

## Short communication

Organophosphonate derivatives of titanium and niobium alkoxoanions<sup>1</sup>R. John Errington<sup>\*</sup>, John Ridland, Kathryn J. Willett, William Clegg, Robert A. Coxall,  
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**Abstract**

The organophosphonate-substituted alkoxides  $[\text{Bu}_4^{\text{n}}\text{N}]_2[\{\text{Ti}(\text{OMe})_3(\text{O}_3\text{PPh})\}_2]$  (**1**) and  $[\text{Bu}_4^{\text{n}}\text{N}]_2[\{\text{Nb}(\text{OMe})_3(\text{O}_3\text{PPh})\}_2(\mu\text{-O})]$  (**2**) have been prepared from  $[\text{Bu}_4^{\text{n}}\text{N}][\text{PhPO}_3\text{H}]$  and the metal alkoxides  $\text{Ti}(\text{OMe})_4$  or  $\text{Nb}(\text{OMe})_5$  respectively. In **1**, the bridging phenylphosphonates occupy *trans* coordination sites, whereas in **2**, a *cis*-bridging geometry is adopted. © 1998 Elsevier Science S.A.

**Keywords:** Titanium; Niobium; Organophosphonate; Alkoxide; Crystal structure

**1. Introduction**

Interest in early transition-metal organophosphonates has been restricted mainly to the layered Group 4 organophosphonates  $\text{M}(\text{O}_3\text{PR})_2$  [1] and the structurally diverse polynuclear oxoanion derivatives of vanadium and molybdenum [2]. The incorporation of organophosphonate groups into polyoxometalate structures provides a means of introducing surface organic functionality into these molecular oxides and, as part of a programme to develop hydrolytic aggregation of alkoxide species as a rational approach to polyoxometalate assembly [3–5], we are investigating low nuclearity transition-metal alkoxophosphonates as building-blocks for subsequent hydrolysis studies. By comparison with the polymeric, layered compounds and the polyoxoanions, smaller molecular organophosphonates of the early transition metals remain remarkably unexplored [6], and we report here the synthesis and crystal structures of the first examples of early transition-metal alkoxides containing organophosphonate ligands.

**2. Results and discussion**

The titanium alkoxophosphonate  $[\text{Bu}_4^{\text{n}}\text{N}]_2[\text{Ti}_2(\text{OMe})_6(\text{O}_3\text{PPh})_2]$  (**1**) was obtained from the reaction between  $\text{Ti}(\text{OMe})_4$  and  $[\text{Bu}_4^{\text{n}}\text{N}][\text{PhPO}_3\text{H}]$  in acetonitrile. Although well formed prisms of **1** · MeCN were grown from a cooled acetonitrile solution, they were unsuitable for X-ray crystallography, and crystals of a toluene solvate grown from acetonitrile-toluene were used for the X-ray crystal structure determination. The structure of one of the two crystallographically independent binuclear anions of **1** is shown in Fig. 1 together with selected bond lengths and angles. Each anion has an exact  $C_2$  axis passing through the two Ti atoms and approximate  $C_{2h}$  symmetry overall (ignoring the orientations of the organic substituents). The distorted octahedral titanium centres are bridged by *trans* bidentate  $\text{PhPO}_3^{2-}$  ligands with the phenyl substituents in an *anti* arrangement, and each titanium is displaced from an ideal octahedral position towards the terminal methoxide ligands as indicated by the selected angles (Fig. 1).

In the IR spectrum of **1**, we assign a band at  $1152\text{ cm}^{-1}$  to  $\nu(\text{PO})$  of terminal P=O, bands between  $1120$  and  $1050\text{ cm}^{-1}$  to  $\nu(\text{CO})$  of the alkoxides and bands at  $993$  and  $937\text{ cm}^{-1}$  to  $\nu(\text{PO})$  of the phosphonate bridges. The NMR spectra of **1** suggest the presence of isomers in solution. The  $^1\text{H}$  NMR contains two major peaks at

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<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday, in appreciation of his friendly help and advice over the years.

