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Hydrothermal Synthesis and Characterization of Four Oxalatotitanates with $Ti_4O_4(C_2O_4)_8$ Tetramers as Basic Building Blocks

Yunlong Fu, Yunling Liu, Zhan Shi, Baozong Li, and Wenqin Pang[1]

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China

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Four oxalatotitanates have been prepared hydrothermally in the presence of organic amine and their structures solved by means of single-crystal X-ray diffraction. The compound $Ti_4O_4(C_2O_4)_8 \cdot 4C_2N_2H_{10} \cdot 4H_2O$ 1 crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.7587(7)$ Å, $b = 11.3180(7)$ Å, $c = 11.5940(8)$ Å, $\alpha = 114.8650(10)^\circ$, $\beta = 109.2980(10)^\circ$, $\gamma = 95.7160(10)^\circ$, $V = 1161.07(13)$ Å^3, $Z = 1$, $R = 0.0357$, w$R = 0.1019$. The compound $Ti_4O_4(C_2O_4)_8 \cdot 4C_4N_2H_{12} \cdot 8H_2O$ 2 crystallizes in the tetragonal space group $I4(1)/a$ with $a = 13.2270(10)$ Å, $b = 13.2270(10)$ Å, $c = 32.799(4)$ Å, $V = 5738.2(9)$ Å^3, $Z = 4$, $R = 0.0529$, w$R = 0.1496$. The compound $Ti_4O_4(C_2O_4)_8 \cdot 4C_6N_2H_{14} \cdot 10H_2O$ 3 crystallizes in the monoclinic space group $P2(1)/c$ with $a = 13.1613(7)$ Å, $b = 18.2394(11)$ Å, $c = 13.8579(7)$ Å, $\alpha = 90^\circ$, $\beta = 104.8600(10)^\circ$, $\gamma = 90^\circ$, $V = 3215.4(3)$ Å^3, $Z = 2$, $R = 0.0445$, w$R = 0.1188$. These compounds are all composed of $Ti_4O_4(C_2O_4)_8$ tetramer anions and protonated organic amine cations. The fourth compound $Ti_4O_4(C_2O_4)_7 \cdot 3C_4N_2H_{12} \cdot 2H_2O$ 4 crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 9.5187(13)$ Å, $b = 11.4926(15)$ Å, $c = 11.6349(15)$ Å, $\alpha = 67.405(3)^\circ$, $\beta = 81.407(3)^\circ$, $\gamma = 66.906(3)^\circ$, $V = 1080.9(2)$ Å^3, $Z = 1$, $R = 0.0356$, w$R = 0.0932$. For 4, the $Ti_4O_4(C_2O_4)_8$ tetramers are connected by sharing the oxalates as bridging ligands and form a one-dimensional chain with negative charges which are neutralized by protonated piperazine cations. The as-synthesized products are characterized by X-ray powder diffraction, IR spectroscopy, inductively coupled plasma analysis, thermogravimetric analysis, and differential thermal analysis. © 2002 Elsevier Science (USA)

Key Words: **hydrothermal synthesis; characterization; oxalatotitanates; tetramer; 1D chain.**

INTRODUCTION

Inorganic open-framework materials, in particular those formed by metal phosphates, have been investigated widely during the past decade (1, 2). The metal phosphates with an open framework are generally synthesized hydrothermally in the presence of organic amines. In the past few years considerable efforts have been devoted to designing open-framework inorganic materials other than phosphates, such as chalcogenides, pnictides, cyanides, and thiopnictides (3, 4). Due to the multidentate character of these groups, some materials composed of metal carboxylates have been made wherein the carboxylates cross-link the extended metal–oxygen networks, giving rise to a three-dimensional connectivity with channels (5–9). The recent reports of novel tin(II) oxalates and zinc oxalates with open architecture synthesized in the presence of structure-directing amines showed more possibilities in the synthesis of new materials with an open framework (10–12). Hence, we made some attempts to synthesize titanium oxalates in the presence of organic amines. Although transition metal oxalates with layered and other architectures containing amines and layered titanium phosphates pillared with organic compounds have been reported (13–16), few titanium oxalates of well-defined structures with organic amine cations and one-dimensional chains have been reported.

Titanium oxalates are widely used as precursors in the synthesis of electronic and ceramic materials (17, 18). Their compositions and structures have been studied widely in recent years (19, 20). More attention is focused on the structure of titanium oxo clusters and relevant compounds due to their role in the mixed-valence systems, as models for heterogeneous catalysts, and in the research of sol–gel process (21, 22). In this paper we report the synthesis and characterization of four novel oxalatotitanates with $Ti_4O_4(C_2O_4)_8$ tetramers as basic building blocks.

EXPERIMENTAL

Synthesis and Characterization

The compounds were hydrothermally synthesized from a mixture of TBOT (tetrabutyl titanate, 99%), oxalic acid ($H_2C_2O_4 \cdot 2H_2O$, 99.8%), organic amine [ethylenediamine (en, $C_2N_2H_8$), piperazine (pip, $C_4N_2H_{10}$), and 1,4-diazabicyclo[2.2.2]octane (dabco, $C_6N_2H_{12}$), AR, 99%], and distilled water. The compositions of the starting mixtures

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[1] To whom the correspondence should be addressed. Fax: + 86-431-5671974. E-mail: wqpang@mail.jlu.edu.cn.

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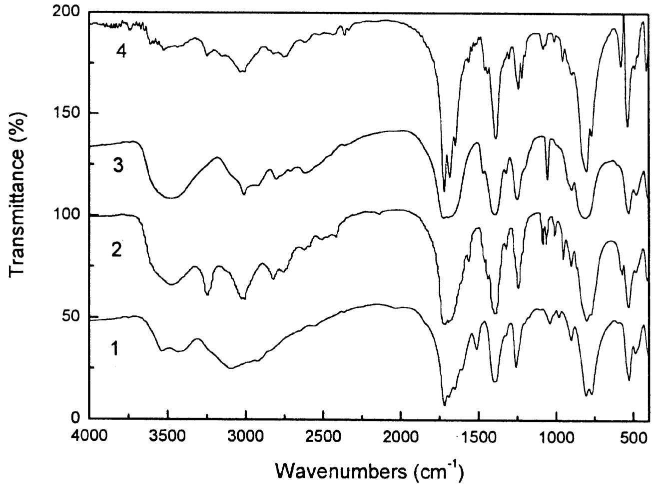


