized U tensor.

oxo O(1) and carbonato O(9) atoms occupying the axial positions. The five equatorial oxygen atoms have a mean deviation of 0.102(4) Å from their least-squares plane and the titanium atom is displaced 0.302(2) Å from this plane toward the oxo ligand. This coordination polyhedron is very similar to that in the seven-coordinate titanium(IV) complex $TiCl(S_2CNMe_2)_3$ [13]. The short interatomic distance

TABLE 3. Bond lengths (Å) and bond angles (°)

Coordination geometry about Ti atom			
Ti–O(1)	1.680(2)	Ti–O(2)	2.158(2)
Ti–O(3)	2.083(2)	Ti–O(5)	2.138(2)
Ti–O(6)	2.088(2)	Ti–O(8)	2.071(2)
Ti–O(9)	2.230(2)		
O(1)–Ti–O(2)	94.7(1)	O(1)–Ti–O(3)	99.7(1)
O(2)–Ti–O(3)	61.2(1)	O(1)–Ti–O(5)	94.3(1)
O(2)–Ti–O(5)	158.2(1)	O(3)–Ti–O(5)	136.2(1)
O(1)–Ti–O(6)	101.8(1)	O(2)–Ti–O(6)	135.3(1)
O(3)–Ti–O(6)	75.1(1)	O(5)–Ti–O(6)	61.5(1)
O(1)–Ti–O(8)	101.3(1)	O(2)–Ti–O(8)	79.2(1)
O(3)–Ti–O(8)	136.3(1)	O(5)–Ti–O(8)	79.6(1)
O(6)–Ti–O(8)	135.7(1)	O(1)–Ti–O(9)	162.3(1)
O(2)–Ti–O(9)	82.0(1)	O(3)–Ti–O(9)	94.0(1)
O(5)–Ti–O(9)	83.4(1)	O(6)–Ti–O(9)	92.6(1)
O(8)–Ti–O(9)	61.0(1)	Ti–O(2)–C(1)	91.4(1)
Ti–O(3)–C(1)	94.1(2)	Ti–O(5)–C(2)	91.4(2)
Ti–O(6)–C(2)	93.5(2)	Ti–O(8)–C(3)	95.8(2)
Ti–O(9)–C(3)	88.7(2)		
Carbonato ligands			
C(1)–O(2)	1.282(4)	C(1)–O(3)	1.308(3)
C(1)–O(4)	1.246(4)	C(2)–O(5)	1.290(4)
C(2)–O(6)	1.297(4)	C(2)–O(7)	1.253(3)
C(3)–O(8)	1.300(4)	C(3)–O(9)	1.298(4)
C(3)–O(10)	1.249(4)		
O(2)–C(1)–O(3)	113.0(2)	O(2)–C(1)–O(4)	124.9(2)
O(3)–C(1)–O(4)	122.1(3)	O(5)–C(2)–O(6)	113.3(2)
O(5)–C(2)–O(7)	124.5(3)	O(6)–C(2)–O(7)	122.3(3)
O(8)–C(3)–O(9)	114.6(2)	O(8)–C(3)–O(10)	122.6(3)
O(9)–C(3)–O(10)	122.8(3)		
Guanidinium cations			
C(4)–N(1)	1.321(4)	C(4)–N(2)	1.328(4)
C(4)–N(3)	1.322(4)	C(5)–N(4)	1.322(4)
C(5)–N(5)	1.316(4)	C(5)–N(6)	1.336(4)
C(6)–N(7)	1.323(4)	C(6)–N(8)	1.320(4)
C(6)–N(9)	1.328(5)	C(7)–N(10)	1.307(4)
C(7)–N(11)	1.322(5)	C(7)–N(12)	1.325(5)
N(1)–C(4)–N(2)	120.1(3)	N(1)–C(4)–N(3)	120.7(2)
N(2)–C(4)–N(3)	119.2(3)	N(4)–C(5)–N(5)	120.4(3)
N(4)–C(5)–N(6)	119.5(3)	N(5)–C(5)–N(6)	120.1(3)
N(7)–C(6)–N(8)	120.5(3)	N(7)–C(6)–N(9)	120.2(3)
N(8)–C(6)–N(9)	119.3(3)	N(10)–C(7)–N(11)	120.0(3)
N(10)–C(7)–N(12)	119.7(4)	N(11)–C(7)–N(12)	120.3(3)

of 1.680(2) Å between Ti and O(1) is consistent with a $Ti{=}O$ double bond, as compared to those in $(Et_4N)_2TiOCl_4$ (1.79 Å) [14] and porphyrin complexes of Ti(IV) (about 1.62 Å) [15]. In the present structure, all three carbonato groups act as chelating bidentate ligands and, like the nitrato group does in $Ti(NO_3)_4$ [16] their dimensions differ from those of a discrete uncomplexed anion, having an average C–O distance of 1.296(4) Å for bonds adjacent to the titanium atom and 1.249(4) Å for the terminal C–O bond. Furthermore, the O–C–O bond angle involving both ligating oxygen atoms in each carbonato group has an average value of 113.6(2)°, considerably smaller than the remaining O–C–O angles at 123.2(3)°. All four independent guanidinium cations are trigonal planar (Fig. 2) with three equivalent C–N bonds (av. 1.323(4) Å) in each moiety, which are in excellent agreement with the literature values ($\bar{d}$(C–N) = 1.325(4) Å and $\bar{\alpha}$ = 120.9(9)° [17]).

