Selective Formation of Alkoxo-bridged Titanium(IV) Polynuclear Complexes with Polyaminopolycarboxylate: First Titanium(IV) Octanuclear Complex Containing Cubic-type $\{Ti_4(\mu\text{-oxo})_4\}_2(\mu\text{-alkoxo})_4$ Core

Yoshitaro Miyashita,* Md. Monirul Islam, Nagina Amir, Kiyoshi Fujisawa, and Ken-ichi Okamoto
Department of Chemistry, University of Tsukuba, Tsukuba 305-8571

(Received August 31, 2004; CL-041025)

Two kinds of alkoxo-bridged Ti(IV) polynuclear complexes were selectively obtained depending on reaction conditions. Crystal structures of the dinuclear complex $[Ti_2(\mu\text{-dptaO})_2]^{2-}$ and the novel octanuclear complex $[\{Ti_4(\mu\text{-O})_4\}_2(\mu\text{-dptaO})_4]^{4-}$ (H_4dptaOH = 2-hydroxypropane-1,3-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) were determined. The obtained complexes were spectrochemically characterized.

In order to prepare polynuclear complexes, many polynucleating ligands have been used for a long time. For example, 2-hydroxypropane-1,3-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4dptaOH) is one of the most typical dinucleating ligands. In V(III),[1] Mn(II/III),[2] Fe(III),[3] Cu(II),[4] and Ru(III)[5] complexes synthesized as biological model compounds or metal-substituted derivatives, two hexacoordinated metal centers are alkoxo-bridged by one deprotonated ligand (dptaO) and carboxylate coligand(s). On the other hand, a dinuclear V(III) complex $[V_2(\mu\text{-HdptaO})_2]^{2-}$ without coligand(s) has heptacoordinated V(III) ions.[6] A tetranuclear V(IV/V) complex $[V_4O_4(\mu\text{-O})_2(\mu\text{-dptaO})_2]^{4-}$ containing hexacoordinated metal ions and oxo-bridges was also reported.[7] Moreover, we have reported dinuclear Ln(III) complexes $[Ln_2(\mu\text{-dptaO})_2]^{4-}$; the stereochemically characterized Yb(III) complex contains octacoordinated Yb(III) ions.[8] Thus, early transition metal ions including Ln(III) ions can take various coordination numbers and geometries. Ti(IV) ion, which is one of the early transition metal ion, also indicates complicated stereochemistry due to the formation of many kinds of oxotitanium clusters. Among them, various Ti_4O_4 clusters have been recognized.[9] From the reaction using Ti(IV) ion and H_4dptaOH, not only a dinuclear complex, which resembles the Yb(III) complex, but also an octanuclear complex containing a unique cubic-type core were formed. Here we report crystal structures of the selectively obtained two types of alkoxo-bridged Ti(IV) polynuclear complexes. A similar dinuclear complex containing octacoordinated Zr(IV) ions, which has been reported quite recently, is formed regardless of pH of solution.[10]

Chemical oxidation of an acidic aqueous solution containing $TiCl_3$, H_4dptaOH, and Na_2CO_3 produced two types of colorless crystals, depending on pH of reaction mixture.[11] The block-shaped crystal obtained from pale yellow solution (pH $\approx$ 5) is a sandwich-type dinuclear Ti(IV) complex, $Na_2[Ti_2(\mu\text{-dptaO})_2]$ (Figure 1).[12] Two Ti(IV) ions are alkoxo-bridged by two dptaO ligands. Each Ti(IV) ion is coordinated by two amino N atoms, four carboxylato O atoms (O_{ca}), and two bridging alkoxo O atoms (O_{al}), forming an octacoordinated structure. This geometry is similar to those of Yb(III) and Zr(IV) complexes.[8,10] The Ti–O_{ca} (av 2.033(2) Å) and Ti–N (av 2.385(2) Å) distances in $[Ti_2(\mu\text{-dptaO})_2]^{2-}$ are longer than the Ti–O_{ca} (av 1.953(2) Å) and Ti–N (av 2.303(2) Å) distances in the heptacoordinated complex $[Ti(edta)(H_2O)]$, respectively.[13] Each Na(I) ion binds to the O_{ca} atoms of the complex anions, forming a three-dimensional network in the crystal. The Na–O_{ca} distances (av 2.451(4) Å) are typical for polyaminopolycarboxylato complexes.[10]

