Inorganic Chemistry

ARTICLE

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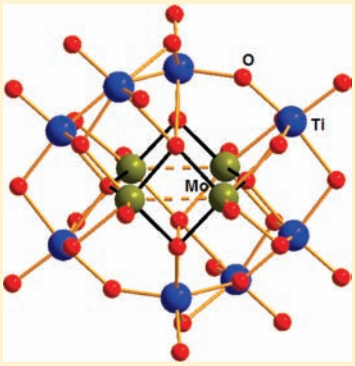
Extending the Family of Titanium Heterometallic−oxo−alkoxy Cages

Salvador Eslava,* Benjamin P. R. Goodwill, Mary McPartlin, and Dominic S. Wright

Department of Chemistry, University of Cambridge, Lensfield Road CB2 1EW, Cambridge, U.K.

S *Supporting Information*

ABSTRACT: Here we investigate the synthesis of high-nuclearity heterometallic titanium oxo−alkoxy cages using the reactions of metal chlorides with $[Ti(OEt)_4]$ or the pre-formed homometallic titanium−oxo−alkoxy cage $[Ti_7O_4(OEt)_{20}]$ (**A**). The octanuclear Ti_7Co^{II} cage $[Ti_7CoO_5(OEt)_{19}Cl]$ (**1**) (whose low-yielding synthesis we reported earlier) can be made in better yield, reproducibly by the reaction of a mixture of heptanuclear $[Ti_7O_4(OEt)_{20}]$ (**A**) and $[KOEt]$ with $[Co^{II}Cl_2]$ in toluene. **A** alone reacts with $[Co^{II}Cl_2]$ and $[Fe^{II}Cl_2]$ to form $[Ti_7Co^{II}O_5(OEt)_{18}Cl_2]$ (**2**) and $[Ti_7Fe^{II}O_5(OEt)_{18}Cl_2]$ (**3**), respectively. Like **1**, compounds **2** and **3** retain the original Ti_7 fragment of **A** and the II-oxidation state of the transition metal ions (Tm). In contrast, from the reaction of $[Ti(OEt)_4]$ with $[Cr^{II}Cl_2]$ it is possible to isolate $[Ti_3Cr^VO(OEt)_{14}Cl]$ (**4**) in low yield, containing a Ti_3Cr^V core in which oxidation of Cr from the II to V oxidation state has occurred. Reaction of $[Mo^VCl_5]$ with $[Ti(OEt)]_4$ in $[EtOH]$ gives the $Ti_8Mo^V{}_4$ cage $[\{Ti_4Mo_2O_8(OEt)_{10}\}_2]$ (**5**). The single-crystal X-ray structures of the new cages **2**, **3**, **4**, and **5** are reported. The results show that the size of the heterometallic cage formed can be influenced by the nuclearity of the precursor. In the case of **5**, the presence of homometallic Mo−Mo bonding also appears to be a significant factor in the final structure.



INTRODUCTION

Heterometallic cages with organic ligands such as alkoxides, carboxylates, and β-diketonates are of broad interest because of their well-defined structures and their applications as single-source precursors (SSP)[1−10] and catalysts.[11−13] As they contain labile organic ligands, they could also serve as building blocks in the assembly of inorganic−organic composite materials as is the case for titanium oxo-alkoxy cages.[14−26] The structural patterns observed in heterometallic cages can be seen to be governed by the principal factors of the difference in electronegativity between metal atoms (Lewis acid−base interactions), the formation of heterometallic metal−metal bonds, and the isomorphous substitution of metal atoms.[27]

Bearing in mind the numerous applications of titanium oxide materials in photovoltaic, photocatalytic, and sensing devices, we started to search for heterometallic oxo−alkoxy cages containing titanium.[28−30] Thus, we reported the synthesis and solid-state structures of the pentanuclear heterometallic metal(II) titanium(IV) oxo−alkoxy cages $[Ti_4TmO(OEt)_{15}Cl]$ [Tm = Co, Zn, Fe, Cu] (Figure 1) and $[Ti_4Mn_2O(OEt)_{15}Cl_3]$.[31] These were isolated by crystallization from toluene after solvothermal reactions of $[Ti(OEt)_4]$ with metal dichlorides ($[M^{II}Cl_2]$, M = Co, Zn, Fe, Cu, Mn) in dry ethanol. It can be noted from the literature, however, that the reaction of a metal halide and a metal alkoxide do not always lead to the isolation of oxo complexes; for example, reactions of $[Ti(OEt)_4]$ with main group metal chlorides such as $[SnCl_4]$ and $[MgCl_2]$ have resulted into molecular complexes with simple addition formulas.[7,32]

The larger octanuclear cage $[Ti_7CoO_5(OEt)_{19}Cl]$ (**1**) was also obtained (unexpectedly) in low yield from the reaction of $[K\{Ti_2(OEt)_9\}]$ with $[CoCl_2]$ in toluene, but the mechanism involved in its formation was unclear.[33] Other heterometallic cages containing Ti or Zr have also been reported, such as $[Co_2Ti_2(acac)_2(O^iPr)_{10}]$,[3] $[Pb_2Ti_2O(O^iPr)_{10}]$,[10] $[Tm\{Ti_2(OR)_9\}Xl]_x$ [Tm = Cu, Co, Ni, Sn, Pb; Xl = halogen],[34−37] $[Ti_4(N,N\text{-dimethylaminoethanolate})(OH)O_6Cu_6(\text{benzoate})_9]$,[38] and $[Sr_2Zr_2(OH)_2(O^iPr)_{10}(^iPrOH)_4]$.[39]

