*Inorg. Chem.* **1992**, *31*, 2920–2928

Contribution from the Departments of Chemistry, Columbia University, New York, New York 10027,
University of Nebraska, Lincoln, Nebraska 68588, and University of Illinois, Urbana, Illinois 61801

# Mono- and Diprotonation of the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ and $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})]^{3-}$ Anions

T. M. Che,[1a] V. W. Day,*[,1b] L. C. Francesconi,[1a,c] W. G. Klemperer,*[,1a,c] D. J. Main,[1c] A. Yagasaki,[1c] and O. M. Yaghi[1c]

*Received December 12, 1991*

Reaction of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$ with trichloroacetic acid in ethanol/dichloromethane followed by crystallization from nitroethane/*p*-xylene yields $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5[C_6H_4(CH_3)_2]$, which, according to a single-crystal X-ray diffraction study [$a = 12.519$ (4) Å, $b = 12.957$ (4) Å, $c = 17.364$ (6) Å, $\alpha = 92.95$ (3)°, $\beta = 97.22$ (2)°, $\gamma = 99.28$ (2)°, $Z = 2$, space group $P\bar{1}\text{-}C_i^1$ (No. 2)], contains hydrogen-bonded dimers of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ ions protonated at OTiW doubly-bridging oxygens. Diprotonation can be achieved using HCl in $CH_3CN$ to obtain the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ ion according to an X-ray crystallographic study [$a = 12.744$ (2) Å, $b = 12.720$ (2) Å, $c = 16.754$ (3) Å, $\alpha = 95.88$ (2)°, $\beta = 99.52$ (2)°, $\gamma = 90.37$ (2)°, $Z = 2$, space group $P\bar{1}\text{-}C_i^1$ (No. 2)] of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$. Here, a pair of *cis*-OTiW oxygens are protonated, and comparison with the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ structure [$a = 17.287$ (3) Å, $b = 23.868$ (5) Å, $c = 18.032$ (4) Å, $\beta = 91.05$ (2)°, $Z = 4$, space group $P2_1/n$ (an alternate setting of $P2_1/c$, No. 14)] shows an induced pattern of trans bond length alternation throughout the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ anion structure. The pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})]^{3-}$, $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H)]^{2-}$, and $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H_2)]^-$ have also been prepared in crystalline form as tetra-*n*-butylammonium salts. According to infrared spectroscopy, these species have the same metal–oxygen structural framework observed for their unsubstituted cyclopentadienyl analogues.

## Introduction

The recently-reported[2] $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ anions are both sufficiently basic to react with protic acids in solution. In the case of $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$, the conjugate acid is apparently unstable and readily decomposes with degradation of its metal oxide framework.[3] The $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ anion, however, forms conjugate acids, $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$, that are easily isolated as crystalline $[(n\text{-}C_4H_9)_4N]^+$ salts. These species, the focus of the present study, are of interest on two different grounds. First, identification of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ protonation sites in the conjugate acids provides a good measure of surface charge distribution given the small steric size of a proton. Second, the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ anions are both protic acids that are likely to be useful starting materials for the synthesis of new heteropolyanion derivatives. Unfortunately, the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ anion cannot be conveniently prepared on a large scale and is therefore not well-suited for synthetic studies. Its pentamethylcyclopentadienyl analogue $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})]^{3-}$ is easily prepared in good yield, however, as a tetra-*n*-butylammonium salt and can also be converted to $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H)]^{2-}$ and $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H_2)]^-$. The synthesis and characterization of these three new species are therefore included in the present report.

## Experimental Section

**Reagents, Solvents, and General Procedures.** The following were purchased from commercial sources and used without further purification: electronic grade gaseous HCl (Union Carbide Corp., Linde Division), $^{17}O$-enriched water (Monsanto Research), nitromethane (Baker), ethanol (Midwest Grain Products), 1-propanol and xylene (Fisher), and hydrochloric acid (Mallinckrodt). Solutions of HCl were prepared by bubbling gaseous HCl through acetonitrile. The normality of the resulting solution was determined by diluting 0.2 mL of acetonitrile solution with deionized water (30 mL) and titrating with NaOH to a phenolphthalein end point. These $HCl/CH_3CN$ solutions were used immediately after preparation.

Procedures described in ref 2 were followed for the preparation of $(WO_4)[(n\text{-}C_4H_9)_4N]_2$ and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$. $^{17}O$-enriched material[2] was used to prepare $^{17}O$-enriched $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})H)][(n\text{-}C_4H_9)_4N]_2$ following the preparative procedures given below. A literature procedure[4] was employed to prepare $(\eta^5\text{-}C_5Me_5)TiCl_3$.

Methylene chloride (Baker), nitroethane (Aldrich), and chloroform (Fisher) were distilled once from $P_4O_{10}$, and acetonitrile (Aldrich, 99%) was distilled either from $P_4O_{10}$ or $CaH_2$. Diethyl ether (Fisher or Mallinckrodt, anhydrous) was distilled from sodium benzophenone ketyl. Deuterated acetonitrile (Merck or ICN Biomedicals) was dried over $CaH_2$. Trichloroacetic acid was sublimed at 30 °C under vacuum or recrystallized by cooling a saturated chloroform solution, saturated at ambient temperature, to 0 °C. The recrystallized product was then dried in vacuo over $P_4O_{10}$.

**Analytical Procedures.** Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois.

Infrared spectra were recorded from KBr pellets using a Perkin-Elmer Model 1330 spectrometer and were referenced to the 1028-cm$^{-1}$ band of a 0.05-mm polystyrene film. Absorptions are described as follows: very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh).

$^1H$ NMR spectra were recorded on a Nicolet NT-360 (360 MHz) spectrometer and referenced internally to $(CH_3)_4Si$. All the spectra described below displayed $^1H$ NMR resonances for the $[(n\text{-}C_4H_9)_4N]^+$ cation at $\delta$ 3.11 (m, $NCH_2$), 1.62 (m, $NCH_2CH_2CH_2CH_3$), 1.37 (m, $NCH_2CH_2CH_2CH_3$), and 0.97 (m, $CH_3$). $^{17}O$ FTNMR spectra were measured at 33.93 MHz in 12-mm sample tubes using a spectrometer equipped with a 5.87-T Oxford Instruments magnet and a Nicolet NIC-80 data system and referenced externally to fresh tap water at 25 °C. Chemical shifts for all nuclei are reported as positive values for resonances that are observed at higher frequency (lower field) than the appropriate reference.

**Preparation of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})H][(n\text{-}C_4H_9)_4N]_2$.** A solution of $Cl_3CCOOH$ (0.11 g, 0.67 mmol) in 5 mL of ethanol was added rapidly, with vigorous stirring, to a solution of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$ (1.3 g, 0.63 mmol) in 3 mL of $CH_2Cl_2$. Upon addition of the acid, the resulting solution turned bright yellow. The solution was stirred for 3 min, and 25 mL of ethanol was then added slowly (over 2 min) to the solution with stirring. A yellow powder formed after stirring for 5 min. This suspension was stirred for a further 30 min. The powder was collected by suction filtration, washed with 2 × 5 mL of ethanol and then 2 × 10 mL of diethyl ether, and dried in vacuo to give 1.0 g of crude product. Crystallization was accomplished by dissolving the crude product in 3 mL of $CH_2Cl_2$, filtering off a small amount of insoluble solid, adding ethanol to the point of near permanent cloudiness (ca. 10 mL), and then allowing the $CH_2Cl_2$ to slowly evaporate under a flow of $N_2$. Over a period of 10 h, yellow rectangular shaped crystals separated from the solution. These were collected by suction filtration, washed with 2 mL of ethanol, and then with 5 mL of diethyl ether. In order to obtain product completely free of ethanol, it was necessary to keep the product under vacuum ($10^{-3}$ mmHg) at 60 °C for 10 h (0.63 g, 0.35 mmol, 55%

---

(1) (a) Columbia University. (b) University of Nebraska. (c) University of Illinois.

(2) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1985**, *24*, 4055–4062.

(3) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597–3599.

(4) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383–393.

0020-1669/92/1331-2920$03.00/0 © 1992 American Chemical Society

**Table I.** Crystallographic Data for $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ (A), $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5[C_6H_4(CH_3)_2]$ (B), and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C)

| | A | B | C |
|---|---|---|---|
| formula | $C_{53}H_{115}N_3TiW_5O_{19}$ | $C_{41}H_{83}N_2TiW_5O_{18}$ | $C_{37}H_{79}N_2TiW_5O_{19}Cl$ |
| fw | 2065.6 | 1859.2 | 1842.6 |
| space group | $P2_1/n$, an alternate setting of $P2_1/c\text{-}C_{2h}^5$ (No. 14) | $P\bar{1}\text{-}C_i^1$ (No. 2) | $P\bar{1}\text{-}C_i^1$ (No. 2) |
| cell constants | | | |
| $a$, Å | 17.287 (3) | 12.519 (4) | 12.744 (2) |
| $b$, Å | 23.868 (5) | 12.957 (4) | 12.720 (2) |
| $c$, Å | 18.032 (4) | 17.364 (6) | 16.754 (3) |
| $\alpha$, deg | 90.00 | 92.95 (3) | 95.88 (2) |
| $\beta$, deg | 91.05 (2) | 97.22 (2) | 99.52 (2) |
| $\gamma$, deg | 90.00 | 99.28 (2) | 90.37 (2) |
| $V$, Å$^3$ | 7439 (3) | 2750 (1) | 2664 (1) |
| $Z$ | 4 | 2 | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.844 | 2.245 | 2.297 |
| temp, °C | 20 | 20 | 20 |
| $\mu$, mm$^{-1}$ | 8.03 | 10.8 | 11.2 |
| transm coeff | 0.473–1.000 | 0.367–1.000 | 0.256–1.000 |
| radiation | Mo K$\bar{\alpha}$ | Mo K$\bar{\alpha}$ | Mo K$\bar{\alpha}$ |
| $R(F_o)$ | 0.052 | 0.054 | 0.054 |
| $R_w(F_o)$ | 0.060 | 0.064 | 0.066 |

based on W). Anal. Calcd for $C_{37}H_{78}N_2TiW_5O_{18}$: C, 24.61; H, 4.35; N, 1.55; Ti, 2.65; W, 50.90. Found: C, 24.60; H, 4.37; N, 1.53; Ti, 2.56; W, 50.78. IR (KBr, 1000–350 cm$^{-1}$): 981 (sh), 959 (s), 884 (w), 814 (s), 764 (sh), 645 (sh), 619 (w), 561 (sh), 553 (w), 482 (2), 438 (m), 420 (sh), 377 (m). $^1$H NMR ($CD_3CN$, 360 MHz): $\delta$ 6.33 (s, $C_5H_5$). $^{17}$O NMR ($CD_3CN$, 65 °C, 33.9 MHz): $\delta$ 741 (OW), 561 (OTiW), 411 ($OW_2$), 396 ($OW_2$), −46 ($OTiW_5$).

**Preparation of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$.** A solution of HCl in $CH_3CN$ (0.75 N, 1.5 mL, 1.1 mmol) was added slowly over ca. 0.5 min to a stirring solution of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$ (1.2 g, 0.59 mmol) in 10 mL of $CH_3CN$. Upon addition of the acid, the resulting solution turned bright yellow. After the mixture was stirred for ca. 5 min, a yellow powder precipitated. The suspension was stirred for a further 10 min after which diethyl ether (100 mL) was added to the stirring suspension to precipitate more yellow solid. This was stirred for a further 15 min, collected by suction filtration, washed with 2 × 10 mL of diethyl ether, and dried in vacuo to yield 0.74 g of crude product. Crystallization was accomplished by dissolving the crude product in ca. 35 mL of $CH_3CN$ and then adding 60 mL of diethyl ether while swirling the flask until crystals begin to form. Additional ether (20 mL) was then added. The flask was capped and cooled to 0 °C. After a period of 10 h, small yellow rectangular crystals were isolated by suction filtration, washed with 2 × 5 mL of diethyl ether, and dried in vacuo to yield 0.69 g of yellow powder (0.37 mmol, 64%). Anal. Calcd for $C_{37}H_{79}N_2TiW_5O_{18}Cl$: C, 24.12; H, 4.32; N, 1.52; Ti, 2.60; W, 49.89; Cl, 1.92. Found: C, 24.10; H, 4.49; N, 1.37; Ti, 2.6; W, 49.7; Cl, 1.91, IR (KBr, 1000–350 cm$^{-1}$): 994 (m), 977 (s), 969 (s), 963 (s), 950 (sh), 884 (w), 844 (sh), 806 (s), 737 (s), 630 (w), 584 (w), 567 (sh), 530 (w), 481 (w), 444 (m), 424 (sh), 377 (m). $^1$H NMR ($CD_3CN$, 360 MHz): $\delta$ 6.54 (s, $C_5H_5$).