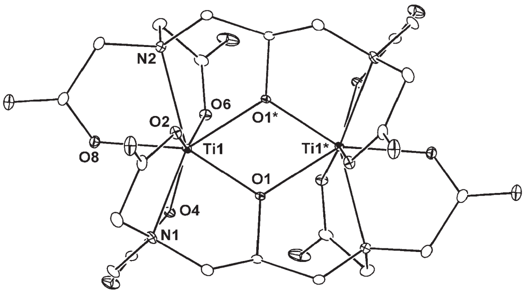

Figure 1. A structure of $[Ti_2(\mu\text{-dptaO})_2]^{2-}$. Ti···Ti, 3.3438(6); Ti1–O1, 1.969(2); Ti1–O1*, 2.086(2); Ti1–O2, 2.022(2); Ti1–O4, 2.051(2); Ti–O6, 2.032(2); Ti1–O8, 2.027(2); Ti1–N1, 2.404(2); Ti1–N2, 2.365(2) Å. * Symmetry code: $-x + 1/2$, $-y + 1/2$, z.

The plate-shaped crystal obtained from colorless solution (pH $\approx$ 3) is an octanuclear Ti(IV) complex, $Na_2H_2[\{Ti_4(\mu\text{-O})_4\}_2(\mu\text{-dptaO})_4]$. Since the crystals of Na(I) salt decay easily,[14] the corresponding crystals of Cs(I) salt were obtained by using Cs_2CO_3 instead of Na_2CO_3;[15] the complex anion of the Cs(I) salt is shown in Figure 2.[16] Two Ti_4O_4 eight-membered rings are alkoxo-bridged by four dptaO ligands, forming a novel octanuclear structure. This is the first example of the complex with a cubic-type $\{Ti_4(\mu\text{-oxo})_4\}_2(\mu\text{-alkoxo})_4$ core, although some complexes with a $Ti_8(\mu\text{-oxo})_{12}$ core are known.[17] Each Ti(IV) ion has a distorted octahedral geometry formed by coordination of one amino N, two O_{ca}, one O_{al}, and two oxo O atoms (O_{ox}). The oxo-bridges are not symmetric; a short Ti–O_{ox} distance is av 1.737(8) Å and a longer one is av 1.896(8) Å. Since the N atom occupies *trans* position to the short Ti–O_{ox} bond, there is a pseudo four fold axis through the center of two Ti_4O_4 rings. This behavior is observed in the complex with the cyclic Ti_4O_4 unit and nitrilotriacetate ligands.[18] The Ti–O_{al} bond (av 2.032(7) Å) is longer than the Ti–O_{ox} bond. The Ti–O_{ca} bond *trans* to O_{ox} (av 2.029(9) Å) is slightly longer than that *trans* to O_{al} (av 1.991(7) Å), reflecting the difference of Ti–O_{ox} and Ti–O_{al} distances. The Ti–N distances (av 2.28(1) Å) in $[\{Ti_4(\mu\text{-O})_4\}_2(\mu\text{-dptaO})_4]^{4-}$ are significantly shorter than those in $[Ti_2(\mu\text{-dptaO})_2]^{2-}$. The Ti–$O_{ox}$–Ti (av 161.5(5)°) and O_{ox}–Ti–O_{ox} (av 102.7(4)°) angles are comparable with the other cyclic Ti_4O_4 units.[18] Although the Ti–O_{al}–Ti angles (av 127.3(4)°) imply contraction of the Ti_8O_{12} cube along the four fold axis, adjacent Ti···Ti distances via O_{al} (av 3.641(2) Å) are somewhat longer than those via O_{ox} (av 3.586(3) Å). Short intramolecular $O_{ox}\cdots O_{ox}$ contacts, which are observed in the tetranuclear Fe(III) complex $[\{Fe_2(\mu\text{-}O)(\mu\text{-}CO_3)\}_2(\mu\text{-dptaO})_2]^{6-}$,[19] are not observed in the present complex. The O_{ca} atoms bind to Cs(I) ions, i.e., the $\{Ti_4(\mu\text{-oxo})_4\}_2(\mu\text{-alkoxo})_4$ cube is capped by two Cs(I) ions. Further, each Cs(I) ion binds to neighboring complexes, forming a two-dimensional network in the crystal. The Cs–O_{ca} distances (av 3.27(2) Å) are also typical.[10] The observed molar conductivity in H_2O[11,15] of the Na(I) salt is fairly in agreement with those of 4:1 electrolytes.[8] Considering the charge balance, the complex anion seems to be tetravalent and two hydrogen ions exist.

