Inorganic Chemistry

Article

Synthesis and Structure of New Water-Soluble and Stable Tantalum Compound: Ammonium Tetralactatodiperoxo-μ-oxo-ditantalate(V)

Valery Petrykin,[†] Masato Kakihana,*,[†] Kohtaro Yoshioka,[‡] Satoshi Sasaki,[‡] Yoshihiro Ueda,[†] Koji Tomita,[†] Yoshiyuki Nakamura,[§] Motoo Shiro,[||] and Akihiko Kudo[⊥]

IMRAM, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Miyagi, Japan, Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan, Chemical Resources Laboratory Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan, X-ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196-0003, Japan, Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan, and CREST, JST 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

The stable water-soluble tantalum complex with lactic acid (ammonium tetralactatodiperoxo-μ-oxo-ditantalate(V)), $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]\cdot3H_2O$, was prepared in the crystalline form. According to the single-crystal X-ray diffraction data, this compound forms a monoclinic cell with $a = 13.85(2)$ Å, $b = 9.06(1)$ Å, $c = 12.32(2)$ Å, and $\beta = 116.30°$, space group $C2$ (No. 2), and has $Z = 2$ molecules per unit cell. The solid-state ^{13}C NMR data and low flack parameter are consistent with the determined structure. Appearance of the same vibration modes in Raman and IR spectra supports the choice of the space group without inversion symmetry. The solution of the tantalum complex was successfully applied for the synthesis of two photocatalytic materials, $NaTaO_3$ and $Sr_2Ta_2O_7$.

Introduction

Design and synthesis of water-soluble tantalum compounds is an exciting challenge for inorganic chemists and a matter of outstanding demand from materials chemistry. In recent years one can witness an increasing importance of oxide materials containing tantalum. They include optical and dielectric materials based on pure Ta_2O_5 in solid-state devices,[1] ferromagnetic materials in which Ta_2O_5 additives prevent grain growth and thus limit the size of the magnetic domains,[2] more complex compositions in the SrBiTaO system for capacitors in computer memory,[3] and photocatalytic materials for photoassisted water decomposition and hydrogen production.[4]

At the same time the increasing trend toward miniaturization emphasizes the importance of solution-based synthesis techniques for materials fabrication. Obviously, insoluble Ta_2O_5, a common source of tantalum in conventional ceramic synthesis, is an inappropriate precursor for solution methods. Alternatively, tantalum compounds utilized as starting materials for sol–gel methods, tantalum pentachloride, tantalum ethoxide, and tantalum oxalate, are relatively toxic; the former two are moisture sensitive and incompatible with water-based processing methods. Tantalum oxalate is an appealing precursor and can be applied for a preparation of a limited set of multicomponent oxide materials since oxalate ion yields precipitates with many cations.

On the other hand, water-soluble tetraperoxo complexes of tantalum and niobium have been known for over 100 years.[5] Although their direct use for preparation of oxide materials is not immediately possible due to the presence of alkaline metal as a counterion or due to extreme instability and the lowest solubility in water of the corresponding ammonium salts,[6,7] these compounds show promise for development of new water-soluble tantalum precursors.

The chemistry of niobium and tantalum peroxo complexes was thoroughly reviewed recently by D. Bayot and M.

* To whom correspondence should be addressed. E-mail: kakihana@tagen.tohoku.ac.jp. Tel/Fax: +81-22-217-5649.
† Tohoku University.
‡ Materials and Structures Laboratory, Tokyo Institute of Technology.
§ Chemical Resources Laboratory, Tokyo Institute of Technology.
|| Rigaku Corporation.
⊥ Science University of Tokyo and CREST/JST.

(1) Chaneliere, C.; Autran, J. L.; Devine, R. A. B.; Balland, B. *Mater. Sci. Eng.* **1998**, *R22*, 269.
(2) Sugimoto, M. *J. Am. Ceram. Soc.* **1999**, *82*, 269.
(3) Scott, J. F. *Annu. Rev. Mater. Sci.* **1998**, *28*, 79.
(4) Kato, H.; Asakura, K.; Kudo, A. *J. Am. Chem. Soc.* **2003**, *125*, 3082.
(5) Melikoff, P.; Pissarjewsky, L. *Z. Anorg. Allg. Chem.* **1899**, *20*, 340.
(6) Titova, V. A.; Slatinskaya, I. G. *Russ. J. Inorg. Chem.* **1967**, *12* (6), 767.