Following on from our studies of the formation of heterometallic cages containing II-oxidation state transition metal ions, we describe here our investigations of a range of other cages of this type employing a variety of synthetic approaches. We show that the octanuclear cages $[Ti_7CoO_5(OEt)_{19}Cl]$ (**1**), $[Ti_7CoO_5(OEt)_{18}Cl_2)]$ (**2**), and $[Ti_7FeO_5(OEt)_{18}Cl_2]$ (**3**) can be obtained by reactions of $[Ti_7O_4(OEt)_{20}]$ (**A**) with the corresponding Tm^{2+} salts. However, the only isolatable, crystalline product from the reaction of $[Ti(OEt)_4]$ with $[CrCl_2]$ is the tetranuclear $[Ti_3CrO(OEt)_{14}Cl]$ (**4**), in which oxidation of Cr^{II} to Cr^V has occurred (obtained in low yield). We also find that the reaction of $[Ti(OEt)_4]$ with $[Mo^VCl_5]$ leads to the new compound $[\{Ti_4Mo^V{}_2O_8(OEt)_{10}\}_2]$ (**5**). Finally, we show that the reaction of $[ZnCl_2]$ with $[Zr(OEt)_4]$ permits the isolation of a crystalline product that is tentatively assigned to $[Zr_4ZnO(OEt)_{15}Cl]$ (**6**); having a similar structure to $[Ti_4Tm^{II}O(OEt)_{15}Cl]$ [Tm = Co, Zn, Fe, Cu] obtained previously from $[Ti(OEt)_4]$ and $[Tm^{II}Cl_2]$.[31,33]

EXPERIMENTAL SECTION

Synthetic Procedures and Characterization of 1−6. Strict inert-atmospheric conditions and a dry, O_2-free atmosphere were used

Received: February 18, 2011
Published: May 23, 2011

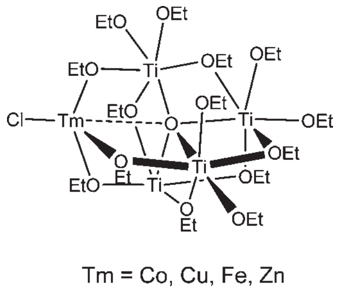


Figure 1. Structure of $[Ti_4TmO(OEt)_{15}Cl]$ [Tm = Co, Zn, Fe, Cu].

throughout all of the syntheses. Ultra-pure, anhydrous salts ($M^{II}Cl_2$), titanium(IV) ethoxide and zirconium(IV) ethoxide were acquired from the Aldrich and Alfa-Aesar chemical companies. Solvents used were dried by distillation over Mg turnings (*Et*OH) and sodium/benzophenone (toluene). The use of dry reactants and solvents was necessary to avoid the formation of the $[Ti_7O_4(OEt)_{20}]$ cage (**A**) as a by-product. Twenty-three milliliter capacity Teflon-lined autoclaves (model 4749, Parr) were used for all experiments. Autoclaves were heated using a Binder ED53 53 L oven with natural convection. All analytical and spectroscopic samples were prepared inside a Saffron Scientific (type β) glovebox, equipped with a closed-loop recirculation system for the removal of moisture and oxygen (operating at ca. 0.1−0.5 vppm O_2). Melting points were recorded on a standard melting point apparatus. IR spectra were recorded as Nujol mulls using a Perkin-Elmer 1710 FT spectrophotometer and CsI windows. Both carbon and hydrogen analyses were obtained by using a Perkin-Elmer 240 Elemental analyzer, and chlorine analysis was obtained by titration against silver nitrate using a radiometer TTT85 titrator. NMR spectroscopic samples were dissolved in 0.75 mL of dry, $[C_6D_6]$ in the glovebox in Wilmad 528PP NMR tubes and were sealed with tight-fitting caps and parafilm prior to immediate acquisition of the spectra. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance Cryo Ultrashield 500 MHz spectrometer (500.05 MHz for ^1H, 125.75 MHz for ^{13}C), with both being referenced to the internal solvent peaks. Since **1** has only been structurally characterized previously, full characterizational data is included here.

Synthesis of $[Ti_7O_4(OEt)_{20}]$ *(**A**)*[19]. A mixture of distilled water (0.34 mmol, 19 mmol) and ethanol (5.0 mL, 86 mmol) was added dropwise to a solution of titanium(IV) ethoxide (7.0 mL, 33 mmol) in dry toluene (15 mL) with vigorous stirring. The mixture was stirred for 2 h and then cooled down to −24 °C. After 5 days, crystals of **A** were isolated from the reactant solution, rinsed with dry toluene, and dried under vacuum (3.0 g, 48% yield, with respect to titanium ethoxide supplied). Melting point: 105 °C. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1350(w), 1137(s), 1101(m), 1065(s), 1050(w), 913(m), 894(m), 645(w), 607(s), 538(s), 517(w), 458(w). Elemental analysis (%) calcd for $C_{40}H_{100}O_{24}Ti_7$: C 36.9, H 7.8; found: C 36.9, H 7.8. ^1H NMR (+25 °C, C_6D_6, δ ppm), collection of multiplets in the ranges 5.2−4.5 (40 H in $-OCH_2CH_3$) and 1.8−1.3 (60 H, $-OCH_2CH_3$). ^{13}C NMR (+25 °C, C_6D_6, δppm), 71.53, 71.48, 71.3, 71.2, 70.7, 70.6, 70.2 ($-OCH_2CH_3$); 19.5, 19.40 19.3, 18.98, 18.8, 18.6, 18.3 ($-OCH_2CH_3$).