**Preparation of $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$.** The initial steps of preparation, up to the washing with $H_2O$, were carried out in a dry nitrogen atmosphere. Trichloroacetic acid (0.90 g, 5.5 mmol) and $(WO_4)[(n\text{-}C_4H_9)N]_2$ (5.0 g, 6.8 mmol) were dissolved in 8 mL of $CH_3CN$. To this solution was added a solution of $(\eta^5\text{-}C_5Me_5)TiCl_3$ (0.40 g, 1.4 mmol) in 18 mL of $CH_3CN$ with stirring. After the mixture was stirred for 3 h, the solution volume was reduced to ca. $^1/_3$ under vacuum. Yellow stickly solid appeared on addition of diethyl ether (200 mL). The solvent was filtered off, and the remaining solid was dried under vacuum for 40 min. The solid was then washed with 20 mL of $H_2O$, collected on a coarse filter frit, and dried in a desiccator over $P_4O_{10}$ overnight to give 2.2 g of product as a yellow powder (1.0 mmol, 76% based on W). Anal. Calcd for $C_{58}H_{123}N_3TiW_5O_{18}$: C, 32.89; H, 5.85; N, 1.98; Ti, 2.26; W, 43.41. Found: C, 32.84; H, 5.88; N, 1.99; Ti, 2.41; W, 43.25. IR (KBr, 1000–350 cm$^{-1}$): 961 (m), 942 (sh), 934 (vs), 881 (w), 805 (vs), 643 (w), 580 (w), 558 (w), 542 (w), 470 (w), 441 (s), 403 (sh), 388 (m). $^1$H NMR ($CD_3CN$, 360 MHz): $\delta$ 1.91 (s, $CH_3$). The compound can be crystallized either by dissolving it in water and slowly evaporating the solvent or by dissolving it in acetonitrile and diffusing diethyl ether vapor into the solution. The former method gives needlelike crystals, and the latter gives block-shaped crystals.

**Preparation of $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2$.** This preparation was carried out in a dry nitrogen atmosphere. Aqueous 12 N hydrochloric acid (0.07 mL, 0.8 mmol) was added to a solution of $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$ (1.0 g, 0.47 mmol) in 10 mL of $CH_3CN$ with stirring. A small amount of precipitate appeared on addition. The mixture was stirred for 1 h and then filtered into 100 mL of diethyl ether. A yellow precipitate appeared immediately. This powder was collected by filtration, washed with 2 × 5 mL of diethyl ether, and dried under vacuum to yield 0.74 g of product (0.39 mmol, 84% based on W). Anal. Calcd for $C_{42}H_{88}N_2TiW_5O_{18}$: C, 26.87; H, 4.73; N, 1.49; Ti, 2.55; W, 48.99. Found: C, 26.86; H, 4.75; N, 1.59; Ti, 2.43; W, 48.84. IR (KBr, 1000–350 cm$^{-1}$): 977 (w), 956 (s), 880 (sh), 823 (s), 784 (s), 655 (sh), 638 (w), 563 (sh), 554 (w), 485 (w), 443 (m), 432 (sh), 392 (m). $^1$H NMR ($CD_3CN$, 360 MHz): $\delta$ 2.01 (s, $CH_3$). The compound can be crystallized as thin plates by diffusion of diethyl ether into an acetonitrile solution.

**Preparation of $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]$.** This preparation was carried out in a dry dinitrogen atmosphere. In a mixture of 1 mL of $CH_3CN$ and 10 mL of $CHCl_3$ was dissolved $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2$ (0.50 g, 0.27 mmol). A solution of $CCl_3COOH$ (0.25 g, 1.5 mmol) in 4 mL of $CHCl_3$ was added to this solution with stirring. The color of the solution changed from yellow to orange. An orange precipitate appeared after adding 15 mL of $CHCl_3$ to the solution, and the mixture was left stirring for 30 min. The precipitate was collected by filtration, washed with 2 × 2 mL of $CHCl_3$, and dried under vacuum to yield 0.22 g of product (0.13 mmol, 50% based on W). Anal. Calcd for $C_{26}H_{53}NTiW_5O_{18}$: C, 19.10; H, 3.27; N, 0.86; Ti, 2.93; W, 56.23. Found: C, 19.20; H, 3.24; N, 0.88; Ti, 3.05; W, 56.17. IR (KBr, 1000–350 cm$^{-1}$): 993 (m), 977 (s), 945 (m), 850 (sh), 825 (s), 769 (s), 659 (w), 575 (w), 552 (w), 530 (sh), 465 (w), 423 (m), 405 (sh), 390 (m). $^1$H NMR ($CD_3CN$, 360 MHz): $\delta$ 2.12 (s, $CH_3$). The compound can be crystallized as parallelepipeds by dissolving it in warm $CH_3CN$ and cooling the solution to room temperature.

**X-ray Crystallographic Studies[5] of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$, $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5[C_6H_4(CH_3)_2]$, and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$.** Single crystals of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ (A) suitable for X-ray diffraction studies were grown by slow evaporation of a saturated, moist 1-propanol solution while those of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5[C_6H_4(CH_3)_2]$ (B) were grown by dissolving the compound in nitromethane, adding xylene to the point of saturation, and slowly evaporating the solvent. Single crystals of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C) suitable for X-ray diffraction studies were grown by adding 0.2 g of crystalline material to 8 mL of $CH_3NO_2$ in a vial, supersaturating this solution with 20 mL of xylene, and capping the vial. After 15 h at room temperature, yellow block-shaped crystals formed. Details of the crystal structure determinations for A–C are summarized in Table I.

Totals of 8543 (A), 10085 (B), and 12256 (C) independent reflections having $2\theta$(Mo K$\bar{\alpha}$) < 43° (A), 50.7° (B), and 55.0° (C) [the equivalent of 0.50 (A), 0.80 (B), and 1.00 (C) limiting Cu K$\bar{\alpha}$ spheres] were collected on a computer-controlled Nicolet autodiffractometer in concentric shells of increasing $2\theta$ using 1.00°-wide (A), 1.00°-wide (B), or 0.90°-wide (C) $\omega$ scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation for approximately cube-shaped (A and C) or rectangular parallelep-

---

(5) See paragraph at end of paper regarding supplementary material.

(6) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I: (a) p 99; (b) p 75.

(7) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 55–66; (b) pp 99–101; (c) pp 149–150.