Devillers.[8] Therefore, we will make only a brief survey necessary to discuss our results. Usually Ta(V) and Nb(V) complexes are discussed together. These elements belong to the same group in the Periodic Table, and due to the lanthanoid contraction, they have almost identical ionic radii; therefore, Nb(V) and Ta(V) possess very close chemical properties. In the tetraperoxo complexes $[M(O_2)_4]^{3-}$ (M = Nb or Ta) the central metal is coordinated by eight oxygen atoms of four peroxo groups,[9] which are responsible for the unstable nature of the compounds. Their ammonium salts have been utilized for synthesis of pure Nb_2O_5 and Ta_2O_5 by thermal decomposition.[10] However, the tetraperoxo complexes seem to be too unstable for a wider use. In the late 1960s and beginning of 1970s of the last century, several research groups attempted to obtain more stable complexes by replacement of one or more peroxo groups with well-known strong ligands such as fluoride,[11] oxalate,[12,13] EDTA,[14] citrate,[15] etc. Mainly these efforts were related to "wet" analytical chemistry of niobium and tantalum, and therefore very few adequate characterizations of their structures were carried out. Structural reports appeared for several soluble niobium complexes during the past few years.[16,17] Perhaps, to date the most systematic efforts in characterization of novel soluble complexes of Nb and Ta and their possible applications for synthesis of inorganic oxide materials have been carried out by the M. Devillers group.[18−21]

As a part of our continuous efforts to broaden the panel of water-soluble precursors of d^0-transition metal ions,[22−24] in this paper we report the synthesis and crystal structure of the stable and water-soluble tantalum peroxo-lactate complex.

Experimental Section

Synthesis of $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]\cdot 3H_2O$. In the typical synthesis 6 g of $TaCl_5$ (99.9%, Furuchi) was dissolved in absolute methanol. Then this solution was diluted slowly with approximately 100 mL of water. The precipitation of $Ta_2O_5\cdot nH_2O$ from the obtained solution was accomplished by addition of NH_3(aq) (28−30% Kanto Kagaku) until the pH of the solution became 10. The

(7) Shchelokov, R. N.; Traggeim, E. N.; Michnik, M. A. *Z. Neorg. Khimii* **1971**, *16*, 402.
(8) Bayot, D.; Devillers M. *Coord. Chem. Rev.* **2006**, *250*, 2610
(9) Wehrum, G.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1315.
(10) Selezneva, K. I.; Niselson, L. A. Russ. *J. Inorg. Chem.* **1968**, *13*, 45.
(11) Vuletic, N.; Djordjevic, C. *J. Less-Common Metals* **1976**, *45*, 85.
(12) Mathern, G.; Weiss, R. *Acta Crystallogr.* **1971**, *B27*, 1572.
(13) Shchelokov, R. N.; Traggeim, E. N.; Petrov, K. I.; Michnik, M. A. *Z. Neorg. Khimii* **1972**, *17*, 2433.
(14) Vuletic, N.; Prcic, E.; Djordjevic, C. *Z. Anorg. Allg. Chem.* **1979**, *450*, 67.
(15) Dengel, A. C.; Griffith, W. P. *Polyhedron* **1989**, *8*, 1371.
(16) Passoni, L. C.; Siddiqui, M. R. H.; Steiner, A.; Kozhevnikov, I. V. *J. Mol. Catal.* **2000**, *A153*, 103.
(17) de Oliveira, V.; San Gil, R. A. D.; Lachter, E. R. *Polyhedron* **2001**, *20*, 2647.
(18) Bayot, D.; Tinant, B.; Devillers, M. *Catal. Today* **2003**, *78*, 439.
(19) Bayot, D.; Tinant, B.; Mathieu, B.; Declercq, J. P.; Devillers, M. *Eur. J. Inorg. Chem.* **2003**, *4*, 737.
(20) Bayot, D. A.; Tinant, B.; Devillers, M. *Abs. Papers Am. Chem. Soc.* **2003**, *226*, U764.
(21) Bayot, D.; Tinant, B.; Devillers, M. *Inorg. Chem.* **2004**, *43*, 5999.
(22) Camargo, E. R.; Kakihana, M. *Chem. Mater.* **2001**, *13*, 1905.
(23) Tada, M.; Yamashita, Y.; Petrykin, V.; Osada, M.; Yoshida, K.; Kakihana, M. *Chem. Mater.* **2002**, *14*, 2845.
(24) Kakihana, M.; Tomita, K.; Petrykin, V.; Tada, M.; Sasaki, S.; Nakamura, Y. *Inorg. Chem.* **2004**, *43*, 4546.

white precipitate of "tantalic acid" was filtered out and repeatedly washed with H_2O until chloride ions could not be detected in the mother liquor by the analytical reaction with $AgNO_3$ solution. Thus, the obtained fresh wet precipitate of $Ta_2O_5\cdot nH_2O$ was transferred into lactic acid (90% L-lactic acid Acros Organics) with an approximate mole ratio of Ta:lactic acid = 1:8. After 40 mL of H_2O_2 (30−35% Kanto Kagaku) was added and cooled to 4 °C, NH_3(aq) was introduced dropwise until full dissolution of the $Ta_2O_5\cdot nH_2O$ precipitate. Usually this step requires ∼20 mL of ammonia solution until the final pH approaches 6. The transparent solution was kept under ambient conditions for gradual evaporation of water and formation of white transparent plate-like crystals. The obtained crystals were separated and recrystallized from water one time. The crystals were dried in the desiccator. For structural analysis the suitable crystals were picked up directly from the solution. We have not attempted to optimize the yield of the solid product. The yield of the dissolved Ta as the peroxo-lactate complex with respect to $TaCl_5$ was 87−90%.