Synthesis of $[Ti_7CoO_5(OEt)_{19}Cl]$ *(**1**)*. Crystals of **A** (1.00 g, 0.769 mmol), cobalt(II) chloride (0.100 g, 0.769 mmol), and potassium ethoxide (95%, 0.068 g, 0.77 mmol) were suspended in anhydrous toluene (5 mL) and stirred at room temperature. After the crystals of **A** dissolved, the mixture was heated in an oil bath for 2 h at 60−65 °C while stirring. An apparently clear dark-blue solution was eventually obtained. The solution was then filtered at room temperature. A whitish product (0.03 g) was collected and confirmed to be potassium chloride by elemental analysis (% calcd for KCl: Cl 47.6; % found: Cl 44.6). The filtered solution was concentrated to 3 mL of toluene and cooled to −24 °C. After 2 days dichroic purple-green crystals of **1** were isolated and dried (0.16 g, 16% yield). Melting point: 145 °C. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1124(s), 1097(w), 1071(s), 1046(s), 928(m), 908(w), 896(m), 631(s), 603(w), 586(w), 565(w), 544(s), 477(m), 412(w), 376(w). Elemental analysis (%) calcd for $C_{38}H_{95}ClO_{24}Ti_7Co$: C 33.4, H 7.0, Cl 2.6; found: C 33.5, H 6.9, Cl 2.6. ^1H NMR (+25 °C, C_6D_6, δ ppm), collection of broad resonances range 13—-1. ^{13}C NMR (+25 °C, C_6D_6, δppm): 77.9, 70.1, 70.0, 69.9, 69.5, 69.2, 68.2 ($-OCH_2CH_3$) and 32.4, 27.2, 23.3, 20.6, 18.8, 18.6, 18.0, 17.9, 17.0, 16.4 ($-OCH_2CH_3$).

Synthesis of $[Ti_7CoO_5(OEt)_{18}Cl_2)]$ *(**2**)*. Crystals of **A** (1.00 g, 0.769 mmol) and cobalt(II) chloride (0.100 g, 0.769 mmol) were suspended in anhydrous toluene (5 mL) and stirred at room temperature. After the crystals of **A** dissolved, the mixture was heated in an oil bath for 2 h at 60−65 °C while stirring. A clear dark-blue solution was eventually obtained. Cooling to −24 °C for 2 weeks produced dichroic purple-green crystals of **2** (0.13 g, 12% yield). Melting point: 155 °C. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1126(s), 1095(w), 1074(s), 1045(s), 931(m), 893(m), 738(w), 657(w), 630(m), 590(m), 546(m), 479(m), 412(w), 403(w). Elemental analysis (%) calcd for $C_{36}H_{90}Cl_2O_{23}Ti_7Co$, C 31.9, H 6.7, Cl 5.2; found: C 32.1, H 6.5, Cl 5.1. ^1H NMR (C_6D_6, δ ppm), collection of broad resonances in the range 14—-5. ^{13}C NMR (+25 °C, C_6D_6, δ ppm): collection of sharp signals in the ranges 77−67 ($-OCH_2CH_3$) and 19−16 ($-OCH_2CH_3$).

Synthesis of $[Ti_7FeO_5(OEt)_{18}Cl_2)]$ *(**3**)*. Crystals of **A** (1.00 g, 0.769 mmol) and iron(II) chloride (0.098 g, 0.77 mmol) were suspended in anhydrous toluene (5 mL) and stirred at room temperature. After the crystals of **A** dissolved, the mixture was heated in an oil bath for 2 h at 60−65 °C while stirring. A clear brown solution was eventually obtained. Cooling to −24 °C for 2 weeks produced a polycrystalline brown solid and a few single crystals (15 mg, 1.4% yield with respect to $[FeCl_2]$ supplied). Melting point: 125 °C. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1134(s), 1073(m), 1044(s), 1045(s), 931(m), 894(m), 804(w), 619(w), 592(s), 549(s), 491(w), 443(w), 423(w). Elemental analysis (%), calcd for $C_{36}H_{90}Cl_2O_{23}Ti_7Fe$: C 32.1, H 6.7, Cl 5.2; found: C 32.1, H 6.6, Cl 5.3. ^1H NMR (+25 °C, C_6D_6, δ ppm), collection of broad resonances all around the range 15—2. ^{13}C NMR (+25 °C, C_6D_6, δ ppm), collection of sharp singlets in the ranges 78−66 ($-OCH_2CH_3$) and 23−15 ($-OCH_2CH_3$).

Synthesis of $[Ti_3CrO(OEt)_{14}Cl]$ *(**4**)*. Titanium(IV) ethoxide (7.00 mL, 33.4 mmol), chromium(II) chloride (762 mg, 6.20 mmol), and anhydrous ethanol (7.00 mL, 120 mmol) were placed in a Teflon-lined autoclave and heated at 100 °C for 1 day. After slow cooling overnight to room temperature, the green solid and liquid formed were transferred to a Schlenk tube. Ethanol (12 mL) was added, and the temperature lowered to −14 °C. Most of the green solid remained undissolved. After one month, elongated 3 mm crystals of **4** were formed on the surface of the Schlenk tube (0.05 g, 1% yield). Melting point: 90 °C. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1133(s), 1103(s), 1066(s), 923(m), 898(m), 586(s), 506(m). Elemental analysis (%), calcd for $C_{28}H_{70}ClO_{15}Ti_3Cr$: C 38.3, H 8.0, Cl 4.0; found: C 37.9, H 8.1, Cl 4.1. ^1H and ^{13}C NMR in C_6D_6 was not informative because of paramagnetic line broadening caused by the presence of the Cr^V center.