**Table II.** Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3 \cdot H_2O$[a]

| atom type[b] | fractional coordinates | | | equiv isotropic thermal param $10B$, Å$^{2c}$ | atom type[b] | fractional coordinates | | | equiv isotropic thermal param $10B$, Å$^{2c}$ |
|---|---|---|---|---|---|---|---|---|---|
| | $10^4x$ | $10^4y$ | $10^4z$ | | | $10^4x$ | $10^4y$ | $10^4z$ | |
| | | | | | Anion | | | | |
| $W_1$ | 2576 (1) | 1426 (1) | 3499 (1) | 47 (1) | $O_{D1}$ | 1618 (8) | 1079 (6) | 3622 (8) | 51 (5) |
| $W_2$ | 1658 (1) | 1900 (1) | 2024 (1) | 52 (1) | $O_{D2}$ | 881 (8) | 1459 (6) | 2434 (8) | 49 (5) |
| $W_3$ | 845 (1) | 2867 (1) | 3029 (1) | 51 (1) | $O_{D3}$ | 218 (8) | 2261 (7) | 3243 (8) | 54 (5) |
| $W_4$ | 1752 (1) | 2397 (1) | 4500 (1) | 45 (1) | $O_{D4}$ | 939 (8) | 1882 (6) | 4455 (8) | 53 (5) |
| $W_5$ | 2749 (1) | 2754 (1) | 3037 (1) | 42 (1) | $O_E$ | 3473 (10) | 3195 (6) | 2854 (8) | 67 (6) |
| Ti | 687 (3) | 1549 (2) | 3487 (3) | 55 (2) | $O_{F1}$ | 3225 (10) | 922 (7) | 3668 (11) | 78 (7) |
| $O_A$ | 1715 (6) | 2155 (6) | 3267 (6) | 32 (4) | $O_{F2}$ | 1659 (12) | 1720 (8) | 1094 (9) | 87 (7) |
| $O_{B1}$ | 2401 (8) | 1395 (6) | 2452 (8) | 51 (5) | $O_{F3}$ | 258 (11) | 3403 (7) | 2848 (10) | 77 (6) |
| $O_{B2}$ | 1018 (10) | 2534 (7) | 2075 (8) | 63 (6) | $O_{F4}$ | 1790 (8) | 2590 (8) | 5410 (8) | 69 (6) |
| $O_{B3}$ | 1063 (8) | 2951 (6) | 4062 (8) | 51 (5) | $C_1$ | 128 (26) | 656 (15) | 4006 (29) | 156 (21) |
| $O_{B4}$ | 2434 (8) | 1784 (6) | 4457 (7) | 45 (5) | $C_2$ | −1 (23) | 704 (22) | 3272 (23) | 152 (22) |
| $O_{C1}$ | 3221 (8) | 2073 (6) | 3252 (8) | 51 (5) | $C_3$ | −516 (19) | 1043 (19) | 3059 (22) | 133 (19) |
| $O_{C2}$ | 2481 (10) | 2423 (6) | 2095 (7) | 58 (5) | $C_4$ | −587 (24) | 1305 (16) | 3684 (20) | 111 (17) |
| $O_{C3}$ | 1845 (10) | 3218 (6) | 2892 (7) | 58 (5) | $C_5$ | −306 (19) | 1098 (14) | 4306 (20) | 95 (14) |
| $O_{C4}$ | 2567 (8) | 2847 (5) | 4085 (7) | 38 (4) | | | | | |
| | | | | | Cation 1 | | | | |
| $N_1$ | −2372 (12) | 247 (8) | 8300 (11) | 58 (7) | $C_{1g1}$ | −1866 (19) | 622 (13) | 6263 (16) | 86 (12) |
| $C_{1a1}$ | −2148 (15) | 564 (10) | 7607 (12) | 58 (9) | $C_{1g2}$ | −4443 (19) | −145 (14) | 7889 (17) | 88 (12) |
| $C_{1a2}$ | −3116 (14) | −113 (10) | 8226 (14) | 59 (9) | $C_{1g3}$ | −2690 (21) | 948 (13) | 10229 (18) | 102 (14) |
| $C_{1a3}$ | −2418 (16) | 710 (11) | 8929 (14) | 67 (9) | $C_{1g4}$ | −383 (15) | −471 (13) | 8860 (15) | 75 (11) |
| $C_{1a4}$ | −1743 (15) | −184 (10) | 8510 (14) | 57 (8) | $C_{1d1}$ | −1832 (22) | 333 (15) | 5535 (17) | 113 (15) |
| $C_{1b1}$ | −2098 (14) | 229 (10) | 6908 (14) | 59 (9) | $C_{1d2}$ | −5208 (19) | 132 (15) | 7662 (19) | 112 (15) |
| $C_{1b2}$ | −3789 (16) | 270 (13) | 7987 (17) | 76 (11) | $C_{1d3}$ | −2895 (27) | 735 (17) | 11039 (16) | 147 (19) |
| $C_{1b3}$ | −2583 (16) | 451 (11) | 9709 (14) | 64 (9) | $C_{1d4}$ | 450 (16) | −253 (14) | 8961 (18) | 94 (12) |
| $C_{1b4}$ | −896 (18) | 40 (12) | 8619 (17) | 80 (11) | | | | | |
| | | | | | Cation 2 | | | | |
| $N_2$ | −444 (14) | 2718 (11) | 6069 (13) | 77 (9) | $C_{2g1}$ | 161 (35) | 3333 (26) | 7855 (29) | 177 (26) |
| $C_{2a1}$ | −511 (19) | 2966 (14) | 6835 (19) | 95 (13) | $C_{2g2}$[d] | 37 (45) | 3920 (20) | 4777 (29) | 264 (36) |
| $C_{2a2}$ | −147 (16) | 3139 (14) | 5473 (16) | 75 (11) | $C_{2g2'}$[d] | −473 (37) | 4307 (30) | 4711 (36) | 278 (28) |
| $C_{2a3}$ | −1339 (13) | 2521 (14) | 5895 (20) | 85 (12) | $C_{2g3}$ | −2480 (32) | 2120 (30) | 5234 (26) | 189 (28) |
| $C_{2a4}$ | 68 (15) | 2217 (13) | 6036 (15) | 63 (9) | $C_{2g4}$ | 487 (26) | 1444 (16) | 6541 (24) | 143 (19) |
| $C_{2b1}$ | 285 (19) | 3251 (15) | 7042 (16) | 104 (14) | $C_{2d1}$ | 732 (45) | 3619 (26) | 8155 (30) | 223 (37) |
| $C_{2b2}$ | −631 (20) | 3665 (13) | 5398 (18) | 97 (13) | $C_{2d3}$ | −2561 (30) | 1939 (32) | 4572 (31) | 214 (33) |
| $C_{2b3}$ | −1443 (17) | 2272 (16) | 5099 (19) | 103 (14) | $C_{2d4}$ | 442 (23) | 939 (21) | 6950 (40) | 219 (32) |
| $C_{2b4}$ | −185 (24) | 1754 (17) | 6628 (29) | 165 (21) | | | | | |
| | | | | | Cation 3 | | | | |
| $N_3$ | 4198 (14) | 1863 (12) | 5871 (14) | 92 (10) | $C_{3g1}$ | 3349 (43) | 2867 (39) | 7118 (50) | 306 (47) |
| $C_{3a1}$ | 4039 (18) | 2188 (15) | 6634 (18) | 99 (13) | $C_{3g2}$ | 2652 (26) | 624 (16) | 6010 (21) | 128 (18) |
| $C_{3a2}$ | 3513 (18) | 1460 (15) | 5669 (17) | 95 (13) | $C_{3g3}$ | 5835 (29) | 787 (27) | 5456 (21) | 188 (28) |
| $C_{3a3}$ | 4969 (16) | 1560 (14) | 5990 (15) | 85 (12) | $C_{3g4}$[d] | 5015 (40) | 2786 (40) | 4434 (65) | 372 (59) |
| $C_{3a4}$ | 4188 (18) | 2203 (17) | 5143 (22) | 124 (16) | $C_{3g4'}$[d] | 4655 (29) | 3323 (19) | 4570 (25) | 185 (22) |
| $C_{3b1}$ | 3331 (28) | 2514 (21) | 6594 (30) | 175 (23) | $C_{3d1}$ | 2834 (41) | 3019 (40) | 7375 (40) | 257 (47) |
| $C_{3b2}$ | 3409 (18) | 957 (16) | 6262 (17) | 97 (13) | $C_{3d2}$ | 2548 (25) | 130 (20) | 6541 (24) | 144 (20) |
| $C_{3b3}$ | 5131 (22) | 1203 (20) | 5266 (22) | 135 (18) | $C_{3d3}$[d] | 5748 (38) | 411 (50) | 5820 (40) | 193 (50) |
| $C_{3b4}$ | 4793 (30) | 2717 (34) | 5309 (23) | 197 (31) | $C_{3d3'}$[d] | 6085 (42) | 344 (39) | 4920 (39) | 141 (36) |
| | | | | | Water Molecule of Crystallization | | | | |
| $O_{1w}$ | 2241 (18) | 1101 (11) | −169 (22) | 218 (18) | | | | | |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 1 and S1. [c] For atom $C_{2g2'}$, this is the refined value of the isotropic thermal parameter. For all remaining atoms, this is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] The second butyl group of cation 2 and fourth butyl group of cation 3 appear to be severely disordered; neither of the terminal methyl groups could be located or refined, and the carbon of the third methylene group appears to be statistically disordered between two half-occupancy sites ($C_{2g2}$ and $C_{2g2'}$ for cation 2 and $C_{3g4}$ and $C_{3g4'}$ for cation 3) in the lattice. The carbon of the terminal methyl group for the third butyl group of cation 3 appears to be statistically disordered between two half-occupancy sites ($C_{3d3}$ and $C_{3d3'}$) in the lattice. Carbon atom $C_{2g2'}$ could not be satisfactorily refined as an anisotropic atom.

iped-shaped (B) specimens with edge lengths or dimensions of 0.42 mm (A), 0.40 × 0.48 × 0.52 mm (B), and 0.52 mm (C), respectively. All three crystals were sealed with mother liquor in thin-walled glass capillaries and mounted on diffractometer with their (longest) edge nearly parallel to the $\phi$ axis. Fixed scanning rates of 6, 4, or 3°/min were used for the various shells of data for the three compounds. The data collection and reduction procedures that were used are described elsewhere.[8] In all three of the present studies, counts were accumulated for 17 equal time intervals during the scan, and those 13 contiguous intervals that had the highest single accumulated count at their midpoint were used to calculate the net intensity; the scan width and step-off for background measurements were both 1.00° (A), 1.00° (B), or 0.90° (C), and the ratio of total background counting time to net scanning time was 0.50 for all three compounds. The intensity data for all three compounds were corrected empirically for variable absorption effects by using $\psi$ scans for five (A) or six (B and C) reflections having $2\theta$ between 6.6 and 31.1°; the relative transmission factors ranged from 0.47 (A), 0.37 (B), and 0.26 (C) to 1.00. The metal and chlorine atoms of the asymmetric units were located by using (SHELXTL) "direct-methods" techniques, and counter-weighted[9] anisotropic full-matrix least-squares refinement of the structural parameters for these metals and chlorine atoms gave $R$ (unweighted, based on $F$)[10] = 0.140 (A), 0.121 (B), and 0.122 (C) for 4473 (A), 5833 (B), and 7338 (C) independent absorption-corrected reflections having $I > 3\sigma(I)$ and $2\theta(\text{Mo } K\bar{\alpha}) < 43°$ (A), 50.7° (B), and 55.0° (C). A series of difference Fourier syntheses based on increasingly more complete structural models for all three compounds revealed the remainder of the non-hydrogen atoms for each anion and most (A) or all (B and C) of the non-hydrogen atoms for the cations and solvent mole-

---

(8) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.

(9) For counter weights: $\sigma(F) = \{[\sigma(F_o)]^2 + (p|F_o|)^2\}^{1/2}$, where the "ignorance factor", $p$, has the value 0.03 for all three compounds.

**Table III.** Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2{\cdot}0.5[C_6H_4(CH_3)_2]$[a]

| atom type[b] | fractional coordinates $10^4x$ | $10^4y$ | $10^4z$ | equiv isotropic thermal param $10B$, Å$^2$ [c] | atom type[b] | fractional coordinates $10^4x$ | $10^4y$ | $10^4z$ | equiv isotropic thermal param $10B$, Å$^2$ [c] |
|---|---|---|---|---|---|---|---|---|---|
| Anion | | | | | | | | | |
| $W_1$ | 4868 (1) | 936 (1) | 3745 (1) | 26 (1) | $O_{D1}$ | 3584 (9) | 7 (9) | 4138 (7) | 25 (3) |
| $W_2$ | 3801 (1) | −569 (1) | 2188 (1) | 27 (1) | $O_{D2}$ | 2806 (9) | −1117 (10) | 2806 (6) | 28 (3) |
| $W_3$ | 1989 (1) | 950 (1) | 1775 (1) | 33 (1) | $O_{D3}$ | 1324 (10) | 139 (11) | 2464 (8) | 37 (4) |
| $W_4$ | 2960 (1) | 2352 (1) | 3400 (1) | 31 (1) | $O_{D4}$ | 2097 (11) | 1276 (10) | 3780 (8) | 37 (4) |
| $W_5$ | 4594 (1) | 1987 (1) | 2085 (1) | 29 (1) | $O_E$ | 5494 (11) | 2772 (13) | 1592 (9) | 49 (5) |
| Ti | 2128 (3) | −169 (3) | 3425 (2) | 25 (1) | $O_{F1}$ | 5861 (10) | 869 (12) | 4518 (8) | 40 (4) |
| $O_A$ | 3409 (10) | 888 (10) | 2825 (7) | 25 (3) | $O_{F2}$ | 4151 (12) | −1604 (10) | 1717 (8) | 42 (4) |
| $O_{B1}$ | 4900 (9) | −257 (11) | 3118 (7) | 31 (4) | $O_{F3}$ | 988 (15) | 1003 (14) | 1030 (10) | 60 (6) |
| $O_{B2}$ | 2667 (11) | −180 (10) | 1463 (7) | 35 (4) | $O_{F4}$ | 2716 (13) | 3436 (11) | 3851 (8) | 45 (5) |
| $O_{B3}$ | 1972 (11) | 2148 (10) | 2439 (8) | 39 (4) | $C_1$ | 1648 (19) | −1632 (16) | 4153 (16) | 53 (8) |
| $O_{B4}$ | 4226 (11) | 2037 (10) | 4101 (8) | 39 (4) | $C_2$ | 934 (20) | −1782 (23) | 3483 (16) | 76 (10) |
| $O_{C1}$ | 5548 (9) | 1741 (10) | 3056 (7) | 28 (3) | $C_3$ | 353 (17) | −968 (28) | 3532 (16) | 76 (11) |
| $O_{C2}$ | 4730 (11) | 640 (10) | 1776 (7) | 35 (4) | $C_4$ | 686 (21) | −388 (17) | 4188 (18) | 54 (9) |
| $O_{C3}$ | 3269 (13) | 1815 (13) | 1434 (9) | 53 (6) | $C_5$ | 1522 (21) | −798 (18) | 4589 (12) | 49 (7) |
| $O_{C4}$ | 4102 (11) | 2915 (10) | 2739 (8) | 36 (4) | | | | | |
| Cation 1 | | | | | | | | | |
| $N_1$ | 4528 (13) | 6282 (12) | 3343 (10) | 35 (5) | $C_{1g1}$ | 3508 (19) | 5903 (19) | 5348 (12) | 44 (7) |
| $C_{1a1}$ | 4266 (17) | 5761 (15) | 4113 (12) | 37 (6) | $C_{1g2}$ | 1689 (21) | 5582 (18) | 2137 (17) | 58 (8) |
| $C_{1a2}$ | 3474 (19) | 6397 (17) | 2844 (12) | 45 (7) | $C_{1g3}$ | 6350 (30) | 5278 (25) | 1929 (20) | 83 (13) |
| $C_{1a3}$ | 5203 (21) | 5574 (16) | 2983 (14) | 48 (7) | $C_{1g4}$ | 6919 (20) | 8534 (17) | 4089 (16) | 55 (8) |
| $C_{1a4}$ | 5159 (17) | 7401 (15) | 3504 (14) | 42 (7) | $C_{1d1}$ | 2711 (21) | 6384 (21) | 5830 (15) | 54 (8) |
| $C_{1b1}$ | 3544 (17) | 6368 (19) | 4555 (13) | 44 (7) | $C_{1d2}$ | 846 (25) | 4559 (26) | 1872 (23) | 94 (14) |
| $C_{1b2}$ | 2720 (23) | 5391 (20) | 2626 (16) | 60 (9) | $C_{1d3}$ | 7478 (31) | 5455 (34) | 2406 (20) | 94 (16) |
| $C_{1b3}$ | 5550 (25) | 5983 (22) | 2206 (15) | 64 (10) | $C_{1d4}$ | 7284 (17) | 8865 (22) | 3301 (21) | 74 (11) |
| $C_{1b4}$ | 6268 (17) | 7463 (17) | 4046 (12) | 40 (6) | | | | | |
| Cation 2 | | | | | | | | | |
| $N_2$ | −2013 (14) | 1837 (15) | 616 (10) | 44 (6) | $C_{2g1}$ | −3529 (41) | 4073 (30) | −184 (25) | 116 (19) |
| $C_{2a1}$ | −2775 (46) | 2556 (45) | 261 (34) | 165 (27) | $C_{2g2}$ | −3845 (33) | −949 (25) | 439 (24) | 101 (15) |
| $C_{2a2}$ | −2786 (49) | 899 (24) | 533 (22) | 163 (23) | $C_{2g3}$ | 287 (33) | 2430 (38) | −627 (24) | 119 (19) |
| $C_{2a3}$ | −1075 (35) | 1976 (45) | 220 (28) | 190 (27) | $C_{2g4}$ | −1308 (33) | 2086 (39) | 2826 (23) | 126 (19) |
| $C_{2a4}$ | −1607 (51) | 1941 (47) | 1496 (23) | 207 (28) | $C_{2d1}$ | −3123 (62) | 5166 (41) | −248 (32) | 204 (33) |
| $C_{2b1}$ | −2784 (38) | 3384 (55) | 33 (23) | 142 (26) | $C_{2d2}$ | −3618 (39) | −1915 (37) | 564 (24) | 120 (20) |
| $C_{2b2}$ | −2981 (38) | −115 (36) | 595 (22) | 133 (20) | $C_{2d3}$ | 609 (40) | 2525 (57) | −1291 (32) | 218 (34) |
| $C_{2b3}$ | −680 (36) | 2196 (42) | −342 (29) | 174 (25) | $C_{2d4}$ | −680 (38) | 1913 (32) | 3481 (19) | 113 (18) |
| $C_{2b4}$ | −1529 (43) | 1720 (31) | 2064 (16) | 127 (20) | | | | | |
| Solvent Molecule of Crystallization | | | | | | | | | |
| $C_{1s}$ | 537 (19) | 4581 (20) | 4465 (15) | 50 (8) | $C_{3s}$ | −37 (20) | 4534 (27) | 5774 (20) | 80 (12) |
| $C_{2s}$ | 480 (19) | 4061 (19) | 5172 (15) | 51 (7) | $C_{4s}$ | 953 (23) | 3153 (24) | 5269 (20) | 76 (12) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 2, 3, and S2. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