FIG. 1. IR spectra of **1**, **2**, **3**, and **4**.

for **1–4** are TBOT (1.7 ml):$H_2C_2O_4 \cdot 2H_2O$ (2.5 g):en (0.4 ml):H_2O (10 ml), TBOT (1.7 ml):$H_2C_2O_4 \cdot 2H_2O$ (2.5 g):pip (0.5 ml):H_2O (10 ml), TBOT (1.7 ml):$H_2C_2O_4 \cdot 2H_2O$ (2.5 g):dabco (0.6 ml):H_2O (10 ml), and TBOT (1.7 ml):$H_2C_2O_4 \cdot 2H_2O$ (3.8 g):pip (0.5 g):H_2O (10 ml), respectively. Each mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 393 K for 3 days under autogenous pressure. The respective products were recovered by filtration, washed thoroughly with distilled water, and dried at room temperature. For **1**, yield: 1.60 g, calcd C 22.51, H 3.75, N 8.75, Ti 15.0%, found C 22.12, H 3.79, N 8.73, Ti 14.8%. For **2**, yield: 1.80 g, calcd C 24.88, H 4.14, N 7.26, Ti 12.40%, found C 24.76, H 4.10, N 7.22, Ti 12.36%. For **3**, yield: 1.81 g, calcd. C 30.09, H 4.81, N 7.02, Ti 11.99%, found C 30.21, H 4.72, N 7.07, Ti 12.02%. For **4**, yield: 1.90 g, calcd C 26.64, H 3.45, N 7.17, Ti 16.33%, found C 26.70, H 3.35, N 7.33, Ti 16.35%. IR for **1–4** (Fig. 1): ca 3500 cm^{-1} (br, m), 1700 cm^{-1} (s), 1450 cm^{-1} (s), 1250 cm^{-1} (s), 800 cm^{-1} (s), and 500 cm^{-1} (m).

Powder X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count time was 4 s. The element analyses were performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300 DV ICP spectrometer. The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using

TABLE 1
Crystal Data and Structure Refinement for 1, 2, 3, and 4

Empirical formula	$Ti_4O_4(C_2O_4)_8 \cdot 4C_2N_2H_{10} \cdot 4H_2O$	$Ti_4O_4(C_2O_4)_8 \cdot 4C_4N_2H_{12} \cdot 8H_2O$	$Ti_4O_4(C_2O_4)_8 \cdot 4C_6N_2H_{14} \cdot 10H_2O$	$Ti_4O_4(C_2O_4)_7 \cdot 3C_4N_2H_{12} \cdot 2H_2O$
Formula weight	1280.30	1448.45	1596.69	1172.24
Crystal system	Triclinic	Tetragonal	Monoclinic	Triclinic
Space group	$P\bar{1}$	$I4(1)/a$	$P2(1)/c$	$P\bar{1}$
a (Å)	10.7587(7)	13.2270(10)	13.1613(7)	9.5187(13)
b (Å)	11.3180(7)	13.2270(10)	18.2394(11)	11.4926(15)
c (Å)	11.5940(8)	32.799(4)	13.8579(7)	11.6349(15)
α (°)	114.8650(10)	90	90	67.405(3)
β (°)	109.2980(10)	90	104.8600(10)	81.407(3)
γ (°)	95.7160(10)	90	90	66.906(3)
V (Å^3)	1161.07(13)	5738.2(9)	3215.4(3)	1080.9(2)
Z	1	4	2	1
D_c (g cm^{-3})	1.831	1.677	1.649	1.801
μ (mm^{-1})	0.793	0.657	0.597	0.831
F(000)	656	2976	1656	598
Crystal size (mm)	0.42 × 0.24 × 0.23	0.40 × 0.20 × 0.20	0.40 × 0.40 × 0.40	0.40 × 0.20 × 0.12
θ Range (°)	2.06–23.24	1.66–23.26	1.60–23.28	1.90–23.27
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 12$, $-12 \le l \le 9$	$-12 \le h \le 14$, $-14 \le k \le 14$, $-36 \le l \le 36$	$-14 \le h \le 12$, $-20 \le k \le 16$, $-13 \le l \le 15$	$-10 \le h \le 10$, $-11 \le k \le 12$, $-12 \le l \le 12$
Reflections collected/unique	5697/3299 [R(int) = 0.0221]	14042/2062 [R(int) = 0.0604]	15580/4624 [R(int) = 0.0376]	5330/3092 [R(int) = 0.0241]
Absorption correction	Empirical	Empirical	Empirical	Empirical
Max. and min. transmission	0.6932 and 0.4514	0.6932 and 0.5396	0.6932 and 0.4378	0.6932 and 0.5143
Data/restraints/parameters	3299/0/343	2062/0/199	4624/0/442	3092/0/316
Goodness-of-fit on F^2	1.044	1.051	1.029	1.021
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0357$ $wR2 = 0.1019$	$R1 = 0.0529$ $wR2 = 0.1496$	$R1 = 0.0445$ $wR2 = 0.1188$	$R1 = 0.0356$ $wR2 = 0.0932$
R indices (all data)	$R1 = 0.0429$ $wR2 = 0.1068$	$R1 = 0.0761$ $wR2 = 0.1641$	$R1 = 0.0570$ $wR2 = 0.1272$	$R1 = 0.0478$ $wR2 = 0.0988$
Largest diff. peak and hole	0.525, -0.344 e·Å^{-3}	0.790, -0.510 e·Å^{-3}	0.523, -0.303 e·Å^{-3}	0.381, -0.327 e·Å^{-3}

KBr pellets. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer and a Perkin-Elmer DTA 1700 differential thermal analyzer, respectively, with a heating rate of 20°C min^{-1}.