Preparation of $NaTaO_3$ and $Sr_2Ta_2O_7$ Photocatalysts. The concentration of Ta after dissolution of tantalic acid was analyzed by ICP-Atomic Emission Spectroscopy. For synthesis of $NaTaO_3$ photocatalyst, 10 mol % excess amount of Na_2CO_3 (99.5% Kanto Kagaku) was dissolved into this solution of Ta-peroxo-lactic acid complex. The temperature was gradually increased to 150 °C and kept constant until water evaporation and formation of glass-like matter. The organic compounds were oxidized by annealing at 350 °C for 1 h and then at 450 °C for 3 h in a mantle heater. The oxide precursor was mildly crushed and annealed at 800 °C for 10 h. $Sr_2Ta_2O_7$ was prepared from the same tantalum precursor solution; however, $SrCO_3$ (99.9% Kanto Kagaku) was preliminary dissolved in the lactic acid with the molar ratio of $SrCO_3$:lactic acid = 1:4. Then both solutions were mixed and treated at 150 °C and 450 °C according to the schedule described above. The oxide precursor was annealed in the furnace at 900 °C for 10 h followed by heating at 1000 °C for 5 h. The obtained samples were characterized by powder XRD, and their photocatalytic activities for water splitting under UV-light irradiation were checked.

Elemental Analysis. Carbon, nitrogen, and hydrogen contents were determined in the Analytical Center of Tokyo Institute of Technology. The amount of Ta_2O_5 was established by thermo-gravimetric experiment, and the phase composition of the residue was confirmed independently by Raman spectroscopy and powder XRD. Elemental analysis yielded C 15.94%, N 5.98%, H 4.03%, and ash (as Ta_2O_5) 47.2%. The amount of oxygen estimated from the difference was 35.35%. For $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]\cdot 3H_2O$ composition, the calculated values are C 15.66%, N 6.08%, H 4.12%, O 34.77%, and Ta (in the form of Ta_2O_5) 48.01%.

Structural Analysis. The essential experimental details of single-crystal data collection and refinement are summarized in Table 1. A colorless plate-like crystal of $Ta_2N_4C_{12}O_{21}H_{38}$ has been mounted in a loop. The diffraction data were collected at 93 K using a Rigaku Raxis Rapid imaging plate detector, graphite monochromated Mo Kα radiation, and crystal to detector distance of 127.40 mm. The indexing of the unit cell was performed from 3 oscillations exposed for 36 s. For the crystal structure solution and refinement, 44 oscillation images with a maximum 2Θ value of 60.1° were acquired. A sweep of data was done using ω scans from 130.0° to 190.0° in 5.0° step at χ = 45.0° and φ = 0.0°. The second sweep was carried out using ω scans from 0.0° to 160.0° in 5.0° step at χ = 45.0° and φ = 180.0°. The exposure rate was 270 s/deg. The readout of the images was performed in the 0.100 mm pixel mode. In total, 8125 reflections were collected (3990 reflections were unique). The corrections for the Lorentz, polarization effects and

Table 1. Data Collection and Refinement Details for the $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]\cdot 3H_2O$ Single Crystal

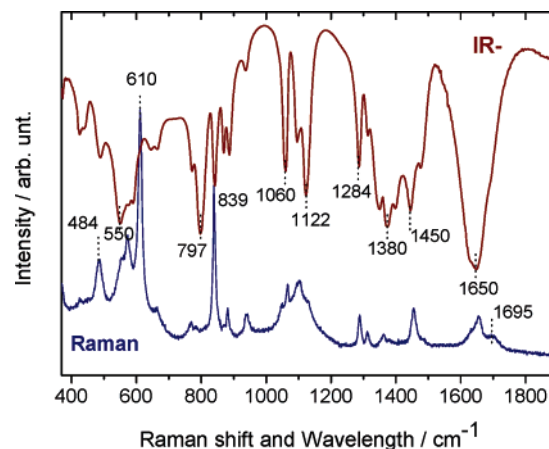|	
diffractometer	Rigaku Raxis Rapid
radiation	0.71075 Å, Mo Kα,
monochromator	graphite
temperature	93 K
formula	$C_{12}H_{38}O_{20}N_4Ta_2$
mol wt	920.34
crystal system	monoclinic
space group	$C2$ (No.5)
a, Å	13.85 (2)
b, Å	9.06 (1)
c, Å	12.32 (2)
β, deg	116.30 (5)
volume, Å^3	1385(3)
Z	2
ρ, g cm^{-3}	2.195
crystal size, mm^3	0.10 0.07 0.02
2θ limit, deg	60.1
μ, cm^{-1}	79.67
reflections, parameters	8125 (3990 unique), 175
R(int)	0.083
final R1 ($I > 2.00\sigma(I))^a$	0.054
R1 (all reflections)	0.086
wR2 (all reflections)	0.120
goodness of fit	0.910