cules of crystallization. The second butyl group of cation 2 and fourth butyl group of cation 3 in A appear to be severely disordered; neither of the terminal methyl groups could be located or refined, and the carbon of the third methylene group appears to be statistically disordered between two half-occupancy sites ($C_{2g2}$ and $C_{2g2'}$ for cation 2 and $C_{3g4}$ and $C_{3g4'}$ for cation 3) in the lattice. The carbon of the terminal methyl group for the third butyl group of cation 3 in A appears to be statistically-disordered between two half-occupancy sites ($C_{3d3}$ and $C_{3d3'}$) in the lattice.

Structural models that utilized anisotropic thermal parameters for all non-hydrogen atoms of all three compounds (except $C_{2g2'}$ of A, which was refined as an isotropic atom) and fixed isotropic thermal parameters for idealized cyclopentadienyl hydrogen atoms were refined to convergence [$R^{10}$ = 0.052 (A), 0.054 (B), and 0.054 (C) and $R_w^{10}$ = 0.060 (A), 0.064 (B), and 0.066 (C) for 4473 (A), 5833 (B), and 7338 (C) independent absorption-corrected reflections having $I > 3\sigma(I)$] using counter-weighted cascade block-diagonal least-squares techniques.

All structure factor calculations for all three compounds employed recent tabulations of atomic form factors[7b] and anomalous dispersion corrections[7c] to the scattering factors of the W, Ti, and Cl atoms. The final cycles of refinement for all three compounds utilized a least-squares-refineable extinction correction.[11] All calculations were performed on a Data General Eclipse S-200 or S-230 computer equipped with 256 K of 16-bit words, a floating-point processor for 32- and 64-bit arithmetic, and versions of the Nicolet EXTL and SHELXTL interactive crystallographic software packages as modified at Crystalytics Co., Lincoln, NE.

## Results and Discussion

**$[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ (1).** The synthesis and characterization of this anion as a tetra-*n*-butylammonium salt have been reported in ref 2. A single-crystal X-ray diffraction study of its water solvate was undertaken to provide structural data for comparison with the protonated species.

X-ray structural analysis of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3{\cdot}H_2O$ revealed the presence of discrete $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ anions **1** (Figure 1), $[(n\text{-}C_4H_9)_4N]^+$ cations (Figure S1[5]), and a water solvent molecule of crystallization. Bond lengths and angles for **1** are given in Tables V and VI, respectively; corresponding data for the cations are given in Tables SVII[5] and SVIII.[5] Anion **1** is seen to contain a $Ti^{IV}$ center sandwiched between $\eta^5\text{-}C_5H_5^-$ and $\kappa^5O\text{-}W_5O_{18}^{6-}$ ligands. The $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ structure is thus formally derived from the $W_6O_{19}^{2-}$ structure[12] through replacement of an $(O{=}W)^{4+}$ unit by a

---

(10) The $R$ values are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where $w = [\sigma(F)]^{-2}$ is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where $K$ is the scale factor.

(11) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(12) (a) Henning, G.; Huellen, A. Z. *Kristallogr., Kristallgeom., Kristallphys., Krastallchem.* **1969**, *130*, 162–72. (b) Kirillova, N. I.; Kolomnikov, I. S.; Zolotarev, Yu. A.; Lysyak, T. V.; Struchkov, Yu. T. *Sov. J. Coord. Chem. (Engl. Transl.)* **1978**, *B34*, 1764–70. (c) Fuchs, V. J.; Freiwald, W.; Hartl, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr., Cryst. Chem.* **1978**, *B34*, 1764–1770. (d) LaRue, W. A.; Liu, A. T.; San Filippo, J., Jr. *Inorg. Chem.* **1980**, *19*, 315–320.

**Table IV.** Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$[a]

| atom type[b] | fractional coordinates $10^4x$ | $10^4y$ | $10^4z$ | equiv isotropic thermal param $10B$, Å$^2$[c] |
|---|---|---|---|---|
| | | Anion 1 | | |
| $W_1$ | −1100 (1) | −299 (1) | −2635 (1) | 25 (1) |
| $W_2$ | 1441 (1) | −259 (1) | −1901 (1) | 24 (1) |
| $W_3$ | 1518 (1) | −2807 (1) | −2436 (1) | 27 (1) |
| $W_4$ | −1033 (1) | −2842 (1) | −3166 (1) | 29 (1) |
| $W_5$ | 588 (1) | −1185 (1) | −3805 (1) | 26 (1) |
| Ti | −198 (2) | −2056 (2) | −1253 (2) | 27 (1) |
| $O_A$ | 165 (7) | −1557 (7) | −2461 (6) | 21 (2) |
| $O_{B1}$ | 134 (8) | 481 (7) | −2026 (6) | 25 (3) |
| $O_{B2}$ | 2248 (7) | −1517 (8) | −1952 (7) | 27 (3) |
| $O_{B3}$ | 291 (9) | −3570 (8) | −3061 (7) | 32 (3) |
| $O_{B4}$ | −1847 (8) | −1544 (8) | −3118 (7) | 29 (3) |
| $O_{C1}$ | −512 (9) | −186 (8) | −3577 (6) | 28 (3) |
| $O_{C2}$ | 1510 (8) | −198 (8) | −2995 (6) | 27 (3) |
| $O_{C3}$ | 1586 (8) | −2188 (8) | −3470 (7) | 30 (3) |
| $O_{C4}$ | −498 (8) | −2223 (8) | −4070 (6) | 29 (3) |
| $O_{D1}$ | −1230 (8) | −844 (8) | −1558 (6) | 29 (3) |
| $O_{D2}$ | 916 (9) | −838 (9) | −968 (6) | 33 (3) |
| $O_{D3}$ | 996 (8) | −2944 (8) | −1510 (7) | 28 (3) |
| $O_{D4}$ | −1140 (8) | −2941 (8) | −2099 (7) | 31 (3) |
| $O_E$ | 883 (10) | −913 (10) | −4721 (7) | 38 (3) |
| $O_{F1}$ | −2054 (9) | 634 (9) | −2666 (8) | 39 (3) |
| $O_{F2}$ | 2333 (9) | 659 (9) | −1399 (7) | 37 (3) |
| $O_{F3}$ | 2518 (9) | −3712 (9) | −2441 (8) | 40 (4) |
| $O_{F4}$ | −1936 (10) | −3752 (10) | −3704 (9) | 48 (4) |
| $C_1$ | −1273 (15) | −1954 (16) | −211 (10) | 40 (5) |
| $C_2$ | −230 (16) | −1661 (17) | 166 (11) | 44 (6) |
| $C_3$ | 403 (16) | −2515 (17) | 71 (12) | 45 (6) |
| $C_4$ | −269 (19) | −3357 (16) | −388 (12) | 52 (7) |
| $C_5$ | −1293 (16) | −2988 (15) | −536 (12) | 41 (5) |
| | | Anion 2 | | |
| Cl | −2439 (4) | 530 (4) | −572 (3) | 45 (1) |
| | | Cation 1 | | |
| $N_1$ | −307 (10) | 6748 (9) | 3154 (8) | 28 (3) |
| $C_{1a1}$ | −796 (16) | 7710 (13) | 3553 (12) | 41 (5) |
| $C_{1a2}$ | −1146 (15) | 6102 (13) | 2525 (11) | 42 (5) |
| $C_{1a3}$ | 559 (15) | 7195 (12) | 2740 (13) | 42 (6) |
| $C_{1a4}$ | 136 (14) | 5967 (13) | 3784 (11) | 38 (5) |
| $C_{1b1}$ | −1701 (17) | 7473 (14) | 4000 (12) | 43 (6) |
| $C_{1b2}$ | −1773 (19) | 6740 (21) | 1896 (15) | 65 (8) |
| $C_{1b3}$ | 1133 (17) | 6266 (14) | 2226 (14) | 48 (6) |
| $C_{1b4}$ | 1201 (14) | 6360 (15) | 4340 (13) | 44 (5) |
| $C_{1g1}$ | −2201 (15) | 8465 (15) | 4301 (13) | 44 (6) |
| $C_{1g2}$ | −2639 (25) | 6086 (26) | 1308 (17) | 83 (10) |
| $C_{1g3}$ | 2065 (18) | 6793 (19) | 1986 (13) | 55 (7) |
| $C_{1g4}$ | 1320 (12) | 5620 (13) | 5018 (11) | 32 (4) |
| $C_{1d1}$ | −3132 (16) | 8225 (18) | 4736 (18) | 63 (8) |
| $C_{1d2}$ | −2223 (35) | 5237 (30) | 857 (23) | 113 (16) |
| $C_{1d3}$ | 2555 (22) | 5982 (22) | 1428 (19) | 76 (10) |
| $C_{1d4}$ | 2480 (16) | 5627 (18) | 5433 (14) | 53 (7) |
| | | Cation 2 | | |
| $N_2$ | 4865 (12) | 1658 (14) | 2541 (10) | 46 (5) |
| $C_{2a1}$ | 5822 (13) | 1708 (18) | 3222 (12) | 46 (6) |
| $C_{2a2}$ | 4317 (15) | 539 (21) | 2435 (13) | 55 (7) |
| $C_{2a3}$ | 5309 (15) | 1836 (20) | 1763 (12) | 51 (6) |
| $C_{2a4}$ | 4018 (18) | 2453 (22) | 2743 (18) | 68 (9) |
| $C_{2b1}$ | 5561 (15) | 1544 (19) | 4072 (12) | 49 (6) |
| $C_{2b2}$ | 5069 (22) | −371 (25) | 2286 (23) | 91 (12) |
| $C_{2b3}$ | 4465 (17) | 1854 (21) | 998 (14) | 63 (8) |
| $C_{2b4}$ | 4420 (36) | 3640 (26) | 2790 (23) | 107 (15) |
| $C_{2g1}$ | 6577 (18) | 1379 (23) | 4625 (14) | 70 (8) |
| $C_{2g2}$ | 4558 (25) | −1436 (28) | 2278 (27) | 110 (15) |
| $C_{2g3}$ | 4996 (23) | 1872 (30) | 241 (15) | 86 (11) |
| $C_{2g4}$ | 4490 (34) | 4229 (35) | 3550 (29) | 127 (18) |
| $C_{2d1}$ | 6429 (22) | 1355 (22) | 5506 (16) | 69 (9) |
| $C_{2d2}$ | 5411 (31) | −2258 (28) | 2247 (25) | 107 (15) |
| $C_{2d3}$ | 5688 (30) | 2850 (34) | 278 (21) | 115 (15) |
| $C_{2d4}$ | 4674 (34) | 5384 (25) | 3601 (32) | 131 (19) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 4, 5, and S3. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