Determination of Crystal Structure

The crystals were mounted on a glass fiber on a Siemens Smart CCD diffractometer equipped for graphite-monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation. Data processing was accomplished with the SAINT processing program (23). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL Version 5.1 (24). All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the amine were placed geometrically ($d_{\text{N–H}} = 0.89$ Å, $d_{\text{C–H}} = 0.97$ Å), and allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. The detailed crystallographic data are listed in Table 1, atomic coordinates in Tables 2–5, and selected bond lengths for **1**–**4** are listed in Table 6.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for 1[a]

	x	y	z	U(eq)
Ti(1)	5061(1)	7468(1)	1375(1)	23(1)
Ti(2)	7292(1)	5534(1)	1497(1)	23(1)
O(1)	6590(2)	6889(2)	1413(2)	29(1)
O(2)	3798(2)	5839(2)	291(2)	29(1)
O(3)	5099(2)	7977(2)	− 56(2)	29(1)
O(4)	3560(2)	8509(2)	1235(2)	30(1)
O(5)	3983(2)	8655(2)	− 1549(2)	37(1)
O(6)	2393(2)	9422(2)	22(3)	40(1)
O(7)	6382(2)	9423(2)	2914(2)	30(1)
O(8)	5040(2)	7605(2)	3154(2)	30(1)
O(9)	7543(3)	10727(2)	5208(3)	48(1)
O(10)	5987(3)	8829(2)	5493(2)	48(1)
O(11)	8525(2)	6808(2)	3619(2)	35(1)
O(12)	6255(2)	4991(2)	2431(2)	28(1)
O(13)	8689(3)	7354(3)	5755(3)	58(1)
O(14)	6095(2)	5480(2)	4436(2)	36(1)
O(15)	8917(2)	6167(2)	1242(2)	29(1)
O(16)	8428(2)	4204(2)	1733(2)	32(1)
O(17)	11034(2)	6048(3)	1508(3)	42(1)
O(18)	10307(3)	3622(3)	1579(4)	70(1)
N(1)	3226(3)	4920(3)	2404(4)	46(1)
N(2)	4443(3)	2683(3)	3108(3)	35(1)
N(3)	8633(3)	10584(3)	2561(3)	39(1)
N(4)	11310(3)	8789(3)	2051(3)	40(1)
C(1)	3045(4)	3467(4)	1520(4)	37(1)
C(2)	3040(3)	2643(3)	2255(4)	35(1)
C(3)	9379(4)	9544(4)	2512(4)	39(1)
C(4)	10342(4)	9588(4)	1825(4)	38(1)
C(5)	4166(3)	8476(3)	− 546(3)	28(1)
C(6)	3272(3)	8844(3)	279(3)	28(1)
C(7)	6672(3)	9721(3)	4177(3)	31(1)
C(8)	5839(3)	8652(3)	4337(3)	31(1)
C(9)	8096(3)	6716(3)	4482(3)	32(1)
C(10)	6701(3)	5651(3)	3776(3)	26(1)
C(11)	9917(3)	5625(3)	1445(3)	31(1)
C(12)	9557(3)	4355(4)	1595(4)	37(1)
O(1W)	8879(3)	3738(4)	3977(3)	73(1)
O(2W)	2801(3)	6701(3)	4760(3)	63(1)

[a] U(equiv) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for 2[a]

	x	y	z	U(eq)
Ti(1)	1691(1)	1966(1)	1122(1)	30(1)
O(1)	1624(3)	2507(2)	561(1)	44(1)
O(2)	2417(4)	3319(4)	66(1)	87(2)
O(3)	3077(3)	2725(3)	1064(1)	55(1)
O(4)	4018(4)	3541(4)	609(2)	120(2)
O(5)	2533(2)	777(2)	877(1)	43(1)
O(6)	3623(4)	− 440(3)	1030(1)	79(1)
O(7)	2276(2)	1301(2)	1616(1)	38(1)
O(8)	3239(3)	53(3)	1850(1)	77(1)
O(9)	530(2)	1261(2)	1073(1)	36(1)
N(1)	5819(4)	5451(4)	212(2)	67(2)
N(2)	407(4)	9484(4)	337(2)	71(2)
C(1)	2374(5)	2970(4)	408(2)	54(2)
C(2)	3243(5)	3111(4)	707(2)	67(2)
C(3)	3023(4)	238(4)	1124(2)	48(1)
C(4)	2858(4)	522(4)	1570(2)	45(1)
C(5)	4131(4)	5609(5)	− 83(2)	63(2)
C(6)	4759(5)	5774(5)	284(2)	64(2)
C(7)	− 304(5)	8968(5)	49(2)	67(2)
C(8)	995(4)	10282(5)	135(2)	57(2)
O(1W)	1390(5)	8036(5)	788(2)	149(3)
O(2W)	5020(6)	− 1178(8)	1689(3)	228(5)

[a] U(equiv) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

Synthesis and Characterization

The experimental results showed that the reaction temperature is critical for the crystallization of the four products. If the temperature is higher than 140°C, the final product is titanium dioxide. In addition, a high concentration of oxalic acid in the initial mixture will lead to the formation of $\mathrm{Ti(C_2O_4)_3^{2-}}$, and a lower concentration of oxalic acid or a higher content of organic amine in the initial mixture gives rise to the amorphous gel. Interestingly, with the increase of piperazine in the initial mixture, the structure of the products changes from one-dimensional chain to zero-dimensional cluster. The powder XRD patterns of the as-synthesized compounds and the patterns simulated on the basis of the single-crystal structures are presented in Fig. 2. Consistent with the single-crystal analysis, the elemental analysis results also demonstrate that the solid samples of the as-synthesized compounds take on the compositions of $Ti_4O_4(C_2O_4)_8 \cdot 4C_2N_2H_{10} \cdot 4H_2O$ **1**, $Ti_4O_4(C_2O_4)_8 \cdot 4C_4N_2H_{12} \cdot 8H_2O$ **2**, $Ti_4O_4(C_2O_4)_8 \cdot 4C_6N_2H_{14} \cdot 10H_2O$ **3**, and $Ti_4O_4(C_2O_4)_7 \cdot 3C_4N_2H_{12} \cdot 2H_2O$ **4**.