Synthesis of $[\{Ti_4Mo_2O_8(OEt)_{10}\}_2]$ *(**5**)*. Titanium(IV) ethoxide (7.00 mL, 33.4 mmol), $[MoCl_5]$ (0.564 g, 2.06 mmol) and anhydrous ethanol were carefully mixed together. After the exothermic reaction had subsided the mixture was placed in a Teflon-lined autoclave and heated at 150 °C for 24 h. After slow cooling to room temperature good quality brown crystals of **5** were formed. (0.51 g, 51% based on $[MoCl_5]$). Decomp. 300 °C to black solid. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1134(s), 1101(s), 1047(m), 960(m, Mo^V=O str.), 928(w), 894(w), 797(m), 712(s), 610(s), 537(m), 453(m). Elemental analysis (%) calcd for $C_{40}H_{100}Mo_4O_{36}Ti_8$, C 25.7, H 5.3; found: C 25.0, H 5.2. ^1H NMR (+25 °C, C_6D_6, δ ppm), collection of overlapping sharp mutiplets 5.4−4.5 (2H, $-CH_2-$, *Et*O), two groups of multiplets each composed of triplets at 1.45−1.23 (1.5H) and 1.85−1.65 (1.5H). ^{13}C NMR

Table 1. Details of the Data Collections and Structural Refinements of the New Compounds 2−5

	2	3	4	5
formula	$C_{36}H_{90}Cl_2CoO_{23}Ti_7$	$C_{36}H_{90}Cl_2FeO_{23}Ti_7$	$C_{28}H_{70}ClCrO_{15}Ti_3$	$C_{40}H_{100}Mo_4O_{34}Ti_8$
M	1356.21	1353.13	877.99	1924.16
cryst. size (mm)	0.32 × 0.05 × 0.02	0.39 × 0.12 × 0.02	0.23 × 0.21 × 0.14	0.23 × 0.18 × 0.10
color	purple-green	brown	green	brown
cryst. system	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P21/c$
a (Å)	12.3220(4)	12.3502(5)	11.1957(1)	14.2373(5)
b (Å)	13.5953(4)	13.7057(5)	13.4346(2)	16.2385(7)
c (Å)	19.3999(7)	19.6221(2)	14.7906(2)	16.7247(6)
α (deg)	80.403(2)	79.843(2)	90.105(1)	90.00
β (deg)	82.370(2)	82.852(2)	92.395(1)	112.548(2)
γ (deg)	70.819(2)	70.308(2)	94.951(1)	90.00
V (Å^3)	3015.89(17)	3070.6(2)	2214.38(5)	3571.1(2)
Z	2	2	2	2
d_{calc} (g cm^{-3})	1.493	1.464	1.317	1.789
μ (mm^{-1})	1.300	1.243	0.875	1.600
F(000)	1410	1408	930	1944
θ range (deg)	3.51 to 22.49	3.57−22.00	3.52−30.07	3.53−28.01
reflections collected	23739	19649	43213	17138
independent refl. [R_{int}]	7814 [0.0606]	7400 [0.0449]	12930 [0.0309]	7670 [0.0768]
R_1, wR_2 [$I > 4\sigma(I)$]	0.053, 0.119	0.083, 0.246	0.053, 0.144	0.075, 0.209
R_1, wR_2 (all data)	0.091, 0.137	0.112, 0.264	0.072, 0.159	0.095, 0.222

(+25 °C, C_6D_6, δ ppm), 75.2−70.0 collection of 10 singlet resonances (75.2, 75.1, 73.7, 73.4, 73.32, 73.26, 72.6, 71.6, 71.2, 70.0), 19.7−17.7 collection of singlet 10 resonances (19.7, 19.5, 19.3, 19.2, 18.9, 18.6, 18.5, 18.05, 18.0, 17.7) ($-OCH_2CH_3$).

*Synthesis of $[Zr_4ZnO(OEt)_{15}Cl]$ (**6**).* Zirconium(IV) ethoxide (2.24 g, 8.26 mmol), zinc(II) chloride (282 mg, 2.07 mmol) and anhydrous ethanol (14 mL) were placed in a Teflon-lined autoclave and heated at 150 °C for 1 day. After slow cooling overnight to room temperature, crystals of **6** were isolated from the reactant solution (1.1 g, 46% yield, with respect to $[ZnCl_2]$ supplied). For characterization, a second crystallization from 2 mL of toluene at −14 °C was performed. Melting point: 330 °C. IR (1500−400 cm^{-1}), ν/cm^{-1} = 1184(w), 1133(s), 1093(w), 1076(m), 1044(s), 921(m), 891(m), 567(m), 533(s), 490(m), 464(w), 400(w). Elemental analysis (%), calcd for $C_{30}H_{75}ClZnO_{16}Zr_4$, C 31.1, H 6.5, Cl 3.1; found: C 30.8, H 6.6, Cl 2.8. ^{1}H NMR (C_6D_6, δ ppm), collection of multiplets in the ranges 4.7−3.9 (30 H in $-OCH_2CH_3$) and 1.8−1.1 (45 H in $-OCH_2CH_3$). ^{13}C NMR (C_6D_6, δ ppm), overlapping resonances in the range 67−63 ($-OCH_2CH_3$) and 21−18 ($-OCH_2CH_3$).

Crystallographic Studies of 2−6. Crystallographic data were collected on a Nonius Kappa CCD device equipped with an Oxford Cryostream low-temperature cooling device (λ = 0.71073 Å). Crystals were mounted directly from solution using a perfluorocarbon oil which freezes at low temperature.[40] The structures were solved and refined by full matrix least-squares on F^2 using the SHELXTL program,[41] with anisotropic displacement parameters for all full occupancy atoms. All crystals diffracted relatively weakly because of considerable disorder of the carbon atoms of the $-OEt$ ligands which had relatively high displacement parameters. Data for the previously characterized compound **1** and the preliminary-characterized compound **6** are not included in Table 1.

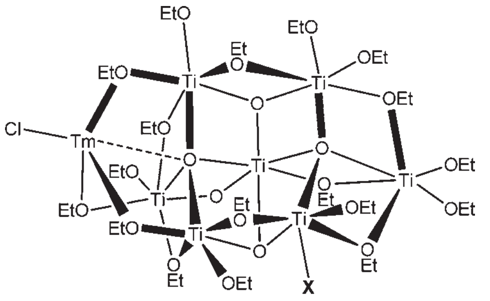
CCDC reference numbers 766941 (**1**), 812600 (**2**), 812601 (**3**), 812602 (**4**), 812603 (**5**), and 812604 (**6**).