^{a} R1 $= \sum||F_o| - |F_c||/\sum|F_o|$ and wR2 $= [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

secondary extinction (coefficient = 0.001440) were applied. After the empirical correction for the absorption, which resulted in transmission factors of 0.416−0.853, the diffraction data were used for structure solution. The *C*2 (No.5) space group was chosen based on the intensity distribution statistics and packing considerations. The structure was solved by direct method[25] and expanded using Fourier technique.[26] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms (except for ammonium and water) were refined using rigid model. The full-matrix least squares refinement was carried out by SHELXL-97[27] against F^2 using 3990 merged reflections and 175 variable parameters. After the convergence, maximum and minimum peaks in the difference Fourier map were 2.16e/A^3 and −2.03e/A^3.

Raman and IR Spectroscopy. Raman spectrum was measured in back-scattering geometry by Jobin-Yvon T64000 triple spectrometer equipped with Atago Bussan microprobe optics and Ar+ laser for excitation (514.5 nm). For micro-Raman characterization of single crystals, the laser beam was focused through the 90× lens of the microscope. The laser power was kept below 50 mW for macro and below 5mW for micro setup. The FT-IR spectrum was recorded by a System 2000 FT-IR Perkin-Elmer spectrometer using KBr for diluting (sample:KBr = 0.3:100). The samples for the IR measurements were prepared and handled in a N$_2$-filled glovebox.

NMR Spectroscopy. The solid-state ^{13}C NMR spectrum of the $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]\cdot 3H_2O$ was acquired by a JEOL NMR-GSX-270 instrument operating at 67.9 MHz with cross-polarization magic spinning. Adamantane ($C_{10}H_{16}$) was used as an external reference, but all the reported values were rescaled by the TMS standard.

Powder XRD Characterization. The phase composition of NaTaO$_3$ and Sr$_2$Ta$_2$O$_7$ samples was examined by powder X-ray

(25) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, *36*, 1103.

(26) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1999.

(27) Sheldrick, G. M. SHELX97; University of Göttingen, Germany, 1997.

Figure 1. Raman and IR spectra of $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]\cdot 3H_2O$ powder.

diffraction analysis using a Rigaku RINT-2200 diffractometer with Cu Kα radiation operating at 40 kV, 30 mA. The patterns were recorded in the range of $2\theta = 10-80$ deg with the scanning speed of 2 deg/min in the Bragg−Brentano geometry.

Photocatalytic Activities Measurements. The experiments were carried out using NiO cocatalyst loaded NiO(0.2 wt %)−NaTaO$_3$ and NiO(0.15 wt %)−Sr$_2$Ta$_2$O$_7$ samples prepared by the impregnation of powders of the host compounds with aqueous solutions of nickel nitrate, followed by appropriate heat treatments.[28] The samples were suspended into an aqueous solution of Ni(NO$_3$)$_2$, and water was evaporated on a water bath. The residue was dried at 100 °C for 5 h. Then the powder was heat-treated at 370 °C in a furnace for 1 h. The photocatalytic reactions were carried out in a gas-closed circulation system using 0.3 g of a photocatalyst suspended by magnetic stirring in 400 mL of pure water in an inner irradiation quartz cell. After thorough degassing, Ar (50−60 Torr) was introduced into the cell. Then photodecomposition of water was carried out under irradiation by the light from a 400 W high-pressure Hg lamp (Ushio, UM-452). H$_2$/O$_2$ gases evolved were analyzed by gas chromatography (Shimadzu, GC-14B, Ar gas carrier, MS-5A Column, TCD).

Results and Discussion

The crystals of the new compound were obtained by dissolving freshly precipitated tantalum oxide Ta$_2$O$_5$·nH$_2$O ("tantalic acid") in the lactic acid and hydrogen peroxide solution, followed by the gradual evaporation of liquid under ambient conditions. Transparent thin plate crystals were separated from the mother liquor, recrystallized from water, and used for further studies. To ensure the purity and single-phase nature of the product, unpolarized micro-Raman spectra were collected for several individual single crystals and compared with the macro-Raman spectra of the powder. Separately, the IR spectrum of the powder diluted with KBr was recorded. Both macro-Raman and IR spectra of the synthesized tantalum complex powder are presented in Figure 1. The vibration bands are active in both Raman and IR spectra, and their intensities are complementary. Appearance of the same bands in Raman and IR spectra allows exclusion of inversion symmetry in the unit cell, and usually such