TABLE 4
Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 3[a]

	x	*y*	*z*	*U*(eq)
Ti(1)	6408(1)	402(1)	4228(1)	28(1)
Ti(2)	3678(1)	48(1)	3322(1)	29(1)
O(1)	5005(2)	385(1)	3869(2)	38(1)
O(2)	6665(2)	254(1)	5560(2)	39(1)
O(3)	6555(2)	– 640(1)	3816(2)	40(1)
O(4)	8020(2)	315(1)	4300(2)	39(1)
O(5)	7652(2)	– 1496(2)	3536(2)	58(1)
O(6)	9193(2)	– 397(2)	3871(3)	74(1)
O(7)	6734(2)	1468(1)	4373(2)	36(1)
O(8)	6421(2)	724(2)	2754(2)	44(1)
O(9)	7566(3)	2354(2)	3768(2)	65(1)
O(10)	7089(2)	1597(2)	1975(2)	65(1)
O(11)	4031(2)	– 977(1)	3039(2)	37(1)
O(12)	3890(2)	120(1)	1879(2)	41(1)
O(13)	4879(2)	– 1645(2)	2144(2)	54(1)
O(14)	4396(3)	– 533(2)	721(2)	64(1)
O(15)	2118(2)	– 71(2)	2530(2)	44(1)
O(16)	3153(2)	1079(1)	3193(2)	41(1)
O(17)	612(3)	532(3)	2079(5)	152(3)
O(18)	1788(3)	1796(2)	2684(5)	162(3)
N(1)	– 1272(3)	2442(2)	7109(3)	50(1)
N(2)	– 57(2)	1631(2)	6528(2)	40(1)
N(3)	3830(3)	2632(2)	745(3)	63(1)
N(4)	4422(2)	1733(2)	– 319(2)	39(1)
C(1)	7456(3)	– 869(2)	3747(3)	41(1)
C(2)	8322(3)	– 276(2)	3988(3)	41(1)
C(3)	7090(3)	1780(2)	3681(3)	38(1)
C(4)	6863(3)	1339(2)	2711(3)	42(1)
C(5)	4412(3)	– 1097(2)	2280(3)	38(1)
C(6)	4225(3)	– 453(2)	1540(3)	41(1)
C(7)	1561(4)	500(3)	2408(4)	69(1)
C(8)	2191(4)	1198(3)	2778(4)	69(1)
C(9)	– 400(4)	2232(3)	7969(4)	76(2)
C(10)	378(4)	1769(3)	7592(4)	69(1)
C(11)	– 1854(3)	1793(3)	6658(4)	68(1)
C(12)	– 1092(3)	1276(3)	6348(4)	71(2)
C(13)	– 840(4)	2842(3)	6375(5)	77(2)
C(14)	– 144(4)	2329(3)	5966(4)	69(1)
C(15)	2936(5)	2429(4)	– 125(5)	98(2)
C(16)	3343(4)	1948(3)	– 822(4)	71(1)
C(17)	4635(5)	2969(3)	340(4)	84(2)
C(18)	5114(5)	2385(3)	– 175(4)	81(2)
C(19)	4208(4)	1982(3)	1338(3)	67(1)
C(20)	4467(5)	1401(3)	666(3)	67(1)
O(1W)	– 8(7)	1151(3)	3941(6)	194(3)
O(2W)	3218(4)	144(2)	8876(3)	102(1)
O(3W)	1081(8)	1262(5)	53(6)	229(4)
O(4W)	1213(6)	69(5)	8980(6)	206(4)
O(5W)	8963(16)	913(6)	9479(10)	416(11)

[a] *U*(equiv) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5
Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 4[a]

	x	*y*	*z*	*U*(eq)
Ti(1)	72(1)	8598(1)	7153(1)	22(1)
Ti(2)	2874(1)	8916(1)	4846(1)	23(1)
O(1)	1365(2)	8566(2)	5792(2)	28(1)
O(2)	– 1752(2)	9529(2)	6412(2)	27(1)
O(3)	2017(2)	7866(2)	8246(2)	28(1)
O(4)	12(2)	10239(2)	7376(2)	31(1)
O(5)	3436(3)	8530(2)	9041(3)	47(1)
O(6)	1081(3)	11097(2)	8260(3)	51(1)
O(7)	271(3)	6690(2)	7423(2)	30(1)
O(8)	– 915(3)	8005(2)	8883(2)	29(1)
O(9)	– 795(3)	5159(2)	8436(3)	46(1)
O(10)	– 2126(3)	6618(3)	10001(2)	43(1)
O(11)	3506(2)	7679(2)	3915(2)	30(1)
O(12)	4604(2)	7278(2)	5952(2)	32(1)
O(13)	5576(3)	6069(3)	3520(2)	50(1)
O(14)	6721(3)	5555(3)	5823(2)	48(1)
O(15)	3312(2)	9920(2)	5784(2)	27(1)
O(16)	4969(2)	9350(2)	3898(2)	29(1)
N(1)	880(3)	5315(3)	5661(3)	40(1)
N(2)	3384(3)	10472(3)	– 81(3)	32(1)
N(3)	– 3433(3)	4816(3)	10037(3)	38(1)
C(1)	2311(4)	8737(3)	8487(3)	31(1)
C(2)	1057(4)	10166(3)	8020(3)	30(1)
C(3)	– 559(4)	6153(3)	8295(3)	29(1)
C(4)	– 1275(4)	6968(3)	9162(3)	28(1)
C(5)	4846(4)	6706(3)	4170(3)	33(1)
C(6)	5467(4)	6458(4)	5431(3)	32(1)
C(7)	5474(4)	9833(3)	4458(3)	24(1)
C(8)	512(5)	4066(4)	6236(3)	44(1)
C(9)	– 308(4)	6421(4)	4740(4)	44(1)
C(10)	5726(4)	8859(4)	1096(3)	38(1)
C(11)	4146(4)	9867(4)	1149(3)	34(1)
C(12)	– 4513(5)	5157(4)	11024(3)	43(1)
C(13)	– 4245(4)	5371(4)	8818(3)	40(1)
O(1W)	– 2320(5)	12602(5)	8319(4)	117(2)

[a] *U*(equiv) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The TGA curves (Fig. 3) of the four compounds show two steps of weight loss corresponding to the loss of lattice water from 100 to 150°C and decomposition of $Ti_4O_4(C_2O_4)_8$ and organic amines from 180 to 500°C. The total weight loss of each compound (75.5% for **1**, 77.9% for **2**, 79.4% for **3**, and 72.9% for **4**) is also consistent with the calculated data (75.3% for **1**, 78.4% for **2**, 79.4% for **3**, and 72.7% for **4**). The DTA curve of each product exhibits mainly two endothermic peaks at ca. 140°C and 300°C corresponding to the loss of water, oxalates, and protonated amine, respectively.