RESULTS AND DISCUSSION

Synthesis and Characterization of 1−6. As noted in the introduction to this paper, we recently reported the unexpected formation of $[Ti_7CoO_5(OEt)_{19}Cl]$ (**1**) (Figure 2) in an attempt to prepare different Co and Ti oxo−alkoxy cages,[33] a reaction that had been previously reported to produce the heterometallic cage $[\{Ti_2(OEt)_9\}_2Co]$.[35] In attempts to obtain **1** more efficiently we reacted commercially-available $[Ti(OEt)_4]$ with $[CoCl_2]$ in ethanol under solvothermal conditions. However, only the pentanuclear Ti_4Co cage $[Ti_4CoO(OEt)_{15}Cl]$ was isolated in good yield.[33] Addition of controlled amounts of water to the reaction of $[Ti(OEt)_4]$ with $[CoCl_2]$ in ethanol did not result in **1**, but in a mixture of $[Ti_4CoO(OEt)_{15}Cl]$ and **A**. Similarly, **1** could not be isolated from the microhydrolysis of $[Ti_4CoO(OEt)_{15}Cl]$. Our interest in higher-nuclearity cages like **1** stems from the higher degree of condensation present than in the pentanuclear cages $[Ti_4Tm^{II}O(OEt)_{15}Cl]$ (i.e., Ti/O 5:7 as opposed to 1:4). After considerable synthetic efforts involving various approaches, we have finally been able to obtain **1** in the current study reproducibly and in better yield (16%) from the reaction of a mixture of the previously reported heptameric cage $[Ti_7O_4(OEt)_{20}]$ (**A**) with $[KOEt]$ and $[Co^{II}Cl_2]$ (1:1:1 equivalents), via a route involving the precipitation of $[KCl]$ and the (presumed) formation of Et_2O (eq 1).

$$\underset{\mathbf{A}}{[Ti_7O_4(OEt)_{20}]} + CoCl_2 + KOEt \rightarrow \underset{\mathbf{1}}{[Ti_7O_5(OEt)_{19}(CoCl)]} + KCl + EtOEt \qquad (1)$$

The outcome of reactions of **A** alone with a broad range of divalent metal halides $[TmCl_2]$ (Tm = Co, Mn, Fe, Cu, Zn) show a marked dependence on the transition metal employed. For example, when **A** was reacted with $[MnCl_2]$ and $[CuCl_2]$ only



Tm = Co, X = EtO (**1**)
Tm = Co, X = Cl (**2**)
Tm = Fe, X = Cl (**3**)

Figure 2. Structures of **1**, **2**, and **3**, which only differ in the substituent *X* at one of the titanium atoms of the core.

the previously reported cages $[Ti_4Mn_2O(OEt)_{15}Cl_3]$ and $[Ti_4CuO(OEt)_{15}Cl]$ were obtained (confirmed by single-crystal X-ray analysis).[31] However, using $[CoCl_2]$ and $[FeCl_2]$ in the current work the new octanuclear cages $[Ti_7Tm^{II}O_5(OEt)_{18}Cl_2)]$ [Tm = Co (**2**), Fe (**3**)] were produced (eq 2). The crystalline yields of both compounds were low although both synthetic methods proved to be completely reproducible (12% for **2** and ca. 1% for **3**). Both **2** and **3** were later shown to have solid-state structures closely-related to **1**, only with one of the O*Et* groups replaced by a Cl atom (Figure 2). Attempts to extend the method used in the synthesis of **1**, **2**, and **3** using the even higher nuclearity cage $[Ti_{16}O_{16}(OEt)_{32}]$ failed to produce thermodynamically stable cages that crystallized.

$$\underset{\mathbf{A}}{[Ti_7O_4(OEt)_{20}]} + TmCl_2 \rightarrow \underset{Tm = Co(2);Fe(3)}{[Ti_7TmO_5(OEt)_{18}Cl_2)]} + Et_2O \qquad (2)$$

Further studies of the solvothermal reactions of titanium(IV) ethoxide with $[CrCl_2]$ in ethanol at either 100 or 150 °C were also undertaken as part of the present study, using a range of different reaction stoichiometries (i.e., Cr/Ti 1:16−5:16). In most of the cases intractable powders were formed, and no crystalline products could be isolated from toluene, *n*-heptane, or tetrahydrofuran. Similar intractable solids were obtained in the absence of $[Ti(OEt)_4]$, indicating that $[CrCl_2]$ itself reacts with ethanol. However, crystallization of the crude product of the 5:16 stoichiometric reaction from ethanol gave $[Ti_3CrO(OEt)_{14}Cl]$ (**4**) (Figure 3) in low yield (∼1%). Although because of this low yield we cannot assume that this complex is the main product of the reaction, it is the only crystalline product that could be isolated, and its synthesis proved to be completely reproducible. We were encouraged by the presence of a Cr^V center in **4** since so far we had only been able to incorporate low oxidation state ions into oxo−alkoxy cages from the reactions of $[Ti(OEt)_4]$ with metal chlorides. We followed this reaction up by exploring the possibility of incorporating other group 6 (Cr, W, Mo) metals into this type of structure directly. The solvothermal reaction of $[MoCl_5]$ with $[Ti(OEt)_4]$ (1:16 mol equiv) in ethanol at 150 °C gave a good yield of the Ti_8Mo_4 cage $[\{Ti_4Mo_2O_8(OEt)_{10}\}_2]$ (**5**) (51%), having a wholly different Ti_8Mo_4 cage arrangement to that of **4** in the solid state (see Figure 7 later).