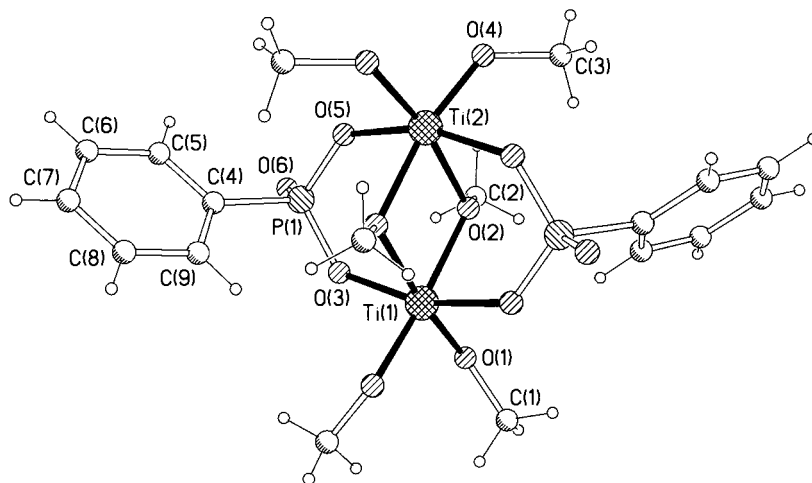


Fig. 1. Structure of one anion of **1** with unique atoms labelled. Selected bond lengths (Å) and angles(°) for this anion: Ti(1)–O(2) 2.037(3), Ti(2)–O(2) 2.045(3), Ti(1)–O(3) 1.979(3), Ti(2)–O(5) 1.981(3), Ti(1)–O(1) 1.847(3), Ti(2)–O(4) 1.842(3), O(2)–Ti(1)–O(2A) 79.53(16), O(2)–Ti(2)–O(2A) 79.15(17), O(3)–Ti(1)–O(1A) 95.1(2), O(4)–Ti(2)–O(4A) 98.4(2), Ti(1)–O(2)–Ti(2) 100.66(8). The geometry of the other anion is essentially the same.

3.94 and 3.66 ppm in the ratio 2:1 due to terminal and bridging OMe groups of the *anti* isomer, while minor peaks at  $\delta$  4.15, 3.93, 3.91 and 3.26 ppm in the ratio 2:2:1:1 can be assigned to the non-equivalent terminal (2:2) and bridging (1:1) OMe groups of the *syn* isomer. From peak integrations, the *anti*:*syn* ratio is *ca.* 4.5:1. The  $^{31}\text{P}$  NMR spectrum at 20°C contains a peak at 8.2 and a smaller one at 7.1 which both broaden slightly on heating the sample to 50°C, and which we assign to the *anti* and *syn* isomers respectively.

The niobium oxoalkoxophosphate  $[\text{Bu}_4\text{N}]_2\text{-}[\text{Nb}_2\text{O}(\text{OMe})_6(\text{O}_3\text{PPh})_2]$  (**2**) was obtained from the reaction between  $\text{Nb}(\text{OMe})_5$  and  $[\text{Bu}_4\text{N}][\text{PhPO}_3\text{H}]$  in acetonitrile. The residue after solvent removal was dissolved in THF, and colourless prisms of **2** formed from this solution over a period of several days. The structure of the binuclear oxoanion in **2** is shown in Fig. 2 together with selected bond lengths and angles. The niobiums are linked by *cis*-bridging phenylphosphonates and also by an oxo ligand, with a NbONb angle of 145.08(12)°. In the IR spectrum of **2**,  $\delta(\text{P}=\text{O})$  appears at 1178  $\text{cm}^{-1}$ ,  $\nu(\text{CO})$  at 1095 and 1003  $\text{cm}^{-1}$ , and  $\nu(\text{PO})$  of the phosphonate bridges at 960  $\text{cm}^{-1}$ , while a peak at 715  $\text{cm}^{-1}$  (which overlaps the aromatic  $\delta(\text{CH})$  peaks) is assigned to  $\nu(\text{NbO})$  of the NbONb linkage. As in the case of **1**, NMR spectra suggest the presence of isomers in solution. Assuming that the same basic structural core is retained, different phosphonate configurations give rise to three isomers as defined in Fig. 3, and in the  $^{31}\text{P}$  NMR spectrum at 20°C, peaks at 7.2 and 5.9 ppm (*exo*, *endo*), 7.1 ppm (*exo*, *exo*) and 6.1 ppm (*endo*, *endo*) in the ratio 3:3:5:1 suggests that while all three isomers are present in solution, the asymmetric *exo*, *endo* isomer is most abundant. The observation of seven methoxide resonances in the  $^1\text{H}$  NMR spectrum is

also consistent with the presence of all three isomers in solution. In a variable-temperature  $^{31}\text{P}$  NMR study, although the peaks did not vary much in relative intensities, they broadened with increasing temperature and had almost collapsed into the baseline at 80°C, suggesting an intramolecular exchange process.