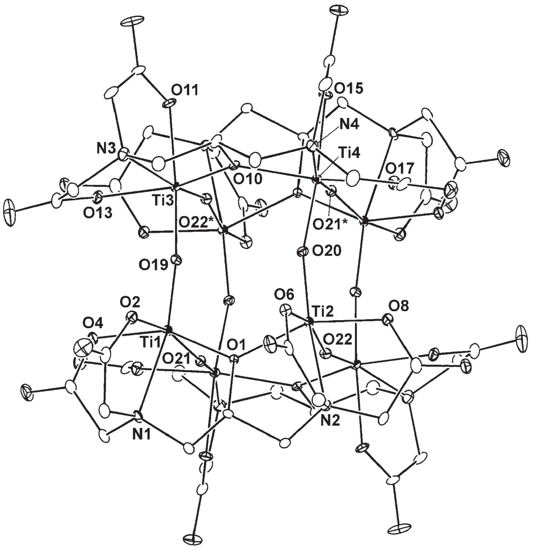

Figure 2. A structure of $[\{Ti_4(\mu\text{-}O)_4\}_2(\mu\text{-dptaO})_4]^{4-}$. Ti1–O1, 2.028(7); Ti1–O2, 2.034(8); Ti1–O4, 1.999(7); Ti1–O19, 1.728(7); Ti1–O21, 1.889(7); Ti1–N1, 2.274(9); Ti2–O1, 2.032(5); Ti2–O6, 2.025(8); Ti2–O8, 1.973(6); Ti2–O20, 1.747(8); Ti2–O22, 1.908(7); Ti2–N2, 2.27(1); Ti3–O10, 2.034(6); Ti3–O11, 2.031(9); Ti3–O13, 1.988(6); Ti3–O19, 1.909(8); Ti3–O22*, 1.733(7); Ti3–N3 2.29(1); Ti4–O10, 2.034(6); Ti4–O15, 2.027(8); Ti4–O17, 2.002(7); Ti4–O20, 1.876(8); Ti4–O21*, 1.741(8); Ti4–N4 2.29(1) Å. * Symmetry code: $-x+1$, $-y+1$, $-z$.

Only $[\{Ti_4(\mu\text{-}O)_4\}_2(\mu\text{-dptaO})_4]^{4-}$ indicated an IR band for oxo-bridges. On the other hand, $[Ti_2(\mu\text{-dptaO})_2]^{2-}$ indicated obviously splitting IR bands for ν_s(COO). The ^{1}H NMR spectrum for $[Ti_2(\mu\text{-dptaO})_2]^{2-}$ exhibits twelve sets of CH_2 signals, whereas that for $[\{Ti_4(\mu\text{-}O)_4\}_2(\mu\text{-dptaO})_4]^{4-}$ exhibits six sets of CH_2 signals. These support that the C_2 symmetry of $[Ti_2(\mu\text{-dptaO})_2]^{2-}$ and the C_{4h} symmetry of $[\{Ti_4(\mu\text{-}O)_4\}_2(\mu\text{-dptaO})_4]^{4-}$ are retained in solution. In the cyclic voltammetry, only $[Ti_2(\mu\text{-dptaO})_2]^{2-}$ showed quasi-reversible redox waves, which may be due to $Ti^{IV/III}$ processes, in a negative potential region. This means the oxidation state of the Ti(IV) ion is highly stabilized in the cubic-type $\{Ti_4(\mu\text{-oxo})_4\}_2(\mu\text{-alkoxo})_4$ core.

This work has been supported by Grants-in-Aid for Scientific Research and 21st Century COE Program from Ministry of Education, Culture, Sports, Science and Technology, and University of Tsukuba Research Projects.