TABLE 6
Selected Bond Lengths (Å) for Compounds 1, 2, 3, and 4

Compound **1**					
Ti(1)–O(1)	1.824(2)	Ti(1)–O(2)	1.802(2)		
Ti(2)–O(1)	1.800(2)	O(2)–Ti(2)*a*	1.846(2)		
Ti(1)–O(3)	1.982(2)	O(3)–C(5)	1.287(4)	O(5)–C(5)	1.220(4)
Ti(1)–O(4)	2.096(2)	O(4)–C(6)	1.272(4)	O(6)–C(6)	1.229(4)
Ti(1)–O(7)	2.116(2)	O(7)–C(7)	1.272(4)	O(9)–C(7)	1.227(4)
Ti(1)–O(8)	2.010(2)	O(8)–C(8)	1.294(4)	O(10)–C(8)	1.220(4)
Ti(2)–O(11)	2.091(2)	O(11)–C(9)	1.268(4)	O(13)–C(9)	1.224(4)
Ti(2)–O(12)	2.005(2)	O(12)–C(10)	1.294(4)	O(14)–C(10)	1.215(4)
Ti(2)–O(15)	1.982(2)	O(15)–C(11)	1.294(4)	O(17)–C(11)	1.216(4)
Ti(2)–O(16)	2.079(2)	O(16)–C(12)	1.281(4)	O(18)–C(12)	1.213(4)
Compound **2**					
Ti(1)–O(9)	1.804(3)	Ti(1)–O(9)*b*	1.826(3)		
Ti(1)–O(1)	1.976(3)	O(1)–C(1)	1.269(6)	O(2)–C(1)	1.217(7)
Ti(1)–O(3)	2.099(4)	O(3)–C(2)	1.297(7)	O(4)–C(2)	1.215(7)
Ti(1)–O(5)	2.089(3)	O(5)–C(3)	1.259(6)	O(6)–C(3)	1.237(6)
Ti(1)–O(7)	1.999(3)	O(7)–C(4)	1.295(6)	O(8)–C(4)	1.217(6)
Compound **3**					
Ti(1)–O(1)	1.785(2)	Ti(1)–O(2)	1.809(2)		
Ti(2)–O(1)	1.824(2)	Ti(2)–O(2)*c*	1.807(2)		
Ti(1)–O(3)	2.009(2)	O(3)–C(1)	1.283(4)	O(5)–C(1)	1.225(5)
Ti(1)–O(4)	2.104(2)	O(4)–C(2)	1.262(4)	O(6)–C(2)	1.218(4)
Ti(1)–O(7)	1.990(2)	O(7)–C(3)	1.301(4)	O(9)–C(3)	1.210(4)
Ti(1)–O(8)	2.130(2)	O(8)–C(4)	1.272(5)	O(10)–C(4)	1.226(4)
Ti(2)–O(11)	1.989(2)	O(11)–C(5)	1.294(4)	O(13)–C(5)	1.213(4)
Ti(2)–O(12)	2.093(3)	O(12)–C(6)	1.271(5)	O(14)–C(6)	1.221(4)
Ti(2)–O(15)	2.076(3)	O(15)–C(7)	1.259(5)	O(17)–C(7)	1.217(6)
Ti(2)–O(16)	1.996(3)	O(16)–C(8)	1.267(5)	O(18)–C(8)	1.207(6)
Compound **4**					
Ti(1)–O(1)	1.857(2)	Ti(1)–O(2)	1.784(2)		
Ti(2)–O(1)	1.754(2)	Ti(2)–O(2)*d*	1.854(2)		
Ti(1)–O(3)	2.101(2)	O(3)–C(1)	1.272(4)	O(5)–C(1)	1.227(4)
Ti(1)–O(4)	1.978(2)	O(4)–C(2)	1.292(4)	O(6)–C(2)	1.214(4)
Ti(1)–O(7)	2.026(2)	O(7)–C(3)	1.302(4)	O(9)–C(3)	1.196(4)
Ti(1)–O(8)	2.069(2)	O(8)–C(4)	1.278(4)	O(10)–C(4)	1.219(4)
Ti(2)–O(11)	1.967(2)	O(11)–C(5)	1.306(4)	O(13)–C(5)	1.208(4)
Ti(2)–O(12)	2.062(2)	O(12)–C(6)	1.270(4)	O(14)–C(6)	1.240(4)
Ti(2)–O(15)	2.045(2)	O(15)–C(7)*e*	1.262(4)	C(7)–O(15)*e*	1.262(4)
Ti(2)–O(16)	2.267(2)	O(16)–C(7)	1.243(4)		

Note. Symmetry transformations used to generate equivalent atoms: *a*, $-x+1, -y+1, -z$; *b*, $-y+\frac{1}{4}, x+\frac{1}{4}, -z+\frac{1}{4}$; *c*, $-x+1, -y, -z+1$; *d*, $-x, -y+2, -z+1$; *e*, $-x+1, -y+2, -z+1$.

After calcination at 700°C for 2 hours, the as-synthesized compounds decompose and convert to rutile phase (JCPDS 01-1292), which has been confirmed by powder X-ray diffraction.

Description of Structure

Compounds **1**, **2**, and **3** are all composed of $[Ti_4O_4(C_2O_4)_8]^{8-}$ anions and diprotonated organic amine cations. They crystallize in $P\bar{1}$, $I4(1)/a$, and $P2(1)/c$ space groups, respectively. Their atom-bonding schemes are shown in Fig. 4. The structure of the $[Ti_4O_4(C_2O_4)_8]$ tetramer was first described by van de Velde *et al.* in 1974 (20), and repeated at least a half dozen times by others later. Li Xiaopin *et al.* reported the crystal structure of three potassium titanyl oxalates (25). However, the crystal structures of compounds **1**–**3** have not been reported, and **4** is a new compound representing a novel model for linking the tetrameric clusters into a 1-D chain.