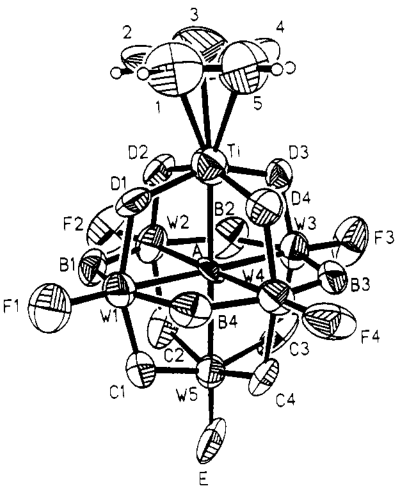


**Figure 1.** Perspective drawing of the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ anion, **1**, present in crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ (A). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; cyclopentadienyl hydrogen atoms are not labeled and are represented by small spheres which are in no way representative of their true thermal motion. Oxygen and carbon atoms are labeled only by their subscripts.

$(C_5H_5Ti)^{3+}$ unit. The $W_6O_{19}{}^{2-}$ structure approximates $O_h$ symmetry and contains three types of oxygen atoms: six terminal oxygen atoms with $d_{W\text{-}O_t} = 1.69$ Å, twelve doubly-bridging oxygen atoms with $d_{W\text{-}O_b} = 1.92$ Å, and a unique 6-fold-bridging central oxygen atom with $d_{W\text{-}O_c} = 2.33$ Å.[12b] Comparison of these distances with the $C_{4v}$-averaged metal–oxygen distances for the $W_5O_{18}{}^{6-}$ anion in **1** (see Table V) shows significant deviation only for the doubly-bridging $d_{W\text{-}O_D}$ oxygens, with $d_{W\text{-}O_D} = 1.86$ Å. This is in marked contrast with the $W_5O_{18}{}^{6-}$ ligand in the $[Ce(W_5O_{18})_2]^{8-}$[13] and $[U(W_5O_{18})_2]^{8-}$[14] structures, where a pattern of trans bond alternation extends throughout the entire ligand, presumably due to even stronger W–$O_D$ bonds.[2] The $Ti^{IV}$–$O_D$ bonds in **1** are thus seen to be weaker than $W^{VI}$–$O_b$ bonds in $W_6O_{19}{}^{2-}$ but stronger than the corresponding $Ce^{IV}$–O and $U^{IV}$–O bonds in the $[M^{IV}(W_5O_{18})_2]^{8-}$ anions (see ref 2).

**$[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ (2).** Reaction of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$ with trichloroacetic acid in ethanol/dichloromethane yields anion **2** as a tetra-*n*-butylammonium salt that can be isolated in pure form in slightly greater than 50% yield. Its formulation, based on elemental analysis as well as $^1H$ and $^{17}O$ NMR spectroscopic data, is supported by the results of an X-ray diffraction study of its crystalline *p*-xylene solvate. This study established that single crystals of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5C_6H_4(CH_3)_2$ are composed of discrete $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ anions (Figure 2), $[(n\text{-}C_4H_9)_4N]^+$ cations (Figure S2[5]), and *p*-xylene solvent molecules of crystallization (Figure S2[5]). Bond lengths and angles for the anion are tabulated in Tables V and VI, respectively, while those for the $[(n\text{-}C_4H_9)_4N]^+$ cations and *p*-xylene solvent molecule of crystallization are given Tables SVII,[5] SVIII,[5] and SIX.[5]

The $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ anions are present in the lattice as hydrogen-bonded dimers about the crystallographic inversion center at ($^1/_2$, 0, $^1/_2$) in the unit cell (Figure 3). A pair of short, 2.71-Å, interionic contacts between $O_{D1}$ and $O'_{F1}$ strongly suggests hydrogen bonding of the type previously observed in $[H_7(\alpha\text{-}PtMo_6O_{24}H)_2]^{7-}$,[15] $[H_7(\alpha\text{-}PtW_6O_{24}H)_2]^{7-}$,[16] $[H_6(V_{10}O_{28})_2]^{6-}$,[17] and

---

(13) Iball, J.; Low, J. N.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2021–2024.

(14) Golubev, A. M.; Muradyan, L. A.; Kazanskii, L. P.; Torchenkova, E. A.; Simonov, V. I.; Spitsyn, V. I. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1977**, *3*, 715–720.

(15) Lee, U.; Sasaki, Y. *Chem. Lett.* **1984**, 1297–1300.

(16) Lee, U.; Sasaki, Y. *J. Kor. Chem. Soc.* **1987**, *31*, 118–120.

(17) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991–3002.

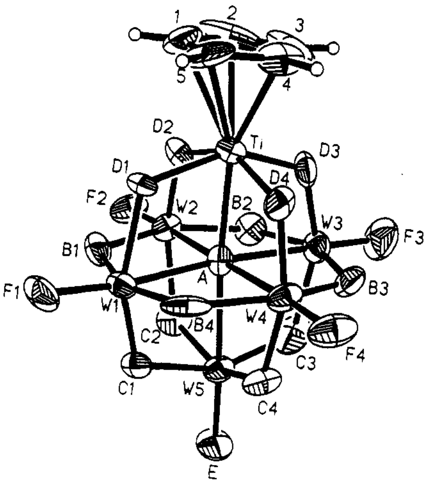


**Figure 2.** Perspective drawing of the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ anion, **2**, present in crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot0.5\text{-}[C_6H_4(CH_3)_2]$ (B). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; cyclopentadienyl hydrogen atoms are not labeled and are represented by small spheres which are in no way representative of their true thermal motion. Oxygen and carbon atoms are labeled only by their subscripts. The single acidic proton (presumably) on $O_{D1}$ could not be located and is not shown.

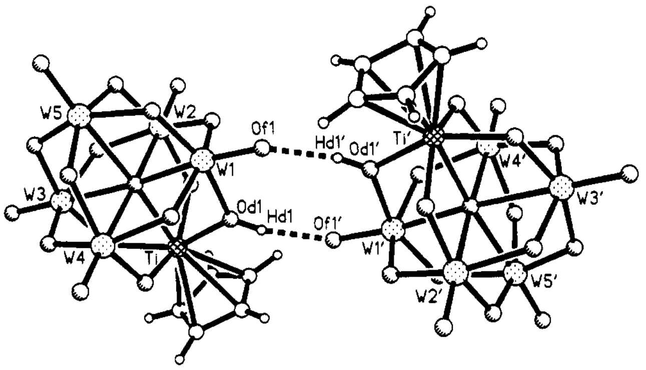


**Figure 3.** Perspective drawing of the (presumably) dimeric hydrogen-bonded $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]_2^{4-}$ moieties present in crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot0.5[C_6H_4(CH_3)_2]$ (B). The protons ($H_{d1}$ and $H_{d1'}$) believed to be involved in the hydrogen bonding are represented by small open spheres and are shown at idealized positions on the $O_{d1}$ oxygen atoms. W, Ti, O, and C atoms are represented by dotted, crosshatched, shaded, and medium-sized open spheres, respectively. Atoms labeled with a prime (′) are related to those labeled without a prime by the crystallographic inversion center at ($^1/_2$, 0, $^1/_2$) in the unit cell. Hydrogen bonds are shown with dashed lines. The $O_{d1}\cdots O_{f1'}$ distance is 2.71 Å, and the $O_{d1}\text{-}H_{d1}\cdots O_{f1'}$ angle is 167°.

$[H_4(SbMo_6O_{24})_2]^{10-}$.[18] Although the acidic proton was not located by X-ray diffraction, its presence and location can be reasonably inferred from a comparison of bond lengths in anions **1** and **2** (see Table V). Specifically, the anomalously long 2.06-Å $W_1\text{-}O_{D1}$ and 2.04-Å $Ti\text{-}O_{D1}$ bonds identify $O_{D1}$ as the protonation site. Nonlocal effects of protonation on metal-oxygen bond strengths cannot be established with much confidence due to the low precision of the structure and perturbations induced by the hydrogen bonds mentioned above. Metal-oxygen bonds do however, as expected, reflect approximate $C_s$ symmetry for **2**. The choice of a bridging oxygen site between a $W^{VI}$ and $Ti^{IV}$ center as the protonation site is not surprising, given that the hexametalate ions $V_2W_4O_{19}^{4-}$ [19] and $Nb_2W_4O_{19}^{4-}$ [20] both protonate at oxygen atoms bridging the pentavalent metal centers. The related Keggin anion $SiV_3W_9O_{40}^{7-}$ is similarly protonated at an oxygen bridging two $V^V$ centers.[21]