(28) Kudo, A.; Sayama, K.; Tanaka, A.; Asakura, K.; Domen, K.; Maruya, K.; Onishi, T. *J. Catal.* **1989**, *120*, 337.

information is helpful for crystal structure solution. Precise interpretation of the characteristic bands in both spectra is difficult due to the possible overlapping of bands of different molecular groups. Nevertheless, one may immediately identify two sets of vibrations at $1300-1450$ cm^{-1} and $1650-1695$ cm^{-1} that correspond to the ν_s(COO) and ν_{as}-(COO) modes of carboxylic groups.[29] The large value of ν_s-(COO) and ν_{as}(COO) separation indicates that COO groups coordinate metal ions in the unidentate manner, while an additional shoulder at 1695 cm^{-1} in Raman spectrum may indicate that there are structurally nonequivalent organic ligands in this complex. Sharp and strong peaks at 839 cm^{-1} 610 and 484 cm^{-1} in Raman spectrum are characteristic to ν(O–O), ν_s(M–O$_2$), and ν_{as}(M–O$_2$) vibrations of a peroxo group.[30,31] In this case, strong single peaks, the particular frequencies of ν(O–O), ν_s(M–O$_2$), and especially appearance of a band at 484 cm^{-1}, may indicate that the metal ion is coordinated by only one η^2–O$_2^{2-}$ ligand. However, the presence of weaker peaks at 869 and 887 cm^{-1}, which may be also attributed to vibrations of O–O groups, makes speculations based on spectroscopic data about coordination by only the single peroxo group less convincing. Several overlapping peaks in the range of $1050-1130$ cm^{-1} can be assigned to C–C stretching mode and vibrations of C–O group of lactic acid coordinated to tantalum. A series of peaks at $550-590$ cm^{-1} are commonly observed as oxygen vibrations of the Ta–O bonds in alkoxides.[32] Perhaps the most puzzling peak is at 797 cm^{-1} in the IR spectrum, which is completely absent in the Raman spectrum. Such a feature could be expected for a centrosymmetric molecule where vibrations of atoms laying in the inversion symmetry are not Raman-active. However, a centrosymmetric molecule cannot be composed of L-lactic acid ligands only and would require the presence of both L- and D-isomers. Perhaps this contradiction can be resolved knowing the structure of the complex anion determined by X-ray analysis. Probably this band should be assigned to the vibrations of the bridging oxo-group in the Ta–O–Ta where the oxygen atom occupies the site with the highest ("nearly inversion") symmetry.

Elemental analysis results led to many reasonable alternative chemical formulas for the prepared tantalum complex. Taking into account the use of lactic acid and charge neutrality, one can obtain Ta$_2$N$_4$C$_{12}$O$_{21}$H$_{38}$ as the closest match for the determined chemical composition. This chemical composition was used to solve the crystal structure of the complex using X-ray diffraction data collected for a single crystal. It has been discovered that the obtained compound crystallizes in the monoclinic unit cell of $a = 13.85(2)$ Å, $b = 9.06(1)$ Å, $c = 12.32(2)$ Å, and $\beta = 116.30°$. The reflection condition $h+k \neq 2n$ indicates that the unit cell is C-centered; however, it does not allow a unique choice of the space group among $C2$, Cm, and $C2/m$. The ambiguity
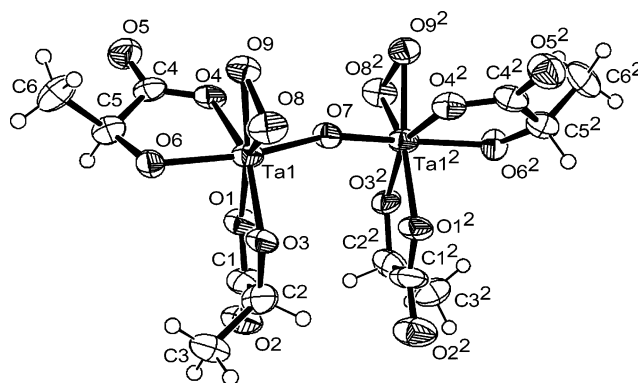

Figure 2. ORTEP view of the [Ta$_2$(C$_3$H$_4$O$_3$)$_4$(O$_2$)$_2$O]$^{4-}$ complex anion structure. Thermal ellipsoids are plotted for 50% probability.