We have yet to determine the origin of the oxo ligand in **2** and it is interesting to note that although the expected alkoxophosphate anion  $[\text{Nb}_2(\text{OMe})_8(\mu\text{-O}_3\text{PPh})_2]^{2-}$  is not isolated from this reaction, the car-

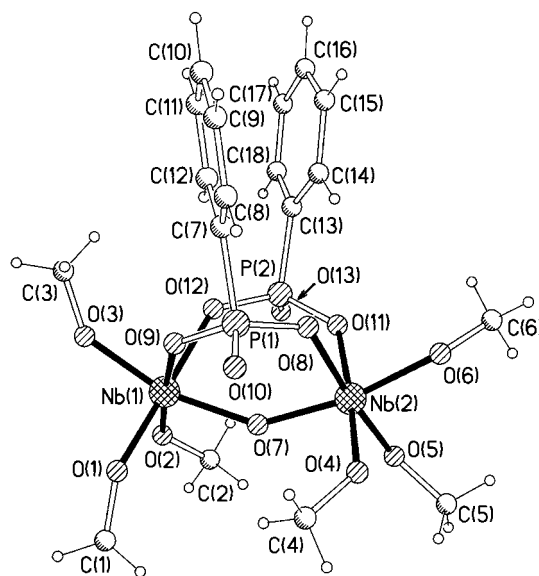


Fig. 2. Structure of the anion of **2** with atoms labelled. Selected bond lengths (Å) and angles(°): Nb(1)–O(7) 1.938(2), Nb(2)–O(7) 1.912(2), Nb(1)–O(9) 2.054(2), Nb(1)–O(12) 2.101(2), Nb(2)–O(8) 2.075(2), Nb(2)–O(11) 2.058(2), Nb(1)–O(1) 1.915(2), Nb(1)–O(2) 1.897(2), Nb(1)–O(3) 1.921(2), Nb(2)–O(4) 1.905(2), Nb(2)–O(5) 1.930(2), Nb(2)–O(6) 1.942(2), Nb(1)–O(7)–Nb(2) 145.08(12).

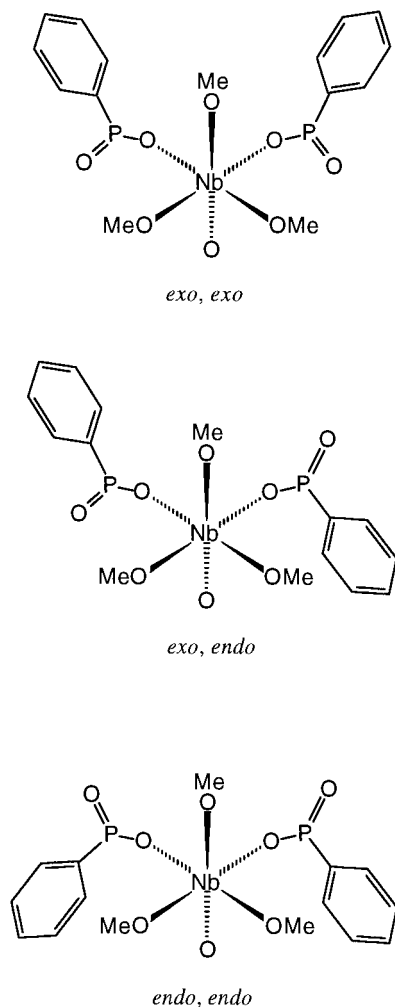


Fig. 3. Isomers of the anion of **2** viewed along the Nb–Nb axis.

boxylate analogue  $[\text{Nb}_2\text{Cl}_4(\text{OEt})_4(\mu\text{-O}_2\text{CPh})_2]$  has been structurally characterised [7]. Additional comparisons with early transition-metal carboxylate derivatives can be made, since the  $\text{M}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2$  core has been observed in the chloro compounds  $[\text{Ti}_2(\mu\text{-O})(\mu\text{-O}_2\text{CPh})_2\text{Cl}_4\text{L}_2]$  (L = THF, EtOAc) [8] and  $[\text{Nb}_2(\mu\text{-O})(\mu\text{-O}_2\text{CPh})_2\text{Cl}_6]$  [9] but, to our knowledge, no Group 4 or 5 carboxylates have been characterised with *trans*-bridging structures analogous to that of **1**.