Lastly, we also explored the use of $[Zr(OEt)_4]$ in this type of reaction in attempts to obtain zirconium(IV) oxo−alkoxy compounds. The solvothermal reactions of a range of transition metal chlorides were undertaken. Only in the case of reaction of $[Zr(OEt)_4]$ with $[ZnCl_2]$ in ethanol could we isolate crystalline material after work-up. The new compound was isolated in good (46%) yield. Elemental analysis and preliminary characterization by X-ray crystallography suggested the compound to be $[Zr_4ZnO(OEt)_{15}Cl]$ (**6**), having a similar structure to that of the previously characterized series of cages $[Ti_4TmO(OEt)_{15}Cl]$ (see Figure 1).[42]

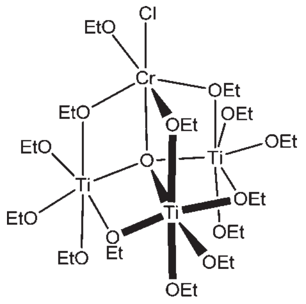


Figure 3. Structure of **4**.

The mechanism of formation of the oxo centers from **A** in **1**−**3** can be explained by the previously reported ether-elimination (Bradley) reaction from the ethoxide groups.[43] We also propose the same mechanism for the formation of oxo centers in **4** and **5** since all the reactants used were anhydrous, and rigorous conditions ensuring the exclusion of water and oxygen were used throughout all syntheses. It is likely that the *Et*O groups in the clusters **4** and **5** are provided by both $[Ti(OEt)_4]$ and by the [*Et*OH] solvent itself. Evidence for this is provided by the observed reaction of $[CrCl_2]$ and $[MoCl_5]$ with [*Et*OH] (which liberates [HCl]). Finally, the presumed method of formation of the oxo center in **6** is loss of an *Et* group and the formation of [*Et*Cl].

All of the new compounds **2**−**6** were fully characterized by elemental analysis and IR, ^1H and ^{13}C NMR, and UV−vis spectroscopy prior to obtaining their low-temperature X-ray structures (see Experimental Section). ^1H and ^{13}C NMR spectroscopy were generally not very useful in the elucidation of the solution structures of **1**−**6** owing to the presence of paramagnetic Tm centers, and only confirmed the presence of *Et* groups in all of the compounds (see Experimental Section). However, the exception to this is the Mo^V cage **5** for which 10 sharp singlets are found in the $-CH_2-$ (δ 75.2−70.0) and $-CH_3$ (19.7−17.7) regions of the ^{13}C NMR spectrum. This is the same number of chemically distinct *Et* groups present in the cage (see Figure 7 later) and suggests that the *intact* cage structure is retained in solution. A further indication of this is also provided by the ^1H NMR spectrum in which the $-CH_3$ region is split into two distinct (1:1) groups of multiplets [δ 1.45−1.23 and 1.85−1.65], presumably for the terminal (10 in total) and μ-O*Et* (10 in total) groups that are present in the cage structure of **5**.

UV−vis spectroscopy of cages **1**−**6** in toluene solution was consistent with the $3d^n$ electronic configurations of the metal ions present (Figure 4). In all the cases, the Ti cages have an absorption edge in the UVA region (315−400 nm) ascribed to the Ti oxo cores. The Co cages **1** and **2** contain absorption bands at 550, 590, and 640 nm corresponding to the expected $^4A_2 \rightarrow {}^4T$ transitions for tetrahedral Co^{II}.[33] The Fe cage **3** shows a broad absorption probably arising from loss of degeneracy of the $^5T_2$

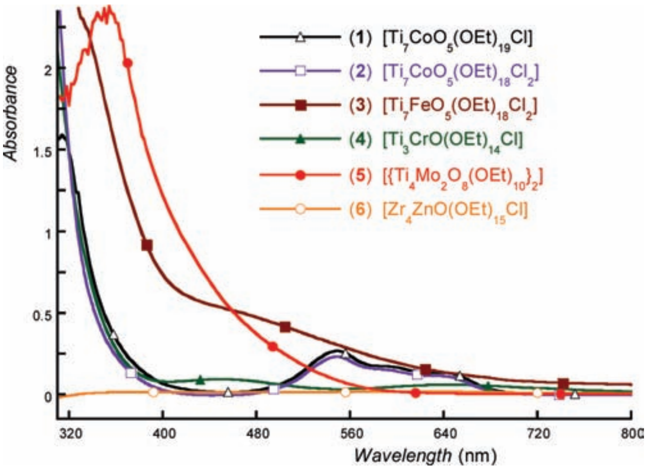


Figure 4. UV−Visible absorbance of the cages **1**−**6** in toluene (concentration of 1 mM for all).

state, similarly to the absorption found in the cage [Ti$_4$FeO(O*Et*)$_{15}$Cl].[31,44] The Cr cage **4** shows two weak absorption bands around 450 and 650 nm, corresponding to the d−d transitions $xy \rightarrow x^2 - y^2$ and $xy \rightarrow xz,yz$ (respectively), the latter being assigned as $^2E \rightarrow {}^2B_2$ and the former (tentatively) to a π-Cr$\overset{\cdot\cdot}{-}$O → xy transition.[45] The Mo^V cage **5** exhibits a single strong absorption at 350 nm. The intensity of this band strongly suggests a charge-transfer transition as opposed to a d−d transition, probably a pπ(O) → dπ(Mo) transition associated with the Mo═O bonds found in the structure of **5**. Finally, the Zn−Zr cage **6** shows no absorptions in the visible region, consistent with the d^{10} electronic configuration of Zn^{2+} and with the Zr oxo core absorbing at lower wavelength.

X-ray Structures of 1−6. The solid-state structures of **1**−**6** were determined using low-temperature [180(2) K] single-crystal X-ray diffraction. Details of the crystal data and structural refinement parameters are summarized in Table 1 (see Experimental Section).