References and Notes

1 K. Kanamori, K. Yamamoto, and K. Okamoto, *Chem. Lett.*, **1993**, 1253; K. Kanamori, K. Yamamoto, T. Okayasu, N. Matsui, K. Okamoto, and W. Mori, *Bull. Chem. Soc. Jpn.*, **70**, 3031 (1997).
2 R. T. Stibrany and S. M. Gorun, *Angew. Chem., Int. Ed. Engl.*, **29**, 1156 (1990).
3 S. Kawata, M. Nakamura, Y. Yamashita, K. Asai, K. Kikuchi, I. Ikemoto, M. Katada, and H. Sano, *Chem. Lett.*, **1992**, 135; M. Kato, Y. Yamada, T. Inagaki, W. Mori, K. Sakai, T. Tsubomura, M. Sato, and S. Yano, *Inorg. Chem.*, **34**, 2645 (1995); S. Yano, T. Inagaki, Y. Yamada, M. Kato, M. Yamasaki, K. Sakai, T. Tsubomura, M. Sato, W. Mori, K. Yamaguchi, and I. Kinoshita, *Chem. Lett.*, **1996**, 61; T. Tanase, T. Inagaki, Y. Yamada, M. Kato, E. Ota, M. Yamazaki, M. Sato, W. Mori, K. Yamaguchi, M. Mikuriya, M. Takahashi, M. Takeda, I. Kinoshita, and S. Yano, *J. Chem. Soc., Dalton Trans.*, **1998**, 713.
4 S. Kawata, H. Kosugi, H. Uda, M. Iwaizumi, and H. Yokoi, *Bull. Chem. Soc. Jpn.*, **65**, 2910 (1992).
5 T. Tanase, M. Kato, Y. Yamada, K. Tanaka, K. Lee, Y. Sugihara, A. Ichimura, I. Kinoshita, M. Haga, Y. Sasaki, Y. Yamamoto, T. Nagano, and S. Yano, *Chem. Lett.*, **1994**, 1853; T. Tanase, Y. Yamada, K. Tanaka, T. Miyazu, M. Kato, K. Lee, Y. Sugihara, W. Mori, A. Ichimura, I. Kinoshita, Y. Yamamoto, M. Haga, Y. Sasaki, and S. Yano, *Inorg. Chem.*, **35**, 6230 (1996).
6 J. C. Robles, M. Shimoi, and H. Ogino, *Chem. Lett.*, **1992**, 309; J. C. Robles, Y. Matsuzaka, S. Inomata, M. Shimoi, W. Mori, and H. Ogino, *Inorg. Chem.*, **32**, 13 (1993).
7 H. Kumagai, S. Kawata, S. Kitagawa, K. Kanamori, and K. Okamoto, *Chem. Lett.*, **1997**, 249.
8 Y. Miyashita, M. Sanada, Y. Yamada, K. Fujisawa, and K. Okamoto, *Chem. Lett.*, **2002**, 840.
9 B. F. G. Johnson, M. C. Klunduk, T. J. O'Connell, C. McIntosh, and J. Ridland, *J. Chem. Soc., Dalton Trans.*, **2001**, 1553.
10 W. Zhong, J. A. Parkinson, S. Parsons, I. D. H. Oswald, R. A. Coxall, and P. J. Sadler, *Inorg. Chem.*, **43**, 3561 (2004).
11 To a purple solution containing 15% $TiCl_3$ HCl solution (Merck; 2.42 g, 2 mmol) in H_2O (20 cm^3), H_4dptaOH (0.64 g, 2 mmol), solid Na_2CO_3, and a small amount of hydroxyammonium chloride were added, whereupon the color of solution was changed into pale yellow or colorless depending on amount of Na_2CO_3. By standing the pale yellow solution (pH ≈ 5) at room temperature, colorless block-shaped crystals appeared. Anal. Found: C, 31.64; H, 3.93; N, 6.76%. Calcd for $Na_2[Ti_2(C_{11}H_{13}N_2O_9)_2]\cdot 3H_2O$: C, 31.83; H, 3.89; N, 6.75%. IR (KBr, ν/cm^{-1}): 1655s (ν_{as}(COO)), 1370s and 1337s (ν_s(COO)). ^{1}H NMR (D_2O, δ/ppm from DSS): 5.08 (1H, tt, $J = 11$, 3 Hz, CH), 4.26 (1H, dd, $J = 17$, 1 Hz, CH_2), 4.07 (1H, d, $J = 17$ Hz, CH_2), 3.86 (1H, d, $J = 17$ Hz, CH_2), 3.82 (2H, m, CH_2), 3.79 (1H, d, $J = 1$ Hz, CH_2), 3.73 (1H, d, $J = 17$ Hz, CH_2), 3.63 (1H, d, $J = 17$ Hz, CH_2), 3.56 (1H, t, $J = 11$ Hz, CH_2), 3.38 (1H, dd, $J = 13$, 3 Hz, CH_2), 3.26 (1H, dd, $J = 12$, 4 Hz, CH_2), 3.13 (1H, t, $J = 12$ Hz, CH_2). Conductivity (H_2O, Λ_m/S cm^2 mol^{-1}): 173. Redox potentials (H_2O, $E^{\circ\prime}$/V vs Ag/AgCl): −0.60, −0.86. From the colorless solution (pH ≈ 3), which is a filtrate after colorless precipitate was removed, colorless plate-shaped crystals appeared. Anal. Found: C, 21.89; H, 4.72; N, 4.67%. Calcd for $Na_2H_2[(Ti_4O_4)_2(C_{11}H_{13}N_2O_9)_4]\cdot 32H_2O$: C, 21.98; H, 4.95; N, 4.66%. IR (KBr, ν/cm^{-1}): 1662s (ν_{as}(COO)), 1370s (ν_s(COO)), 870s (ν(Ti–O–Ti)). ^{1}H NMR (D_2O, δ/ppm from DSS): 4.62 (1H, t, $J = 11$ Hz, CH), 4.37 (2H, d, $J = 17$ Hz, CH_2), 3.85 (2H, d, $J = 19$ Hz, CH_2), 3.82 (2H, d, $J = 19$ Hz, CH_2), 3.73 (4H, m, CH_2), 3.21 (2H, d, $J = 11$ Hz, CH_2). Conductivity (H_2O, Λ_m/S cm^2 mol^{-1}): 390.
12 Crystal data for $Na_2[Ti_2(\mu\text{-dptaO})_2]\cdot 3H_2O$: $C_{22}H_{32}N_4Na_2O_{21}Ti_2 = 830.29$, orthorhombic, *Pccn*, $a = 10.9765(7)$, $b = 14.5063(9)$, $c = 18.993(1)$ Å, $V = 3024.2(3)$ Å^3, $Z = 4$, $R = 0.046$, $R_w = 0.149$, GOF = 1.00. Of 3887 unique reflections measured, 2754 ($I > 3\sigma(I)$) were used in refinements. CCDC No. 248299.
13 J. P. Fackler, Jr., F. J. Kristine, A. M. Mazany, T. J. Moyer, and R. E. Shepherd, *Inorg. Chem.*, **24**, 1857 (1985).
14 The same octanuclear structure with space group $P\bar{1}$ as the Cs(I) salt[16] was observed by a low quality X-ray analysis ($R \approx 0.18$).
15 Anal. Found: C, 20.30; H, 4.25; N, 4.27%. Calcd for $Cs_2H_2[(Ti_4O_4)_2(C_{11}H_{13}N_2O_9)_4]\cdot 30H_2O$: C, 20.42; H, 4.44; N, 4.33%. IR spectral patterns of the Na(I) and Cs(I) salts are essentially the same as each other. Because of poor solubility of the Cs(I) salt, only the Na(I) salt was used for the measurements in solution.
16 Crystal data for $Cs_2H_2[\{Ti_4(\mu\text{-}O)_4\}_2(\mu\text{-dptaO})_4]\cdot 12H_2O$: $C_{44}H_{78}Cs_2N_8O_{56}Ti_8 = 2264.13$, triclinic, $P\bar{1}$, $a = 13.760(6)$, $b = 14.112(7)$, $c = 14.123(6)$ Å, $\alpha = 88.66(2)$, $\beta = 64.62(1)$, $\gamma = 82.28(2)°$, $V = 2453(2)$ Å^3, $Z = 1$, $R = 0.075$, $R_w = 0.214$, GOF = 1.00. Of 11168 unique reflections measured, 5793 ($I > 3\sigma(I)$) were used in refinements. CCDC no. 228490.
17 F. Heshmatpour, S. Wocadlo, W. Massa, K. Dehnicke, F. Bottomley, and R. W. Day, *Z. Naturforsch.*, **49b**, 827 (1994); M. G. Reichmann, F. J. Hollander, and A. T. Bell, *Acta Crystallogr.*, **C43**, 1681 (1987).
18 K. Wieghardt, U. Quilitzsch, J. Weiss, and B. Nuber, *Inorg. Chem.*, **19**, 2514 (1980).
19 D. L. Jameson, C.-L. Xie, D. N. Hendrickson, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **109**, 740 (1987).