### 3. Experimental

All manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques, or in a dry-box fitted with a recirculation system. Hydrocarbon and ether solvents were dried over and distilled from sodium–benzophenone and acetonitrile was dried over and distilled from calcium hydride immediately prior to use. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 598 spec-

trometer or on a Mattson Genesis FTIR spectrometer. NMR spectra were recorded on Bruker WP 200, Bruker WM 300 or JEOL Lambda 500 spectrometers. Elemental analyses were performed by the University of Newcastle upon Tyne microanalytical service. NMR resonances due to  $\text{Bu}_4\text{N}^+$  cations are not listed below and appear as multiplets centered at about  $\delta$  1.0, 1.4, 1.6 and 3.1 in  $^1\text{H}$  NMR spectra.

#### 3.1. $[\text{Bu}_4\text{N}]_2[\text{Ti}_2(\text{OMe})_6(\text{O}_3\text{PPh})_2]$ (**1**)

$\text{Ti}(\text{OMe})_4$  (0.5 g, 2.91 mmol) was suspended in MeCN (15 cm<sup>3</sup>) and treated with a solution of  $[\text{Bu}_4\text{N}][\text{PhPO}_3\text{H}]$  (1.16 g, 2.90 mmol) in MeCN (15 cm<sup>3</sup>) with stirring. After 5 min, the mixture was heated to ca. 50°C to give a clear, colourless solution which was then stirred at room temperature for 16 h. Volatiles were removed from the filtered solution under reduced pressure and the solid residue was washed with hexanes and recrystallised from acetonitrile at –30°C to give large prisms of  $[\text{Bu}_4\text{N}]_2[\text{Ti}_2(\text{OMe})_6(\text{O}_3\text{PPh})_2] \cdot 0.5 \text{ MeCN}$  (1.10 g, 69%). (Found: C, 56.2; H, 9.5; N, 3.2.  $\text{C}_{51}\text{H}_{101.5}\text{N}_{2.5}\text{O}_{12}\text{P}_2\text{Ti}_2$  requires: C, 55.7; H, 9.3; N, 3.2%).

Crystals of  $[\text{Bu}_4\text{N}]_2[\text{Ti}_2(\text{OMe})_6(\text{O}_3\text{PPh})_2] \cdot \text{C}_7\text{H}_8$  suitable for X-ray crystallography were obtained by recrystallisation from acetonitrile–toluene.

##### 3.1.1. Spectroscopic data

$^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{CN}$ ): [ppm] ca. 7.9 (m, 4H, aromatic), ca. 7.2 (m, 6H, aromatic), 4.15 (s, 1.09H, OMe), 3.94 (s, 9.84H, OMe), 3.93 (s, 1.09H, OMe), 3.91 (s, 0.55H, OMe), 3.66 (s, 4.92H, OMe), 3.26 (s, 0.55H, OMe).  $^{31}\text{P}$  NMR (202.35 MHz,  $\text{CD}_3\text{CN}$ , 20°C): [ppm] 8.2, 7.1. IR: [ $\text{cm}^{-1}$ ] 1152 (s), 1116 (s), 1080 (m), 1065 (m), 1052 (s), 993 (s), 937 (s), 882 (w), 747 (m), 714 (m), 698 (m), 585 (s), 532 (s), 492 (m), 465 (m), 440 (m), 366 (m).

##### 3.1.2. Crystal structure determination of **1** · ( $\text{C}_7\text{H}_8$ )

Crystal data:  $[\text{C}_{16}\text{H}_{36}\text{N}]_2^+[\text{C}_{18}\text{H}_{28}\text{O}_{12}\text{P}_2\text{Ti}_2]^{2-} \cdot \text{C}_7\text{H}_8$ ,  $M = 1171.2$ , monoclinic, space group  $C2$  (no. 5),  $a = 22.8666(17)$ ,  $b = 16.7727(13)$ ,  $c = 17.4317(14)$  Å,  $\beta = 107.769(2)^\circ$ ,  $V = 6366.7(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.222 \text{ g cm}^{-3}$ ,  $\mu = 0.36 \text{ mm}^{-1}$  (MoK $\alpha$ ,  $\lambda = 0.71073$  Å),  $F_{000} = 2536$ ,  $T = 160 \text{ K}$ , crystal size  $0.28 \times 0.24 \times 0.14 \text{ mm}$ . Siemens SMART CCD area detector diffractometer,  $\omega$  rotation with  $0.3^\circ$  frames,  $1.5 < \theta < 25.0^\circ$ , 16913 measured reflections, 8714 unique ( $R_{\text{int}} = 0.0352$ ), semi-empirical absorption correction, transmission 0.700–0.880. Structure solution by direct methods, refinement on  $F^2$ , anisotropic displacement parameters, riding hydrogen atoms, disorder of some cation chains and toluene solvent,  $R' = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2} = 0.1107$  for all data, conventional  $R =$