**Table V.** Bond Lengths (Å) in the Anions of Crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ (A), $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot0.5C_6H_4(CH_3)_2$ (B), and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C)[a]

| param[b] | value in A | value in B | value in C |
|---|---|---|---|
| $Ti\text{-}C_1$ | 2.53 (4) | 2.37 (2) | 2.38 (2) |
| $Ti\text{-}C_2$ | 2.37 (5) | 2.38 (3) | 2.39 (2) |
| $Ti\text{-}C_3$ | 2.51 (4) | 2.33 (2) | 2.36 (2) |
| $Ti\text{-}C_4$ | 2.31 (4) | 2.36 (3) | 2.32 (2) |
| $Ti\text{-}C_5$ | 2.53 (4) | 2.38 (2) | 2.37 (2) |
| $Ti\cdots C_g$[c] | 2.18 () | 2.07 () | 2.05 () |
| $W_1\text{-}O_{B1}$ | 1.91 (1) | 1.85 (1) | 1.93 (1) |
| $W_2\text{-}O_{B2}$ | 1.88 (2) | 1.92 (1) | 1.91 (1) |
| $W_3\text{-}O_{B3}$ | 1.91 (1) | 1.89 (1) | 1.93 (1) |
| $W_4\text{-}O_{B4}$ | 1.88 (1) | 1.98 (1) | 1.96 (1) |
| $W_2\text{-}O_{B1}$ | 1.91 (1) | 1.96 (1) | 1.91 (1) |
| $W_3\text{-}O_{B2}$ | 1.92 (2) | 1.90 (1) | 1.92 (1) |
| $W_4\text{-}O_{B3}$ | 1.94 (1) | 1.93 (1) | 1.92 (1) |
| $W_1\text{-}O_{B4}$ | 1.95 (1) | 1.86 (1) | 1.88 (1) |
| $Ti\text{-}O_{D1}$ | 1.97 (1) | 2.04 (1) | 2.08 (1) |
| $Ti\text{-}O_{D2}$ | 1.95 (1) | 1.95 (1) | 2.06 (1) |
| $Ti\text{-}O_{D3}$ | 1.93 (2) | 1.93 (1) | 1.98 (1) |
| $Ti\text{-}O_{D4}$ | 1.96 (1) | 1.95 (1) | 1.95 (1) |
| $W_1\text{-}O_{D1}$ | 1.87 (1) | 2.06 (1) | 2.03 (1) |
| $W_2\text{-}O_{D2}$ | 1.87 (1) | 1.83 (1) | 2.00 (1) |
| $W_3\text{-}O_{D3}$ | 1.85 (1) | 1.83 (1) | 1.81 (1) |
| $W_4\text{-}O_{D4}$ | 1.87 (1) | 1.83 (1) | 1.83 (1) |
| $W_1\text{-}O_{C1}$ | 1.96 (1) | 1.83 (1) | 1.87 (1) |
| $W_2\text{-}O_{C2}$ | 1.90 (2) | 2.01 (1) | 1.86 (1) |
| $W_3\text{-}O_{C3}$ | 1.94 (2) | 1.98 (2) | 1.99 (1) |
| $W_4\text{-}O_{C4}$ | 1.93 (1) | 2.01 (1) | 1.99 (1) |
| $W_5\text{-}O_{C1}$ | 1.86 (1) | 2.01 (1) | 1.96 (1) |
| $W_5\text{-}O_{C2}$ | 1.92 (1) | 1.84 (1) | 1.98 (1) |
| $W_5\text{-}O_{C3}$ | 1.93 (2) | 1.86 (1) | 1.87 (1) |
| $W_5\text{-}O_{C4}$ | 1.93 (1) | 1.84 (1) | 1.87 (1) |
| $Ti\text{-}O_A$ | 2.33 (1) | 2.32 (1) | 2.30 (1) |
| $W_1\text{-}O_A$ | 2.32 (1) | 2.26 (1) | 2.28 (1) |
| $W_2\text{-}O_A$ | 2.32 (1) | 2.29 (1) | 2.32 (1) |
| $W_3\text{-}O_A$ | 2.30 (1) | 2.40 (1) | 2.35 (1) |
| $W_4\text{-}O_A$ | 2.30 (1) | 2.28 (1) | 2.32 (1) |
| $W_5\text{-}O_A$ | 2.33 (1) | 2.42 (1) | 2.49 (1) |
| $W_1\text{-}O_{F1}$ | 1.67 (2) | 1.73 (1) | 1.70 (1) |
| $W_2\text{-}O_{F2}$ | 1.73 (2) | 1.68 (1) | 1.68 (1) |
| $W_3\text{-}O_{F3}$ | 1.66 (2) | 1.70 (2) | 1.72 (1) |
| $W_4\text{-}O_{F4}$ | 1.71 (2) | 1.66 (1) | 1.70 (1) |
| $W_5\text{-}O_E$ | 1.67 (2) | 1.73 (1) | 1.71 (1) |
| $Ti\cdots W_1$ | 3.278 (4) | 3.461 (3) | 3.449 (3) |
| $Ti\cdots W_2$ | 3.262 (5) | 3.262 (4) | 3.459 (3) |
| $Ti\cdots W_3$ | 3.264 (5) | 3.275 (4) | 3.271 (3) |
| $Ti\cdots W_4$ | 3.272 (5) | 3.269 (3) | 3.257 (3) |
| $W_5\cdots W_1$ | 3.292 (1) | 3.254 (1) | 3.272 (1) |
| $W_5\cdots W_2$ | 3.304 (1) | 3.321 (1) | 3.287 (1) |
| $W_5\cdots W_3$ | 3.302 (1) | 3.287 (1) | 3.321 (1) |
| $W_5\cdots W_4$ | 3.289 (1) | 3.317 (1) | 3.316 (1) |
| $W_1\cdots W_2$ | 3.274 (1) | 3.256 (1) | 3.266 (1) |
| $W_1\cdots W_4$ | 3.278 (1) | 3.255 (1) | 3.270 (1) |
| $W_2\cdots W_3$ | 3.267 (2) | 3.273 (1) | 3.279 (1) |
| $W_3\cdots W_4$ | 3.256 (1) | 3.262 (1) | 3.277 (1) |
| $C_1\text{-}C_2$ | 1.34 (7) | 1.36 (3) | 1.40 (3) |
| $C_1\text{-}C_5$ | 1.41 (5) | 1.33 (3) | 1.37 (3) |
| $C_2\text{-}C_3$ | 1.26 (6) | 1.38 (5) | 1.37 (3) |
| $C_3\text{-}C_4$ | 1.30 (5) | 1.31 (4) | 1.44 (3) |
| $C_4\text{-}C_5$ | 1.31 (5) | 1.38 (4) | 1.38 (3) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Tables II–IV and Figures 1–5. [c] $C_g$ is used to denote the center-of-gravity for the five carbons in the cyclopentadienyl ligand; these values are therefore listed without an estimated standard deviation.

**$[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ (3).** Addition of ether to an acetonitrile solution of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3$ containing 2 equiv of HCl yields a solid material that can be crystallized from

---

(18) Ogawa, A.; Yamato, H.; Lee, U.; Ichida, H.; Kobayashi, A.; Sasaki, Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *C44*, 1879–1881.

(19) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891–4893.

(20) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030–6044.

(21) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947–2960.

**Table VI.** Bond Angles (deg) in the Anions of Crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ (A), $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5C_6H_4(CH_3)_2$ (B), and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C)[a]