Figure 5 compares the molecular structures of the previously reported compounds [Ti$_7$O$_4$(O*Et*)$_{20}$] (**A**)[19] and [Ti$_7$CoO$_5$(O*Et*)$_{19}$Cl] (**1**)[33] with the new compounds [Ti$_7$TmO$_5$(O*Et*)$_{18}$Cl$_2$)] [Tm = Co (**2**), Fe (**3**)]. The same numbering scheme has been used in all of the structures presented. It is to be expected on the basis of previous studies of heterometallic complexes that the titanium oxo−alkoxy frameworks will have a dominant effect on structural direction.[4,27] Thus, the cages **1**−**3** have the *same* structural arrangement, but different Tm metal centers or ligands (see, e.g., that Ti(6) contains a Cl ligand in **2** and **3** but a terminal *Et*O group in **1**).

Comparison between **A** and **1**−**3** indicates that to obtain a thermodynamically stable cage including a [TmCl] unit, an [*Et*]$^+$ cation [i.e., the *Et* group from O(72) in Figures 5a and b] has been lost. In addition, this comparison also shows how the three terminal [O*Et*] groups of **A** have coordinated with either Co or Fe metal centers in **1**−**3** to complete the tetrahedral geometries of the Tm^{2+} ions [Co−μ_2-O(32,42,52)−O 1.976(7)−1.988(7) Å range in **1**; Co−μ_2-O(32,42,52) 1.977(4)−1.983(5) Å range in **2**; Fe−μ_2-O(32,42,52) 1.993(8)−2.019(7) Å range in **3**]. In **A**, pseudo-tetrahedral geometry is found at the cage O-atom O(2). However, the coordination of the Co or Fe metal centers in **1**−**3** results in a change to an almost trigonal bipyramidal geometry at O(2), indicating the

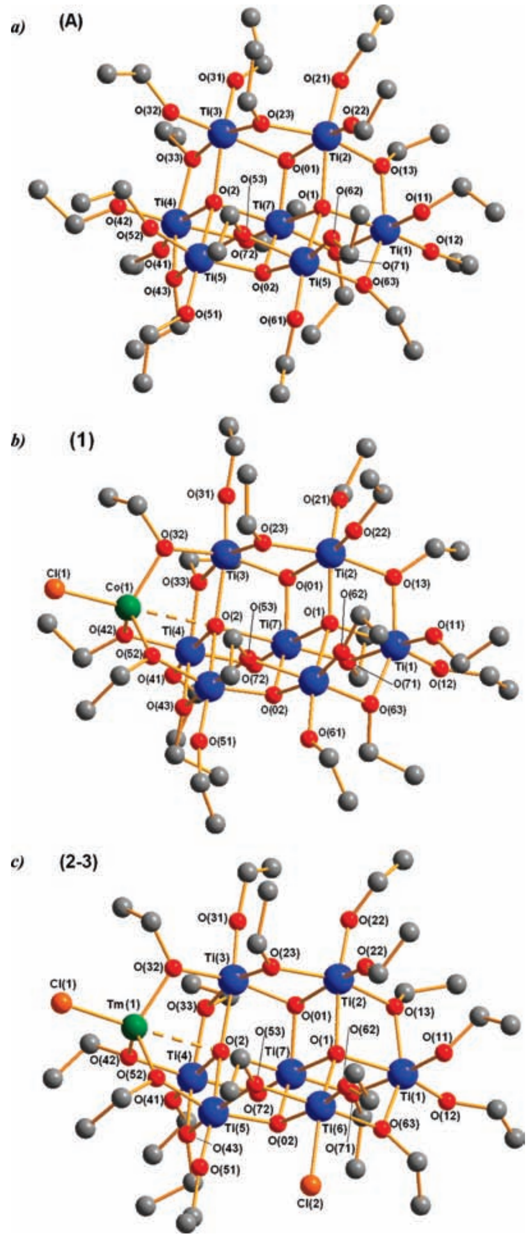


Figure 5. *(a)* Structures of the titanium−oxo−alkoxy cage [Ti$_7$O$_4$(O*Et*)$_{20}$] (**A**),[19] *(b)* the heterometallic [Ti$_7$CoO$_5$(O*Et*)$_{19}$Cl] (**1**),[33] and *(c)* the heterometallic [Ti$_7$TmO$_5$(O*Et*)$_{18}$Cl$_2$] [Tm = Co (**2**) or Fe (**3**)]. H-atoms and the minor components of disorder in some of the *Et*O groups are omitted for clarity. The same numbering scheme has been used for all chemically-related atoms. Selected bond lengths (Å) and angles (deg): Within **1**−**3**, Ti−O*Et*(terminal) range 1.749(10)−1.832(6), Ti−μ_2-O(32,42,52) range 1.954(7)−1.998(6), Ti−(μ_2-O*Et*) range 1.804(6)−2.139(7), Ti−O(1) range 1.939(6)−2.163(5), Ti−O(2) range 2.068(7)−2.170(6), Ti−O(2)−Ti range 88.2(2)−159.3(3), Ti−O(1)−Ti range 96.3(2)−150.2(2), Ti−(μ_2-O*Et*)−Ti range 101.8(2)−106.9(2). In **1**, Co−Cl 2.272(3), Co−μ_2-O(32,42,52) 1.976(7)−1.988(7), Co···O(2) 2.598(6), O−Co−O range 107.4(3)−116.5(7). In **2** (Tm = Co), Ti(6)−Cl(2) 2.367(3), Co−Cl(1) 2.265(2), Co−μ_2-O(32,42,52) 1.977(4)−1.983(5), Co···O(2) 2.591(4), O−Co−O 107.0(2)−118.6(2), Cl(1)−Co−O 106.2(2)−109.9(1), Co−O−Ti 109.8(2)−113.6(2). In **3** (Tm = Fe), Ti(6)−Cl(2) 2.363(5), Fe−Cl(1) 2.287(4), Fe−μ_2-O(32,42,52) 1.993(8)−2.019(7), Fe···O(2) 2.587(5), O−Fe−O 103.1(3)−126.3(3), Cl−Fe−O 105.0(2)−113.8(2), Fe−O−Ti 110.4(4)−112.7(3).