0.0449 on  $F$  values of 7868 reflections with  $F_o^2 > 2\sigma(F_o^2)$ , goodness of fit = 1.120 on  $F^2$  with 740 parameters, residual electron density extremes +0.65 and  $-0.27 \text{ e}\text{\AA}^{-3}$ , absolute structure parameter = 0.04(3) [10]. Programs: standard Siemens control and integration software, SHELXTL [11] and local programs.

### 3.2. $[\text{Bu}_4\text{N}]_2[\text{Nb}_2\text{O}(\text{OMe})_6(\text{O}_3\text{PPh})_2]$ (2)

MeCN ( $15 \text{ cm}^3$ ) was added to a mixture of  $\text{Nb}(\text{OMe})_5$  (0.24 g, 0.97 mmol) and  $[\text{Bu}_4\text{N}][\text{PhPO}_3\text{H}]$  (0.39 g, 0.98 mmol). The solids were dissolved by heating the mixture, and the resulting clear solution was stirred overnight. The solution was filtered and, after removal of the solvent under reduced pressure, the residue was dissolved in THF ( $5 \text{ cm}^3$ ). The colourless crystals of the product deposited over 3 days were isolated, and a further crop was obtained from the mother liquor over a further period of several more days. (Found: C, 50.6; H, 9.2; N, 2.4.  $\text{C}_{50}\text{H}_{100}\text{N}_2\text{Nb}_2\text{O}_{13}\text{P}_2$  requires: C, 50.7; H, 8.5; N, 2.4%).

#### 3.2.1. Spectroscopic data

$^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{CN}$ ): [ppm] 8.23, 7.94, 7.69, 7.29, 7.16, 6.98 (complex multiplets, 10H, aromatic), 4.24, 4.23, 3.99, 3.86, 3.85, 3.83, 3.80 (singlets, 18H, OMe).  $^{31}\text{P}$  NMR (202.35 MHz,  $\text{CD}_3\text{CN}$ ,  $20^\circ\text{C}$ ): [ppm] 7.3, 7.1, 6.1, 5.9. IR: [ $\text{cm}^{-1}$ ] 1178 (s), 1095 (s), 1003 (s), 960 (s), 947 (m), 750 (w), 715 (m), 700 (w), 580 (w), 548 (m), 528 (m), 498 (s), 461 (m).

#### 3.2.2. Crystal structure determination of 2

Crystal data:  $[\text{C}_{16}\text{H}_{36}\text{N}]_2^+ [\text{C}_{18}\text{H}_{28}\text{O}_{13}\text{Nb}_2\text{P}_2]^{2-}$ ,  $M = 1185.1$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 12.3300(5)$ ,  $b = 20.7717(8)$ ,  $c = 24.6580(10) \text{ \AA}$ ,  $\beta$

$= 103.171(2)^\circ$ ,  $V = 6149.2(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.280 \text{ gcm}^{-3}$ ,  $\mu = 0.48 \text{ mm}^{-1}$ ,  $F_{000} = 2520$ ,  $T = 160 \text{ K}$ , crystal size  $0.3 \times 0.2 \times 0.12 \text{ mm}$ . Methods as for **1**:  $\text{C}_7\text{H}_8$ ,  $1.7 < \theta < 28.5^\circ$ , 37779 measured reflections, 14042 unique ( $R_{\text{int}} = 0.0431$ ), transmission 0.784–0.956. No disorder,  $R' = 0.1048$  for all data,  $R = 0.0452$  (9846  $F$  values), goodness of fit = 1.038, 637 parameters, residual electron density extremes +0.87 and  $-0.42 \text{ e}\text{\AA}^{-3}$ .

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