In this paper, we describe the structure of **4** mainly for the sake of conciseness. The compound **4** crystallizes in the triclinic space group $P\bar{1}$ and its asymmetric unit contains 35 nonhydrogen atoms. The atom-bonding scheme of **4** is

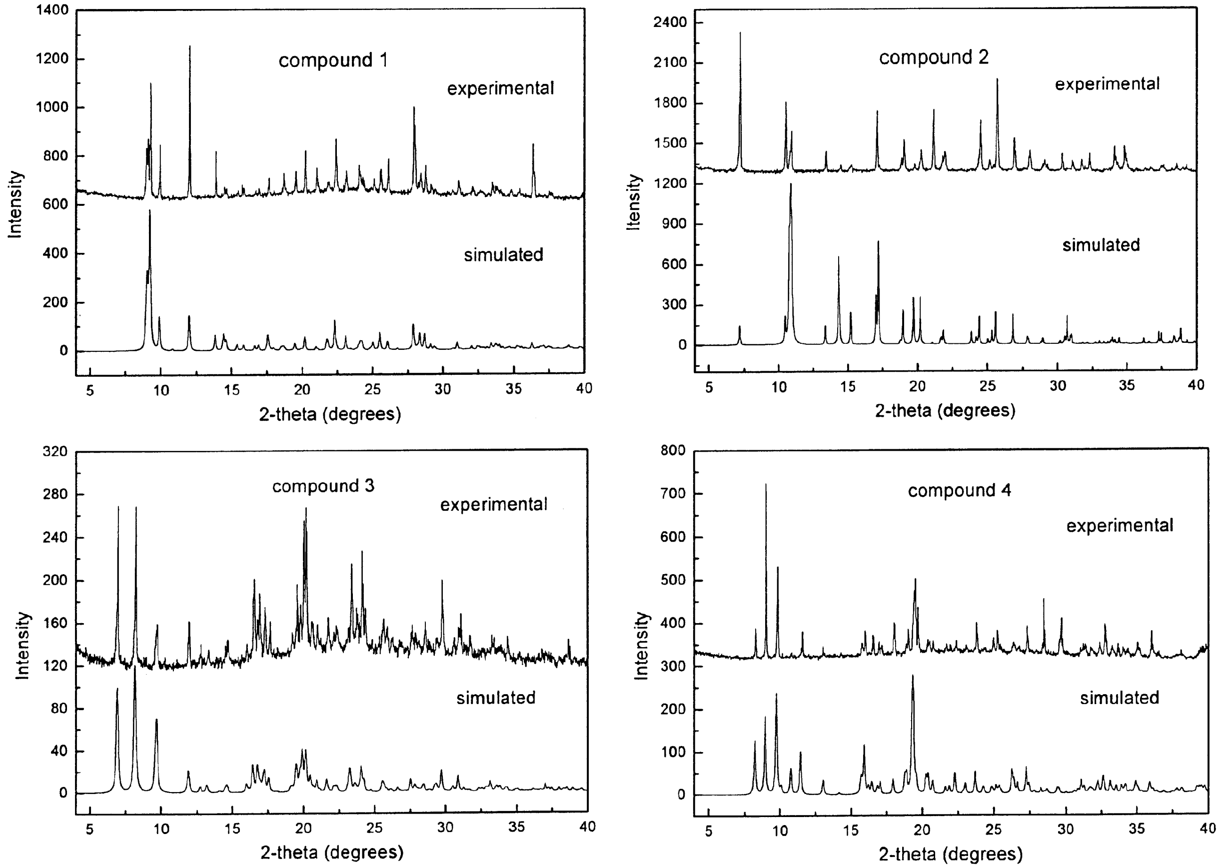


FIG. 2. Experimental and simulated powder X-ray diffraction patterns of **1**, **2**, **3**, and **4**.

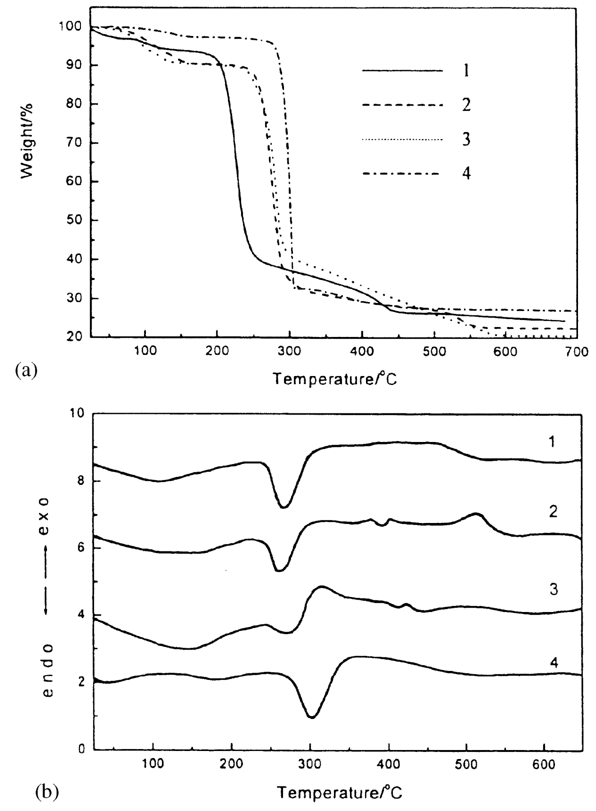
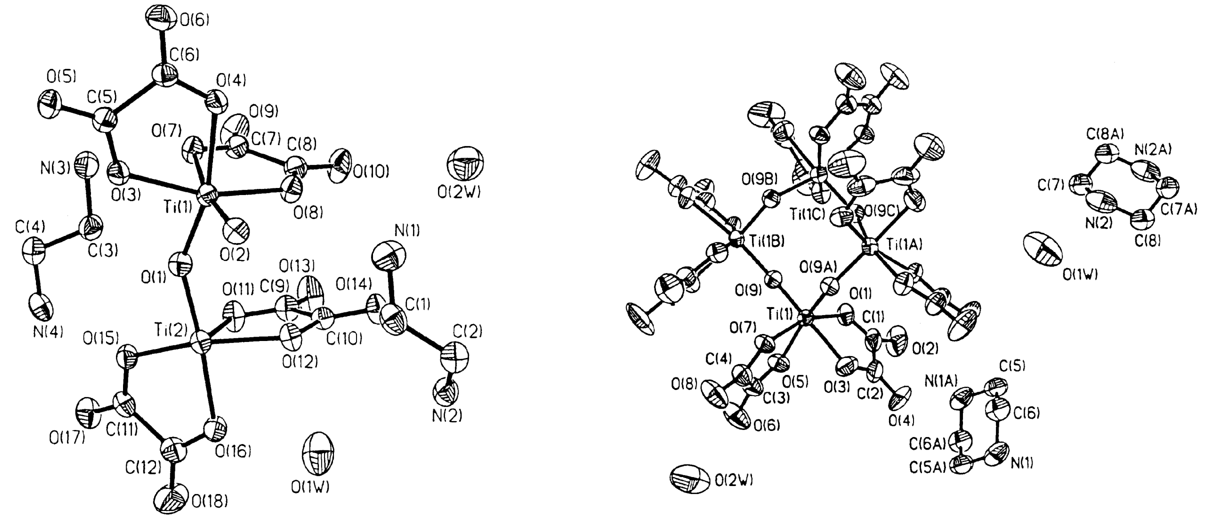


FIG. 3. TGA (a) and DTA (b) curves for **1**, **2**, **3**, and **4**.