| param[b] | value in A | value in B | value in C |
|---|---|---|---|
| $O_ATiO_{D1}$ | 75.6 (5) | 72.9 (4) | 73.5 (4) |
| $O_ATiO_{D2}$ | 76.0 (5) | 73.8 (5) | 72.9 (4) |
| $O_ATiO_{D3}$ | 74.5 (5) | 75.4 (5) | 74.8 (4) |
| $O_ATiO_{D4}$ | 75.0 (5) | 73.2 (5) | 74.8 (4) |
| $O_{D1}TiO_{D2}$ | 84.4 (6) | 83.2 (5) | 83.2 (4) |
| $O_{D2}TiO_{D3}$ | 87.4 (6) | 87.7 (6) | 85.7 (4) |
| $O_{D3}TiO_{D4}$ | 86.0 (6) | 85.7 (6) | 88.3 (4) |
| $O_{D1}TiO_{D4}$ | 87.3 (6) | 85.5 (5) | 85.4 (4) |
| $O_{D1}TiO_{D3}$ | 150.1 (6) | 148.3 (5) | 148.2 (5) |
| $O_{D2}TiO_{D4}$ | 151.0 (6) | 146.9 (6) | 147.6 (5) |
| $O_{F1}W_1O_{B4}$ | 104.5 (8) | 101.6 (6) | 103.8 (5) |
| $O_{F1}W_1O_{B1}$ | 104.2 (8) | 102.7 (6) | 102.1 (5) |
| $O_{F2}W_2O_{B1}$ | 102.8 (8) | 104.2 (6) | 103.4 (5) |
| $O_{F2}W_2O_{B2}$ | 105.0 (8) | 103.5 (6) | 103.5 (5) |
| $O_{F3}W_3O_{B2}$ | 104.3 (8) | 104.6 (7) | 103.9 (5) |
| $O_{F3}W_3O_{B3}$ | 102.7 (7) | 103.9 (8) | 103.5 (5) |
| $O_{F4}W_4O_{B3}$ | 102.7 (7) | 105.3 (7) | 104.1 (5) |
| $O_{F4}W_4O_{B4}$ | 103.7 (7) | 101.6 (6) | 103.2 (5) |
| $O_{F1}W_1O_{C1}$ | 103.0 (7) | 106.0 (6) | 104.2 (6) |
| $O_{F2}W_2O_{C2}$ | 102.4 (8) | 101.8 (6) | 105.0 (5) |
| $O_{F3}W_3O_{C3}$ | 100.6 (7) | 102.3 (7) | 100.5 (6) |
| $O_{F4}W_4O_{C4}$ | 102.0 (7) | 102.6 (6) | 100.4 (6) |
| $O_{C1}W_1O_{B4}$ | 86.5 (6) | 92.2 (6) | 90.8 (5) |
| $O_{C1}W_1O_{B1}$ | 83.5 (6) | 89.7 (6) | 87.9 (4) |
| $O_{C2}W_2O_{B1}$ | 83.7 (6) | 83.8 (5) | 90.2 (4) |
| $O_{C2}W_2O_{B2}$ | 84.7 (7) | 82.9 (5) | 87.8 (5) |
| $O_{C3}W_3O_{B2}$ | 84.9 (6) | 83.5 (6) | 83.3 (4) |
| $O_{C3}W_3O_{B3}$ | 85.3 (6) | 84.3 (6) | 84.0 (5) |
| $O_{C4}W_4O_{B3}$ | 84.9 (6) | 85.1 (6) | 84.0 (5) |
| $O_{C4}W_4O_{B4}$ | 87.4 (6) | 84.0 (6) | 83.4 (5) |
| $O_{D1}W_1O_{B4}$ | 87.9 (6) | 84.1 (5) | 85.7 (5) |
| $O_{D1}W_1O_{B1}$ | 88.5 (6) | 83.6 (5) | 84.9 (4) |
| $O_{D2}W_2O_{B1}$ | 88.1 (6) | 88.8 (5) | 85.0 (5) |
| $O_{D2}W_2O_{B2}$ | 90.3 (7) | 91.3 (5) | 85.1 (5) |
| $O_{D3}W_3O_{B2}$ | 88.1 (7) | 89.8 (6) | 90.6 (5) |
| $O_{D3}W_3O_{B3}$ | 89.1 (6) | 89.0 (6) | 90.0 (5) |
| $O_{D4}W_4O_{B3}$ | 88.5 (6) | 89.3 (6) | 92.0 (5) |
| $O_{D4}W_4O_{B4}$ | 87.6 (6) | 88.7 (6) | 88.7 (5) |
| $O_EW_5O_{C1}$ | 105.3 (7) | 102.8 (6) | 105.1 (5) |
| $O_EW_5O_{C2}$ | 104.7 (7) | 104.4 (7) | 104.6 (5) |
| $O_EW_5O_{C3}$ | 102.7 (7) | 104.1 (7) | 103.7 (6) |
| $O_EW_5O_{C4}$ | 104.8 (6) | 104.4 (7) | 104.6 (5) |
| $O_{C1}W_5O_{C2}$ | 85.6 (6) | 84.0 (5) | 82.8 (4) |
| $O_{C2}W_5O_{C3}$ | 86.3 (6) | 89.1 (7) | 84.3 (4) |
| $O_{C3}W_5O_{C4}$ | 85.4 (5) | 90.0 (7) | 91.4 (4) |
| $O_{C4}W_5O_{C1}$ | 88.6 (6) | 83.7 (6) | 87.1 (4) |
| $O_AW_1O_{F1}$ | 177.6 (7) | 172.2 (6) | 174.3 (5) |
| $O_AW_2O_{F2}$ | 177.4 (7) | 177.2 (6) | 173.9 (5) |
| $O_AW_3O_{F3}$ | 176.9 (7) | 179.6 (4) | 178.5 (5) |
| $O_AW_4O_{F4}$ | 178.8 (6) | 176.2 (6) | 177.9 (5) |
| $O_AW_5O_E$ | 178.3 (6) | 177.2 (5) | 179.2 (4) |
| $O_ATiC_g$[c] | 178.0 () | 178.1 () | 179.6 () |
| $O_{F1}W_1O_{D1}$ | 104.6 (7) | 98.2 (6) | 99.7 (6) |
| $O_{F2}W_2O_{D2}$ | 104.8 (8) | 105.7 (6) | 100.6 (5) |
| $O_{F3}W_3O_{D3}$ | 106.5 (8) | 105.0 (7) | 105.0 (6) |
| $O_{F4}W_4O_{D4}$ | 103.6 (7) | 105.2 (7) | 104.7 (6) |
| $O_AW_1O_{B4}$ | 75.0 (5) | 77.6 (5) | 77.3 (4) |
| $O_AW_1O_{B1}$ | 76.2 (5) | 77.1 (5) | 76.4 (4) |
| $O_AW_2O_{B1}$ | 76.1 (5) | 74.3 (5) | 75.9 (4) |
| $O_AW_2O_{B2}$ | 75.9 (5) | 77.7 (5) | 76.8 (4) |
| $O_AW_3O_{B2}$ | 75.6 (6) | 75.5 (5) | 75.9 (4) |
| $O_AW_3O_{B3}$ | 77.2 (5) | 75.9 (5) | 76.5 (4) |
| $O_AW_4O_{B3}$ | 76.8 (5) | 78.1 (5) | 77.4 (4) |
| $O_AW_4O_{B4}$ | 76.7 (5) | 74.8 (5) | 75.0 (4) |
| $O_AW_1O_{C1}$ | 74.6 (5) | 81.8 (5) | 81.3 (4) |
| $O_AW_2O_{C2}$ | 75.2 (5) | 75.7 (5) | 81.1 (4) |
| $O_AW_3O_{C3}$ | 76.2 (5) | 77.3 (5) | 78.0 (4) |
| $O_AW_4O_{C4}$ | 76.9 (5) | 75.8 (5) | 78.3 (4) |
| $O_AW_1O_{D1}$ | 77.7 (5) | 74.0 (4) | 74.8 (4) |
| $O_AW_2O_{D2}$ | 77.6 (5) | 76.8 (5) | 73.3 (4) |
| $O_AW_3O_{D3}$ | 76.6 (5) | 75.4 (5) | 76.5 (4) |
| $O_AW_4O_{D4}$ | 77.6 (5) | 76.3 (5) | 76.5 (4) |
| $O_AW_5O_{C1}$ | 76.2 (5) | 74.3 (4) | 74.6 (4) |
| $O_AW_5O_{C2}$ | 74.5 (5) | 75.5 (5) | 74.8 (4) |
| $O_AW_5O_{C3}$ | 75.8 (5) | 78.8 (6) | 76.6 (4) |
| $O_AW_5O_{C4}$ | 76.0 (5) | 75.4 (5) | 76.1 (4) |
| $O_{B4}W_1O_{B1}$ | 151.0 (6) | 154.1 (5) | 153.5 (4) |
| $O_{B1}W_2O_{B2}$ | 151.6 (6) | 151.2 (6) | 152.6 (4) |
| $O_{B2}W_3O_{B3}$ | 152.6 (6) | 150.7 (5) | 151.5 (4) |
| $O_{B3}W_4O_{B4}$ | 153.5 (6) | 152.6 (6) | 151.5 (4) |
| $O_{C1}W_1O_{D1}$ | 152.3 (6) | 155.8 (5) | 156.0 (4) |
| $O_{C2}W_2O_{D2}$ | 152.7 (6) | 152.5 (6) | 154.4 (4) |
| $O_{C3}W_3O_{D3}$ | 152.9 (6) | 152.7 (6) | 154.5 (4) |
| $O_{C4}W_4O_{D4}$ | 154.4 (6) | 152.2 (6) | 154.8 (4) |
| $O_{C1}W_5O_{C3}$ | 152.0 (6) | 153.1 (6) | 150.6 (5) |
| $O_{C2}W_5O_{C4}$ | 150.5 (6) | 150.5 (6) | 150.7 (5) |
| $TiO_AW_1$ | 89.6 (5) | 98.1 (5) | 97.6 (4) |
| $TiO_AW_2$ | 89.0 (4) | 90.0 (4) | 96.9 (3) |
| $TiO_AW_3$ | 89.5 (4) | 87.9 (4) | 89.4 (3) |
| $TiO_AW_4$ | 90.0 (4) | 90.5 (5) | 89.7 (3) |
| $W_5O_AW_1$ | 90.1 (4) | 88.0 (4) | 86.4 (3) |
| $W_5O_AW_2$ | 90.4 (4) | 89.6 (4) | 86.1 (3) |
| $W_5O_AW_3$ | 90.8 (5) | 86.0 (4) | 86.6 (3) |
| $W_5O_AW_4$ | 90.6 (4) | 89.7 (4) | 87.1 (3) |
| $W_1O_AW_2$ | 89.6 (4) | 91.4 (5) | 90.3 (3) |
| $W_2O_AW_3$ | 89.8 (4) | 88.6 (4) | 89.1 (3) |
| $W_3O_AW_4$ | 90.1 (4) | 88.4 (4) | 89.2 (3) |
| $W_4O_AW_1$ | 90.4 (4) | 91.6 (4) | 90.6 (3) |
| $TiO_AW_5$ | 179.3 (4) | 173.9 (5) | 174.9 (4) |
| $W_1O_AW_3$ | 179.0 (6) | 174.0 (6) | 173.0 (5) |
| $W_2O_AW_4$ | 179.0 (4) | 176.9 (6) | 173.1 (5) |
| $TiO_{D1}W_1$ | 117.1 (7) | 115.1 (6) | 114.1 (5) |
| $TiO_{D2}W_2$ | 117.4 (7) | 119.2 (7) | 116.7 (5) |
| $TiO_{D3}W_3$ | 119.3 (7) | 121.3 (6) | 119.3 (6) |
| $TiO_{D4}W_4$ | 117.4 (7) | 119.9 (8) | 118.8 (6) |
| $W_5O_{C1}W_1$ | 119.1 (7) | 115.8 (6) | 117.5 (5) |
| $W_5O_{C2}W_2$ | 119.9 (8) | 119.0 (7) | 118.0 (6) |
| $W_5O_{C3}W_3$ | 117.1 (7) | 117.9 (8) | 118.7 (6) |
| $W_5O_{C4}W_4$ | 116.5 (6) | 118.6 (6) | 118.3 (5) |
| $W_1O_{B1}W_2$ | 117.9 (7) | 117.1 (7) | 116.3 (5) |
| $W_2O_{B2}W_3$ | 118.5 (8) | 118.0 (6) | 118.0 (5) |
| $W_3O_{B3}W_4$ | 115.8 (7) | 117.4 (8) | 116.7 (5) |
| $W_4O_{B4}W_1$ | 117.9 (6) | 115.6 (6) | 116.9 (5) |
| $C_1C_2C_3$ | 117 (4) | 104 (2) | 108 (2) |
| $C_2C_3C_4$ | 97 (4) | 111 (2) | 107 (2) |
| $C_3C_4C_5$ | 121 (4) | 108 (2) | 108 (2) |
| $C_4C_5C_1$ | 98 (4) | 106 (2) | 108 (2) |
| $C_5C_1C_2$ | 104 (4) | 111 (2) | 109 (2) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Tables II–IV and Figures 1–5. [c] $C_g$ is used to denote the center-of-gravity for the five carbons in the cyclopentadienyl ligand; these values are therefore listed without an estimated standard deviation.

acetonitrile/ether to give analytically pure $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$. An X-ray structural analysis of material recrystallized from nitromethane/xylene revealed the presence of $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ anions (Figure 4), $(n\text{-}C_4H_9)_4N^+$ cations (Figure S3[5]), and $Cl^-$ anions, which are used to form a pair of $O_D\text{–}H_D\cdots Cl\cdots H_D\text{–}O_D$ hydrogen bonds between two $C_i$-related molecules (Figure 5). Bond lengths and angles for anion **3** are tabulated in Tables V and VI, respectively. Corresponding data for the cations are given in Tables SVII[5] and SVIII.[5]

As was the case for anion **2**, the acidic protons in $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ could not be located X-ray crystallographically. Their locations could be reasonably inferred, however, by comparison of metal–oxygen bond lengths in anions **1** and **3** (see Table V). This comparison shows unusually long bonds to oxygens $O_{D1}$ and $O_{D2}$, thus identifying these oxygen atoms as protonation sites. The entire metal–oxygen framework closely conforms to the implied $C_s$ framework symmetry, and the structure determination is sufficiently precise to discern systematic variations in metal to bridging oxygen bond lengths that are attributable

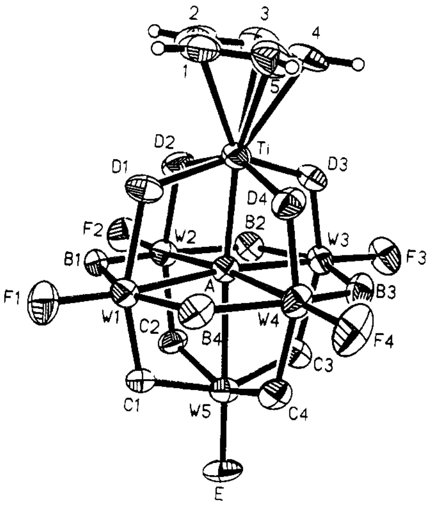


**Figure 4.** Perspective drawing of the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)]^-$ anion, 3, present in crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; cyclopentadienyl hydrogen atoms are not labeled and are represented by small spheres which are in no way representative of their true thermal motion. Oxygen and carbon atoms are labeled only by their subscripts. The two acidic protons (presumably on $O_{D1}$ and $O_{D2}$) could not be located and are not shown.

to $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})]^{3-}$ protonation. This is achieved by examining the three sets of mutually perpendicular, planar $M_4O_4$ rings in the structure: the $W_4O_4$ ring formed by $W_1$–$W_4$ and all four $O_B$ oxygen atoms (see Figure 4) and the two (pseudo) $C_s$-equivalent $TiW_3O_4$ rings formed by Ti, $W_1$, $W_5$, and $W_3$ (or Ti, $W_2$, $W_5$, and $W_4$), plus two $O_C$ and two $O_D$ oxygen atoms. Bond lengths in the $W_4O_4$ ring are relatively constant, with an average value of 1.92 (1, 1, 4, 8) Å[22] and deviate little from the 1.91 (1, 2, 4, 8) Å[22] value observed for anion 1 (see Table V). Bond lengths in the $TiW_3O_4$ rings are given in Table V, and $C_s$-averaged values are shown in Scheme Ia for anion 3. The differences between these average bond lengths and the corresponding $C_{4v}$-averaged bond lengths in anion 1 are given in Scheme Ib, where they are seen to follow a pattern of bond length alternation at $W^{VI}$ (but not $Ti^{IV}$) centers. In short, the bond lengths observed within the $W_4O_4$ and $TiW_3O_4$ rings of anion 3 show a pattern of trans bond length alternation at $W^{VI}$ centers originating from the sites of protonation, where long metal–oxygen bonds are observed. Similar behavior has been noted at $Mo^{VI}$ centers in $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})MoO_2Cl]^{2-}$,[3] at $V^V$ centers in $V_{10}O_{28}H_3^{3-}$,[17] and at $Nb^V/W^{VI}$ centers in $[(\eta^5\text{-}C_5Me_5)Rh(Nb_2W_4O_{19})]^{2-}$ [8] and $[(OC)_3Mn(Nb_2W_4O_{19})]^{3-}$ [23] and can also be discerned at $Mo^{VI}$ centers in the $PMo_{12}O_{40}CH_3^{2-}$ structure.[24]

Since the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]^{2-}$ anion is protonated at an OTiW bridging oxygen, protonation at two OTiW-bridging oxygens in anion 3 is the expected result. Note however that two isomeric structures are possible, and that the cis rather than trans oxygens are protonated. This preference for the cis isomer is a direct consequence of the trans bond length alternation mechanism for charge delocalization just noted. Protonation of one $O_D$ oxygen lengthens the metal–oxygen bonds to it and establishes a pattern of trans bond length alternation that removes electron density from (and deactivates with respect to protonation) the $O_D$ oxygen on Ti which is trans to the protonated oxygen; this would leave the two cis $O_D$ oxygens relatively unperturbed. In other words, diprotonation at *trans*-OTiW oxygens causes the two protons to compete for a charge density from oxygen atoms in the same $TiW_3O_4$ ring but diprotonation at *cis*-OTiW oxygens allows the two protons to withdraw charge from two different $TiW_3O_4$ rings. A similar argument has been made regarding protonation sites in $V_{10}O_{28}H_2^{4-}$.[17]