Table 2. Selected Interatomic Distances and Angles for the (NH$_4$)$_4$[Ta$_2$(C$_3$H$_4$O$_3$)$_4$(O$_2$)$_2$O]·3H$_2$O Tantalum Complex

bond	distance, Å	bond	angle, deg
Ta–O(1)	2.152(13)	Ta–O(7)–Ta	163.99(6)
Ta–O(3)	1.984(15)	O(4)–Ta–O(6)	74.53(34)
Ta–O(4)	2.134(28)	O(4)–Ta–O(7)	83.43(28)
Ta–O(6)	1.998(64)	O(6)–Ta–O(7)	156.90(21)
Ta–O(7)	1.919(76)	O(1)–C(1)–O (2)	121.69(153)
Ta–O(8)	1.947(23)	O(4)–C(4)–O (5)	116.47(101)
Ta–O(9)	2.042(10)	Ta–O(4)–C(4)	117.71(77)
Ta–Ta	3.800(153)	Ta–O(6)–C(5)	123.42(62)
O(8)–O(9)	1.485(21)	C(4)–C(5)–O (6)	107.21(98)

in choice of the space group can be overcome if one considers that both inversion center in $C2/m$ space group and mirror plane symmetry operators in Cm space group would require presence of D- and L-lactic acid molecules in the crystal simultaneously, which is inconsistent with the synthesis of this complex using only L-form of lactic acid. In addition, centrosymmetric $C2/m$ is not compatible with Raman and IR spectroscopy data. Thus, the packing considerations and successful structure solution helped us to determine the space group to be $C2$ (No. 5).

The chemical formula of the synthesized tantalum-lactic acid-peroxo complex can be written based on the result of X-ray structural analysis as (NH$_4$)$_4$[Ta$_2$(C$_3$H$_4$O$_3$)$_4$(O$_2$)$_2$O]· 3H$_2$O. The ORTEP[33] view of the [Ta$_2$(C$_3$H$_4$O$_3$)$_4$(O$_2$)$_2$O]$^{4-}$ complex anion is displayed in Figure 2. The selected interatomic distances and bond angles are presented in Table 2. In this anion, two lactic acid molecules coordinate tantalum atom by carboxylic groups in a unidentate manner with rather similar Ta–O1 and Ta–O4 distances of 2.152 and 2.134 Å and by hydroxyl groups having slightly shorter Ta–O3 and Ta–O6 bonds of 1.984 and 1.998 Å. In this way, tantalum atom and lactic acid molecules form two five-membered rings (Ta–O1–C1–C2–O3 and Ta–O4–C4–C5–O6) located in almost perpendicular planes. Formation of such five-membered rings is believed to be important for the stability of the peroxo complexes of tantalum.[8,15] A low flack parameter of $-0.01(2)$ indicates the correct absolute configuration of lactic acid in the complex. The single peroxo group acts as a η^2–O$_2^{2-}$ ligand with slightly different Ta–O8 and Ta–O9 bond lengths of 1.947 and 2.042 Å and quite a typical O–O distance of 1.485 Å. The seventh oxygen

(29) Nakamoto, K. *Infrared and Raman spectra of Inorganic and Coordination Compounds*; 3rd ed.; John Wiley and Sons: New York, 1978.
(30) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 397.
(31) Bayot, D.; Devillers, M.; Peeters, D. *Eur. J. Inorg. Chem.* **2005**, *20*, 4118.
(32) Barraclough, C. G.; Bradley, D. C.; Lewis, J.; Thomas, I. M. *J. Chem. Soc.* **1961**, *3*, 2601.

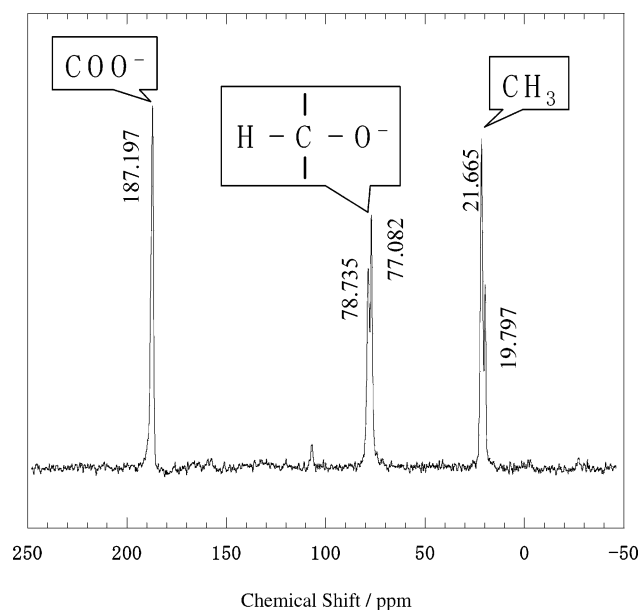(33) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Figure 3. Solid-state ^{13}C NMR spectrum of the $(NH_4)_4[Ta_2(C_3H_4O_3)_4$-$(O_2)_2O]\cdot 3H_2O$ compound.