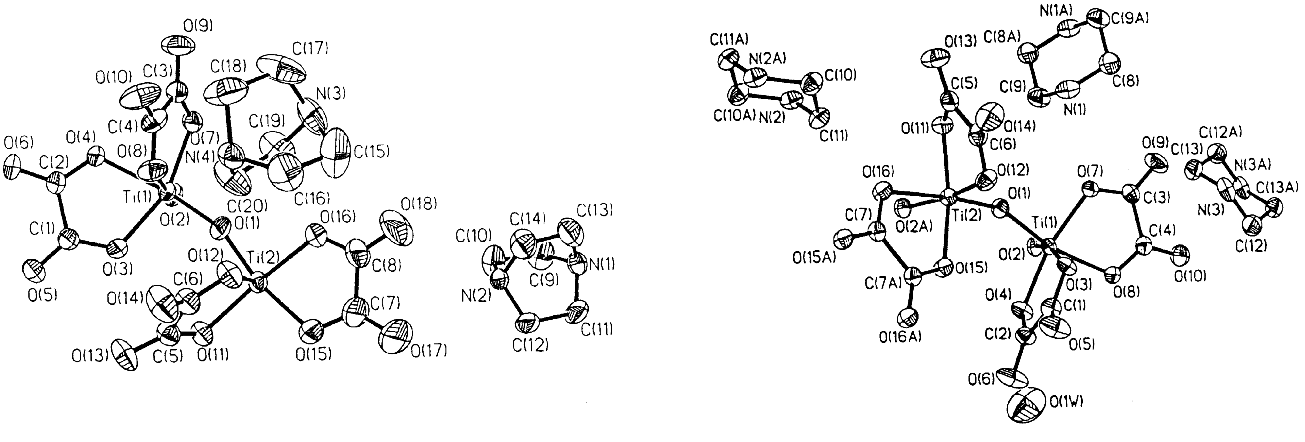
shown in Fig. 4. The structure consists of diprotonated piperazine cations and infinite $[Ti_4O_4(C_2O_4)_7^{6-}]_n$ chains which run parallel to the *a* axis (as shown in Fig. 5). The parallel chains are held together by the interaction between oxygen and diprotonated piperazine cations, so each chain has six neighbours, with no direct linkage between adjacent chains. The piperazine cations lie in the channels between the infinite chains. The various hydrogen bonds between organic amine and oxygen atoms in the chains are listed in Table 7.

The infinite chain $[Ti_4O_4(C_2O_4)_7^{6-}]_n$ is composed of $[Ti_4O_4(C_2O_4)_8]$ tetramer units connected by sharing one oxalate bridging ligand between every two $[Ti_4O_4(C_2O_4)_8]$ tetramers (Fig. 6). Each tetramer unit (Fig. 7) is formed by the Ti_4O_4 eight-membered cyclic nuclei with oxygen bridging atoms and eight oxalates ligands. So each titanium atom is coordinated octahedrally by two oxalates and two oxygen atoms. Bond angles and interatomic distances suggest that there are two severely distorted octahedra of oxygen atoms around the Ti1 and Ti2; the Ti–O distances in the eight-membered cyclic unit of $[Ti_4O_4(C_2O_4)_7^{6-}]_n$ are short (Ti1–O1, 1.857(2) Å; Ti1–O2, 1.784(2) Å; Ti2–O1, 1.754(2) Å; Ti2–O2, 1.854(2) Å), similar to those of the simple anions $[TiO(C_2O_4)_2]_4^{8-}$: 1.824(2) Å, 1.802(2) Å, 1.800(2) Å, 1.846(2) Å in compound **1**; 1.976(3) Å in compound **2**; and 1.785(2) Å, 1.809(2) Å, 1.824(2) Å, 1.807(2) Å in compound **3**. The bond lengths of Ti–O formed by titanium and bridging



compound 1

compound 2



Compound 3

compound 4

FIG. 4. ORTEP views of **1**, **2**, **3**, and **4** structures showing the atom labeling scheme (50% thermal ellipsoids).

oxalates (Ti2–O15, 2.045(2) Å; Ti2–O16, 2.267(2) Å) are generally longer than those between titanium and bidentate oxalate (Ti2–O11, 1.967(2) Å; Ti2–O12, 2.062(2) Å; Ti1–O4, 1.978(2) Å; Ti1–O3, 2.101(2) Å; Ti1–O7, 2.026(2) Å; Ti1–O8, 2.069(2) Å). The oxalate planes connecting with the same titanium are nearly perpendicular to each other and each oxalate is asymmetric despite the bridging oxalate. But the oxalates which connect with different titanium and parallel each other in the eight-membered cyclic unit of $[Ti_4O_4(C_2O_4)_7^{6-}]_n$ have mutually respondent bond parameters. There are then two types of oxalates in the eight-membered cyclic unit of $[Ti_4O_4(C_2O_4)_7^{6-}]_n$: bridging oxalate and bidentate oxalate. Kinomura *et al.* reported the structure of a one-dimensional titanium glycolate complex $Ti(OCH_2CH_2O)_2$, which is composed of parallel chains built up from edge-sharing TiO_6 octahedra and each ethylene glycolate ligand bridging two titanium atoms with one of its oxygen atoms and the other is terminal (26). C. N. R. Rao and co-workers also reported the effects of tetradentate oxalate and many layered or three-dimensional structures were built up in this way (12–16). So it is evident that oxalate as a kind of tetradentate ligand play an important role in the formation of structures with different dimensions. Meanwhile, the shapes and distribution of electric charge of the cations are another key in the formation of a novel structure.