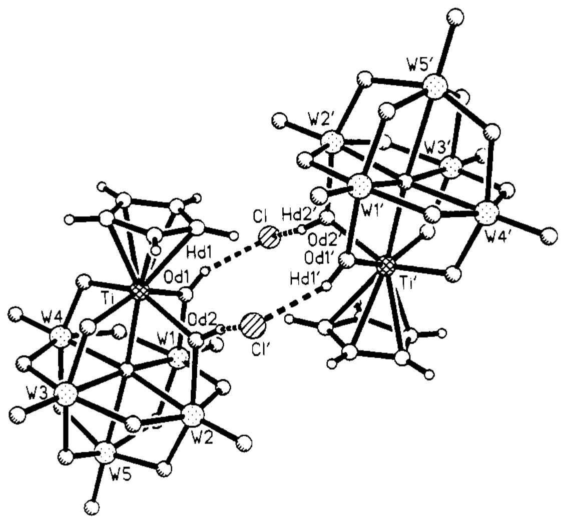
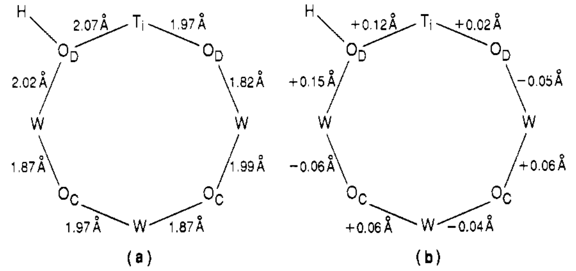


**Figure 5.** Perspective drawing of the (presumably) dimeric hydrogen-bonded $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)Cl]_2^{4-}$ moieties present in crystalline $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C). The protons ($H_{d1}$, $H_{d2}$, $H_{d1'}$, and $H_{d2'}$) believed to be involved in the hydrogen bonding are represented by small open spheres and are shown at idealized positions on the $O_{d1}$ and $O_{d2}$ oxygen atoms. W, Ti, Cl, O, and C atoms are represented by dotted, crosshatched, striped, shaded, and medium-sized open spheres, respectively. Atoms labeled with a prime (′) are related to those labeled without a prime by the crystallographic inversion center at the origin of the unit cell. Hydrogen bonds are shown with dashed lines. The $O_{d1}\cdots Cl$ and $O_{d2'}\cdots Cl$ distances are 2.91 and 2.95 Å, respectively. The $O_{d1}$–$H_{d1}\cdots Cl$, $O_{d2'}$–$H_{d2'}\cdots Cl$, and $H_{d1}\cdots Cl\cdots H_{d2'}$ angles are 158, 147, and 93°, respectively.

**Scheme I**



**$[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})]^{3-}$ (4), $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H)]^{2-}$ (5), and $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18}H_2)]^-$ (6).** Reaction of $(C_5Me_5)TiCl_3$ with acidified $(WO_4)[(n\text{-}C_4H_9)_4N]_2$ in $CH_3CN$ yields anion 4 as a tetra-*n*-butylammonium salt in 76% yield. This salt can be converted to its conjugate monoprotic acid salt 5 in 84% yield by HCl in $H_2O/CH_3CN$ and its conjugate diprotic acid in 50% yield by $CCl_3COOH$ in $CHCl_3/CH_3CN$. All three salts give satisfactory elemental analysis and $^1H$ NMR integrated intensities for $C_5Me_5$ resonances relative to $(n\text{-}C_4H_9)_4N^+$ resonances. The infrared spectra of anions 4–6 in the 1000–350-cm$^{-1}$ region resemble those observed for 1–3, respectively, strongly suggesting a common metal–oxygen structural framework for 1–6. Note that this framework has been characterized X-ray crystallographically in $[(\eta^5\text{-}C_5Me_5)Ti(W_5O_{18})Ir(C_8H_{12})]^{2-}$.[25]

**Acknowledgment.** T.M.C., L.C.F., W.G.K., D.J.M., A.Y., and O.M.Y. are grateful to the National Science Foundation for financial support.

---

(22) The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(23) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44–50.

(24) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265–4266.

(25) Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1989**, 2041–2043.

**Supplementary Material Available:** Crystal structure analysis reports (text and tables), tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, and bond lengths and angles in cations and solvent molecules of crystallization (Tables SI–SIX), and ORTEP plots of cations and solvent molecules of crystallization for $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3\cdot H_2O$ (A), $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2\cdot 0.5[C_6H_4(CH_3)_2]$ (B), and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C) (Figures S1–S3) (41 pages); tables of observed and calculated structure factors for A–C (80 pages). Ordering information is given on any current masthead page.

---

Contribution from the Departments of Chemistry, Indiana University,
Bloomington, Indiana 47405, and University of Durban-Westville, P/B 54001, Durban, South Africa

# Synthesis and Substitution Reactions of Dinuclear Molybdenum Complexes Containing Mo–Mo Quadruple Bonds and Labile Solvent Ligands

Roger H. Cayton,[†] Malcolm H. Chisholm,[*,†] Elena F. Putilina,[†] Kirsten Folting,[†] John C. Huffman,[†] and Kandasamy G. Moodley[‡]

*Received December 2, 1991*

The kinetically labile acetonitrile ligands of $[Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2]^+(BF_4^-)$ (**1**) have been selectively replaced by the anions derived from deprotonation of 6-hydroxy-2-methylpyridine (mhp) and 2,6-dimethylpyridine (dmp) to yield the triscarboxylate complexes $Mo_2(O_2C\text{-}t\text{-}Bu)_3$ (mhp) (**3**) and $Mo_2(O_2C\text{-}t\text{-}Bu)_3$ (dmp) (**4**), respectively. In contrast to complexes containing mixed tetracarboxylate ligand sets, the ligand sets of **3** and **4** were found to be inert with respect to scrambling reactions in solution. **4** crystallized in the centrosymmetric space group $C2/c$, $a = 19.732$ (3) Å, $b = 11.733$ (1) Å, $c = 24.648$ (3) Å, $\beta = 94.57$ (1)°, and $Z = 8$. Treatment of **1** with 1 equiv of 2-(diphenylphosphino)pyridine (dppy) promoted a ligand scrambling reaction to yield equimolar amounts of $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(dppy)_2]^{2+}(BF_4^-)_2$ (**5**) and $Mo_2(O_2C\text{-}t\text{-}Bu)_4$. **5** was also prepared quantitatively by the reaction between $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(MeCN)_6]^{2+}(BF_4^-)_2$ (**2**) and 2 equiv of dppy. The MeCN ligands of **2** were also substituted with $\alpha,\alpha'$-bipyrimidine (bpym) to afford $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(bpym)_2]^{2+}(BF_4^-)_2$ (**6**). The crystal structure of **6** was solved in the monoclinic space group $P2_1/n$ at −177 °C, $a = 11.144$ (1) Å, $b = 10.054$ (1) Å, $c = 35.751$ (6) Å, $\beta = 91.32$ (1)°, and $Z = 4$. The two bpym ligands of **6** each formed five-membered chelate rings employing cis-equatorial positions on the Mo–Mo quadruple bond. Treatment of **6** with an equimolar amount of **2** did not result in a polymer supported by bpym bridges, rather ligand scrambling was again observed. The novel solvated complex $[Mo_2(mhp)_3(MeCN)_2]^+(BF_4^-)$ (**7**) was prepared by alkylation of $Mo_2(mhp)_4$ in acetonitrile. The cation in **7** crystallized as a dimer of $Mo_2$ units connected by two Mo–O axial interactions involving one mhp ligand on each dinuclear cation; at −172 °C, space group = $P2_1/n$, $a = 17.899$ (6) Å, $b = 14.515$ (4) Å, $c = 21.897$ (7) Å, $\beta = 97.04$ (2)°, and $Z = 4$.

## Introduction

The wide variety of electrochemical, magnetic, and photochemical properties associated with complexes possessing metal–metal multiple bonds has prompted us to investigate the viability of preparing low-dimensional materials which incorporate such multiple bond subunits. Our initial efforts concentrated on the synthesis of polymers containing M–M quadruple bonds in a mixed carboxylate framework such as structure I.[1] Unfortunately the

$$\{[M_2(O_2CR)_2](O_2C\text{-}R'\text{-}CO_2)[M_2(O_2CR)_2](O_2C\text{-}R'\text{-}CO_2)\}_n$$

I

$$M = Mo, W$$

generality of polymers of this type turns out to be severely limited by facile carboxylate exchange reactions that often lead to unselective ligand scrambling on the $M_2$ cores.[1b] Such facile scrambling of carboxylate groups on dinuclear compounds was previously observed in a study of the self-exchange reactions of $Mo_2(O_2CCF_3)_4$ with $NaO_2CCF_3$ in acetonitrile by variable temperature $^{19}F$ NMR.[2] More recently, it was found that the rates of self-exchange reactions of $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ with $(n\text{-}Bu_4N)(O_2C\text{-}t\text{-}Bu)$ as determined by variable temperature $^1H$ NMR are quite solvent dependent and in fact different mechanisms are operative in either coordinating or noncoordinating solvents.[3]

The preparation of polymers containing more kinetically persistent coordination spheres about the M–M quadruple bonds rested upon the development of suitable dinuclear starting materials and the selection of the ligand bridge. We found the solvated complexes $[Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2]^+(BF_4^-)$ (**1**) and $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(MeCN)_6]^{2+}(BF_4^-)$ (**2**) to be extremely versatile reagents for the synthesis of tetranuclear complexes of the type shown in structure II[1b,4] and higher oligomers of formula

$$[Mo_2(O_2CR)_3](bridge)[Mo_2(O_2CR)_3]$$

II

$[Mo_2(O_2CR)_2(bridge)]_n$. During the course of this work, we expored a variety of substitution reactions involving the $Mo_2$-containing cations **1** and **2**, along with other related solvated dimolybdenum species, the results of which are presented here.

## Results and Discussion

The replacement of carboxylate ligands in dimolybdenum tetracarboxylate complexes with labile solvent ligands has previously been studied under a variety of conditions.[5] The first such product to be structurally characterized was $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}(BF_4^-)_2$, obtained by the treatment of dimolybdenum tetraacetate with an excess of Meerwein's reagent in acetonitrile.[6] Following a similar reaction we isolated the *t*-Bu analogue, $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(MeCN)_6]^{2+}(BF_4^-)_2$ (**2**) as shown in eq 1.

---

[†] Indiana University.

[‡] University of Durban-Westville.

(1) (a) Cayton, R. H.; Chisholm, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 8921. (b) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. *J. Am. Chem. Soc.* **1991**, *113*, 8709.

(2) Teramoto, K.; Sasaki, Y.; Migita, K.; Iwaizumi, M.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 446.

(3) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Folting, K. Manuscript in preparation.

(4) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 862.

(5) See, for example: (a) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287. (b) Bowen, A. R.; Taube, H. *Inorg. Chem.* **1974**, *13*, 2245. (c) Abbott, E. H.; Schownewolf, F., Jr.; Backstrom, T. *J. Coord. Chem.* **1974**, *3*, 255. (d) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774. (e) Telser, J.; Drago, R. S. *Inorg. Chem.* **1984**, *23*, 1798. (f) Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1991**, *30*, 871.

(6) (a) Cotton, F. A.; Reid, A. H.; Schwotzer, W. *Inorg. Chem.* **1985**, *24*, 3695. (b) Pimblett, G.; Garner, C. G.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1986**, 1257.

0020-1669/92/1331-2928$03.00/0