atom is the bridging μ-oxo group O7, which connects two identical fragments, concluding the structure of the dimeric complex anion having C_2 symmetry. The formation of the dimeric complex may be very useful for future development of mixed Nb−Ta "molecular precursors" similar to Nb−Ta peroxo-tartrato complexes[34] applied for synthesis of Nb/Ta containing oxides. The coordination number of each Ta ion in the $[Ta_2(C_3H_4O_3)_4(O_2)_2O]^{4-}$ complex anion is seven with Ta−O distances ranging from 1.919 to 2.152 Å. The bond valence sum of the tantalum atom in this compound is BVS-(Ta) = 5.40.[35] This value is 8% higher than the expected valence of tantalum and can be considered reasonable, especially, if one takes into account coordination by a peroxo group when bond valence calculations tend to yield higher valence for cations. To the best of our knowledge, this is the first example of Ta peroxo complexes with organic ligands, which contain only one peroxo group attached to the metal ion.[8]

The solid-state ^{13}C NMR spectrum of the crystals (Figure 3) is consistent with the structure determined by X-ray structural analysis. There are three structurally different carbon atoms in the lactic acid molecule and, as one may expect, free lactate ion has three peaks in ^{13}C NMR spectrum at 22.8, 71.2, and 185.1 ppm corresponding to methyl group, tertiary carbon, and carboxylic group, respectively.[36] In the spectrum in Figure 3, one may identify clearly separated signals at 19.8 and 21.66 ppm of methyl groups and two peaks at 77.1 and 78.7 ppm corresponding to the tertiary carbon atom, which indicate that the complex ion contains two structurally nonequivalent molecules of lactic acid. Strictly speaking, the dimeric complex ion contains two pairs of structurally different lactate ligands according to X-ray

structural analysis results, and it is well supported by the NMR data. The shift of the tertiary carbon signal from 71.2 ppm in lactic acid to >77 ppm in this tantalum complex is an important evidence that the alcoholic group attached to this carbon atom is completely deprotonated.[36] Therefore, lactic acid acts as a bidentate ligand with a total charge of −2. The signal of the carboxylic groups is shifted to 187.2 ppm, and apparently, the resolution of the solid state ^{13}C NMR was not sufficient to distinguish two structurally different carboxylic groups.

Formation of five-membered rings composed of tantalum atom and lactic acid molecules, high coordination number and tight environment of tantalum, and net negative charge of the complex ion are the factors that can explain stability of this complex against hydrolysis because they account for steric obstacles for nucleophilic attack by a water molecule. Also the peculiar stability of the new tantalum complex against hydrolysis can be understood in terms of the "partial charge model" advanced by J. Livage.[37,38] The model is based on the electronegativity equalization principle, which states that individual atoms adjust to the same intermediate electronegativity in the compound, and the model also provides the approach to evaluate mean electronegativity of the compound χ and partial charges of atoms δ. As one of the consequences, hydrated metal ions in water, for instance $[Ta(H_2O)_6]^{+5}$ ($\chi = 2.98$), will tend to lose protons to adjust the electronegativity to that of the solution, which is close to the electronegativity of water ($\chi_{H2O} = 2.49$, although it is also dependent on the pH). However, even $\chi = 2.55$ for Ta-$(OH)_5(H_2O)$, the hydrated form of Ta_2O_5, does not reach χ_{H2O}. At the same time, the mean electronegativity of $[Ta_2(C_3H_4O_3)_4$-$(O_2)_2O]^{4-}$ anion is $\chi = 2.45$, which means that further hydrolysis of such complex is unlikely. In other words, large molecular groups and overall negative charge play a stabilizing role by equilibrating electronegativity of the tantalum complex ion with that of a water molecule.

It should be emphasized that the synthesis sequence is very essential for the formation of the lactic acid complex. The addition of $NH_3(aq)$ is the most delicate step. Apart from heating of the solution during neutralization reaction, the dissolution of tantalic acid is normally accomplished at the moment when pH reaches 5−6. If $NH_3(aq)$ is added too rapidly and the solution becomes slightly alkaline, the precipitate remains. At this stage, one may conclude that tantalic acid does not dissolve. In reality, the residual white powder is slightly soluble and can be recrystallized from water to give transparent prismatic crystals. The elemental analysis showed that those crystals did not contain carbon, and their chemical composition was close to $(NH_4)_3[Ta(O_2)_4]$. The unit cell of this compound can be indexed as tetragonal $a = 7.0475(10)$ Å and $c = 8.6168(10)$ Å. However, those single crystals undergo relatively rapid decay under the X-ray beam, and structural analysis using the available data was not possible. The crystal structure of this complex has never been refined, although it is believed that the compound is isostructural to $K_3[Ta(O_2)_4]$.[39] We have attempted to refine

(34) Bayot, D.; Tinant, B.; Devillers, M. *Inorg. Chem.* **2005**, *44*, 1554.
(35) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.
(36) Kakihana, M.; Nagumo, T.; Okamoto, M.; Kakihana, H. *J. Phys. Chem.* **1987**, *91*, 6128.
(37) Livage, J. *Coord. Chem. Rev.* **1998**, *178*, 999.
(38) Livage, J. *Catal. Today* **1998**, *41*, 3.

crystal structure using powder diffraction data, but it also resulted in high R-factors above 15% with particularly large $R(F^2)$ values of above 35%, which means that the sample degradation under the X-ray beam is significant even during relatively high speed of powder data acquisition. When obtained, $(NH_4)_3[Ta(O_2)_4]$ should be treated with care because at 80 °C dry powder undergoes explosion-like decomposition.