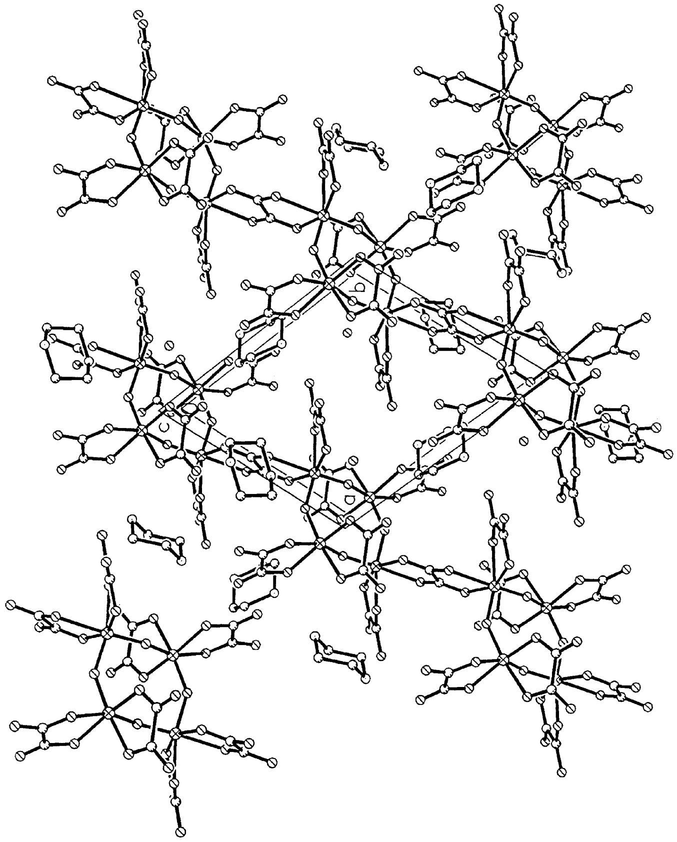


FIG. 5. Structure of **4** viewed along the *c*-direction.

CONCLUSIONS

The present study shows that titanium(IV) in most compounds possesses a strong tendency to form a hexacoordinated state and the Ti_4O_4 oxo cluster is the basic form in

TABLE 7
Hydrogen Bonds for 4

D–H ··· A	d(D–H) (Å)	d(H ··· A) (Å)	d(D ··· A) (Å)	Angle (D–H ··· A) (°)
N(1)–H(1A) ··· O(14)#6	0.90	1.90	2.748(4)	156.3
N(1)–H(1A) ··· O(13)#6	0.90	2.64	3.225(4)	123.1
N(1)–H(1B) ··· O(7)	0.90	2.05	2.906(3)	158.2
N(2)–H(2A) ··· O(8)#1	0.90	2.09	2.864(3)	144.1
N(2)–H(2A) ··· O(10)#1	0.90	2.55	3.113(4)	120.9
N(2)–H(2B) ··· O(5)#7	0.90	1.89	2.771(3)	164.2
N(3)–H(3A) ··· O(3)#8	0.90	2.07	2.850(3)	144.4
N(3)–H(3B) ··· O(10)	0.90	1.98	2.790(4)	148.2
N(3)–H(3B) ··· O(9)	0.90	2.33	2.957(4)	126.9

Note. Symmetry transformations used to generate equivalent atoms: #1, $-x, -y+2, -z+1$ #2, $-x+1, -y+2, -z+1$ #3, $-x+1, -y+2, -z$ #4, $-x, -y+1, -z+1$ #5, $-x-1, -y+1, -z+2$ #6, $-x+1, -y+1, -z+1$ #7, $x, y, z-1$ #8, $-x, -y+1, -z+2$

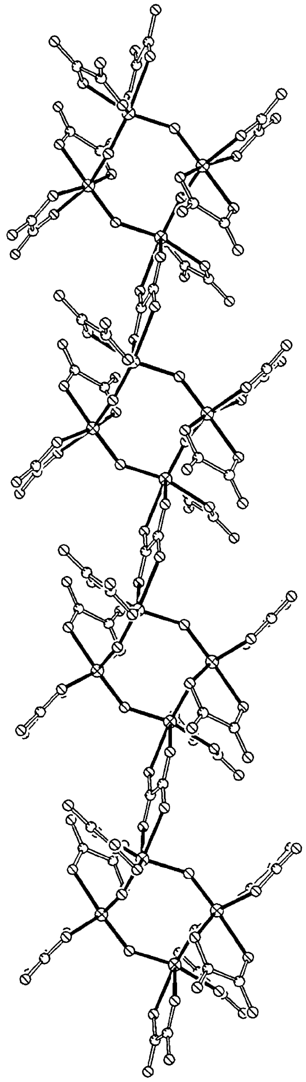


FIG. 6. Section of the $[Ti_4O_4(C_2O_4)_7^{6-}]_n$ chain in the $Ti_4O_4(C_2O_4)_7 \cdot 3C_4N_2H_{12} \cdot 2H_2O$ **4** along the *a* axis.

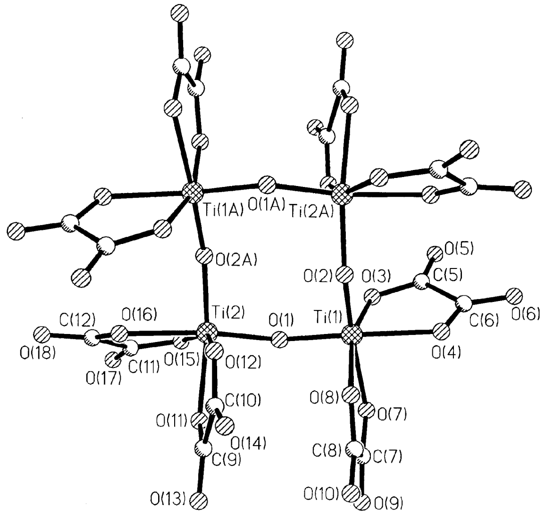


FIG. 7. Structure of the tetramer anions $Ti_4O_4(C_2O_4)_8^{8-}$.

oxalatotitanate compounds; new framework oxalatotitanate can be obtained when the synthesis is carried out in the presence of a specific organic amine with a proper reactant ratio. This new compound with infinite chains is noteworthy as this is the first type of such an architecture based on the Ti_4O_4 and oxalate. The various ways of combination between tetramer Ti_4O_4 nuclei (or TiO_6) and bridging oxalate open up the possibility of synthesizing new oxalatotitanate with a two- or three-dimensional open-framework.

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