One of the notable structural characteristics of the present complex is that the maximum possible number of hydrogen bonds are formed between the oxygen and nitrogen atoms. The oxo atom and nine oxygen atoms from three carbonato groups act as

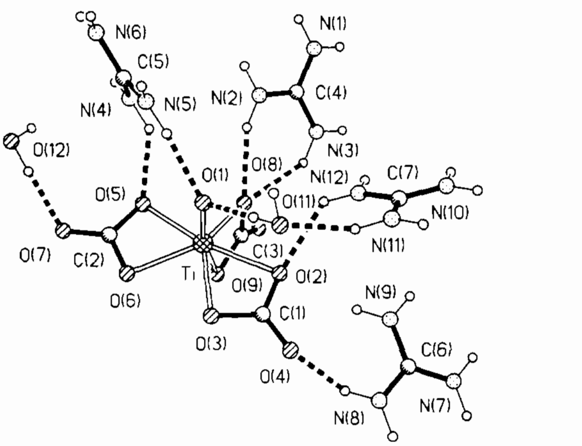

Fig. 2. Perspective view of the $[TiO(CO_3)_3]^{4-}$ anion showing its hydrogen bonding interactions with neighboring groups.

hydrogen bond acceptors, the twelve amino groups from four guanidinium cations as hydrogen bond donors, and the two water molecules (O(11) and O(12)) as both donors and acceptors. Geometrical details of the hydrogen-bonding scheme are given in Table 4.

IR spectra

The Ti=O stretching band at 875 cm^{-1} falls below the usual region of 972 to 890 cm^{-1} [18] because the oxo ligand is involved in the formation of three acceptor hydrogen bonds.

Since the splitting of the degenerate vibrations in a carbonato ligand is generally larger in the bidentate than in the unidentate mode [19], the large splitting (1381s, 1525s–1581s, br cm^{-1}), in conjunction with the appearance of a weak band at 1062 cm^{-1} and a medium band at 750 cm^{-1}, indicates that the carbonato ligands are bidentate which is in accord with the result of the X-ray structural analysis. The guanidinium cation exhibits infrared absorption bands at 1668 s δ(N–H) and 1143w μ(C–N) cm^{-1}. The very broad bands in the region of 3600–2800 cm^{-1} are assigned to the hydrogen-bonded amino groups and water molecules.

Supplementary material

Anisotropic temperature factors, hydrogen coordinates, hydrogen bond angles, and a table of observed and calculated structure factor amplitudes (19 pages) are available from author T.C.W. Mak on request.

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TABLE 4. Hydrogen bond distances (Å)[a]

O(1)···N(1a)	2.983(4)	O(1)···N(5)	2.892(4)
O(1)···O(11)	2.800(4)	O(2)···N(9)	3.267(4)
O(2)···N(12)	2.904(4)	O(3)···N(3a)	2.946(4)
O(3)···N(6b)	3.013(4)	O(4)···N(4c)	2.918(4)
O(4)···N(8)	2.815(4)	O(4)···O(12c)	2.802(4)
O(5)···N(4)	2.826(4)	O(5)···N(8d)	3.114(4)
O(6)···N(5b)	2.971(4)	O(6)···N(7e)	3.024(4)
O(7)···N(9e)	3.020(4)	O(7)···O(11b)	2.754(4)
O(7)···O(12)	2.726(4)	O(8)···N(2)	2.936(4)
O(8)···N(3)	3.111(4)	O(9)···N(1f)	2.873(4)
O(9)···N(10g)	2.860(4)	O(10)···N(2f)	2.956(4)
O(10)···N(7d)	2.950(4)	O(10)···N(11g)	3.126(4)
O(11)···N(6c)	2.978(4)	O(11)···N(11)	2.903(4)
O(12)···N(10e)	2.987(4)	O(12)···N(12e)	2.938(4)

[a] The acceptor atom precedes the donor atom in each hydrogen bond. Symmetry transformations: a $(-1+x, y, z)$; b $(-x, -\frac{1}{2}+y, -z)$; c $(x, y, 1+z)$; d $(x, y, -1+z)$; e $(-1+x, y, -1+z)$; f $(1-x, -\frac{1}{2}+y, -z)$; g $(1-x, -\frac{1}{2}+y, 1-z)$.

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