In contrast, the described $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]$ complex is rather stable. This compound contains only environmentally benign ligands; the products of thermal decomposition are nontoxic, and in addition lactic acid and peroxide do not form precipitates with most of the cations, which makes $(NH_4)_4[Ta_2(C_3H_4O_3)_4(O_2)_2O]$ a rather attractive water-soluble tantalum precursor for synthesis of multicomponent oxides. In water solution the anion does not fully preserve its structure. According to the solution ^{13}C NMR spectrum available as Supporting Information, it exists in equilibrium with lactic acid and the intermediate complexes. However, from the position of the tertiary carbon signal shifted to above 79 ppm and carboxylic group carbon peaks in the range of 191.2−191.9 ppm, one can definitely say that tantalum is still coordinated by lactic acid as a bidentate ligand, which forms a five-membered ring. To test the applicability of the tantalum peroxo-lactato complex for solution-based synthesis of multicomponent oxides, we have prepared $NaTaO_3$ and $Sr_2Ta_2O_7$, two photocatalytic materials for water splitting.[40,41] The actual synthesis procedures are based on the approach proposed by Marcilly.[42] The main idea relies on the tendency of lactates to form amorphous glass-like solids upon water evaporation, and, in this way, to preserve homogeneity achieved in the solution. The XRD patterns of $NaTaO_3$ and $Sr_2Ta_2O_7$ prepared by this method are presented in Figure 4. Both samples were single phase and did not contain a diffuse scattering characteristic to an amorphous impurity. The photocatalytic activities for water splitting were measured under UV irradiation on samples loaded with NiO as a cocatalyst. We are aware of the nonstoichiometric amount of H_2 and O_2 in our measurements, which was partly due to the consumption of oxygen during oxidation of vacuum grease. Considering the amount of sample in our measurements, the activities of the $NaTaO_3$ (evolution rate: H_2 1.67 mmol/h, O_2 0.62 mmol/h), and $Sr_2Ta_2O_7$ (H_2 1.14 mmol/h, O_2 0.38 mmol/h) were higher than

Figure 4. Powder XRD patterns of $NaTaO_3$ (a) and $Sr_2Ta_2O_7$ (b) photocatalysts prepared by a solution method using water solution of $(NH_4)_4$-$[Ta_2(C_3H_4O_3)_4(O_2)_2O]$ complex.

activities of these compounds obtained by the conventional ceramic method and comparable to the best reported values even though our catalyst preparation conditions were not extensively optimized.

Conclusions

We obtained single crystals of the new tantalum-lactic acid complex and solved its crystal structure. The result was consistent with solid-state ^{13}C NMR, Raman, and IR spectra. This is the first example of a tantalum complex with organic ligands where each tantalum atom is coordinated by only one peroxo group. The compound is very convenient for synthesis of multicomonent oxide materials using advanced solution methods. It was demonstrated by solution synthesis of two photocatalytic materials $NaTaO_3$ and $Sr_2Ta_2O_7$. Both materials exhibited a high rate of hydrogen and oxygen evolution from water under UV irradiation even though the catalyst preparation procedures were not thoroughly optimized.

Supporting Information Available: (1) Atomic positions and selected interatomic distances in a separate crystallographic information file (CIF). (2) Stereoview of the $(NH_4)_4[Ta_2(C_3H_4O_3)_4$-$(O_2)_2O]\cdot3H_2O$ unit cell. (3) ^{13}C NMR spectrum of the $(NH_4)_4[Ta_2$-$(C_3H_4O_3)_4(O_2)_2O]$ solution. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060861U

(39) Haxhillazi, G.; Haeuseler, H. *J. Solid State Chem.* **2004**, *177*, 3045.
(40) Kato, H.; Kudo, A. *J. Phys. Chem. B* **2001**, *105*, 4285.
(41) Kudo, A.; Kato, H.; Nakagawa, S. *J. Phys. Chem. B* **2000**, *104*, 571.
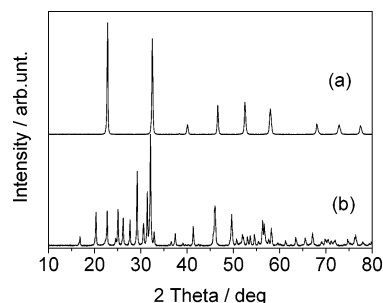(42) Marcilly, C.; Courty, P.; Delmon, B. *J. Am. Ceram. Soc.* **1970**, *53*, 56.