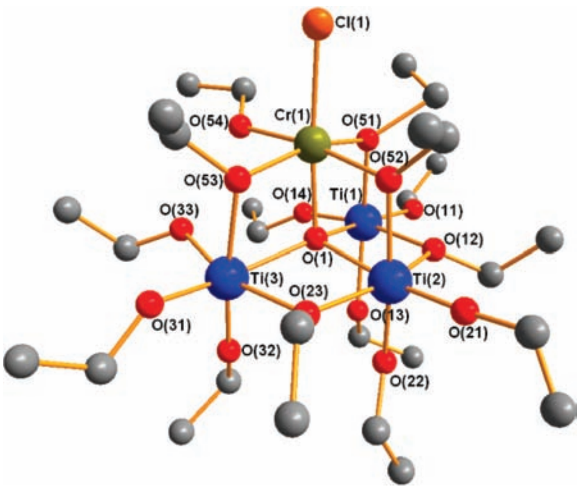


Figure 6. Structure of the heterometallic complex [$Ti_3CrO(OEt)_{14}Cl$] (**4**). H-atoms and the minor disorder components in some of the *Et*O groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−O*Et*(terminal) range 1.780(2)−2.071(2), Ti−(μ_2-O*Et*) range 1.955(2)−2.086(2), Ti−μ_2-O(51,52,53) range 1.977(2)−2.000(2), Ti−O(1) range 2.051(2)−2.130(2), Cr−O(54) 2.020(2), Cr−Cl 2.317(1), Cr−μ_2-O(51,52,53) 1.951(2)−1.994(2), Cr−O(1) 1.992(1), Ti−O(1)−Ti range 100.2(1)−150.1(1), Ti−(μ_2-O*Et*)−Ti 103.3(1)−105.0(1), O−Cr−O range 83.9(1)−171.7(1), Cl−Cr−O range 175.3(0)−90.8(1), Cr−O−Ti 101.8(1)−103.2(1).

presence of Tm···O(2) interactions [Co···O(2) 2.598(6) Å in **1**; Co···O(2) 2.591(4) Å in **2**, Fe···O(2) 2.587(5) Å in **3**].

Figure 6 shows the structure of [$Ti_3CrO(OEt)_{14}Cl$] (**4**). Its core is a heterometallic cage of virtual C_s symmetry containing a tetrahedral Ti_3Cr arrangement, with a μ_4-O atom at the center bridging the metal centers together. The six coordinate, pseudo-octahedral Cr^V center in **4** is bonded to three, titanium bridged μ-O*Et* groups and forms a strong bond to the μ_4-O atom of the cage [Cr−O(1) 1.992(1) Å] (cf. the weak Tm···O interactions found in **1**−**3**), in addition to being coordinated by a terminal Cl atom and a single terminal *Et*O group. The Cr−O bond in **4** is significantly longer than expected for a Cr═O double bond (range 1.38−1.88 Å),[46] for example, in [{HC$\overset{\cdot\cdot}{-}$C(Me)$\overset{\cdot\cdot}{-}$Ndipp}$_2Cr^V(=O)_2$] (Dipp =2,6-$^iPr_2C_6H_3$) (mean 1.75 Å),[47] and there is also no apparent lengthening of the Ti−μ_4-O bonds [range 2.051(2)−2.130(2)Å] compared to **1**−**3** [range 1.939(6)−2.170(6)Å]; both suggesting that there is at best only a small π-bonding contribution to the Cr−O bond in the cage. The presence of a strong Cr−O bond does, however, appear to have a noticeable *trans* influence on the Cr−Cl bond [2.317(1)Å], which is longer than anticipated for a Cr^V−Cl bond in an octahedral arrangement [for example, the Cr−Cl bond length is 2.273(1)−2.292(1) Å in known [$Cr^{III}O_5Cl$] octahedral arrangements].[48,49] To our knowledge **4** represents the first oxo−alkoxy Ti cage of this type to contain a high oxidation state transition metal ion (>+2) and a rare example of a [Cr^VO_5Cl] octahedral arrangement.

The solid-state structure of [{$Ti_4Mo_2O_8(OEt)_{10}$}$_2$] (**5**) is that of a centrosymmetric Ti_8Mo_4 cage (Figure 7). The full gamut of terminal [O(11), O(17)], μ_2-[O(18)], μ_3-[O(12), O(13), O(14)] and μ_4-[O(16)] metal-bonded oxy ligands is seen in this structure (Figure 7b). Significantly, the IR spectrum of solid **5** shows no O−H stretching bands so that none of these oxy ligands is protonated. The cage is built around a rectangular Mo_4 core of two [Mo(=O)(μ-O)]$_2^{2+}$ ring units which are bridged together by the μ_4-bonded O atoms O(16,16A), thus forming a neutral $Mo^V{}_4O_{10}$ fragment at the center of the cage structure. This unit is incorporated into the cage by a combination of μ_3-, μ_4-O and μ_2-O*Et* bridging to Ti^{IV} centers at the periphery of the structure. Although both Mo(1) and Mo(2) have similar distorted octahedral coordination geometries, they have chemically distinct environments, with Mo(1) being bonded to five oxo−ligands and an *Et*O group while Mo(2) is coordinated by four oxo−ligands and two *Et*O groups. Bearing in mind that **5** is

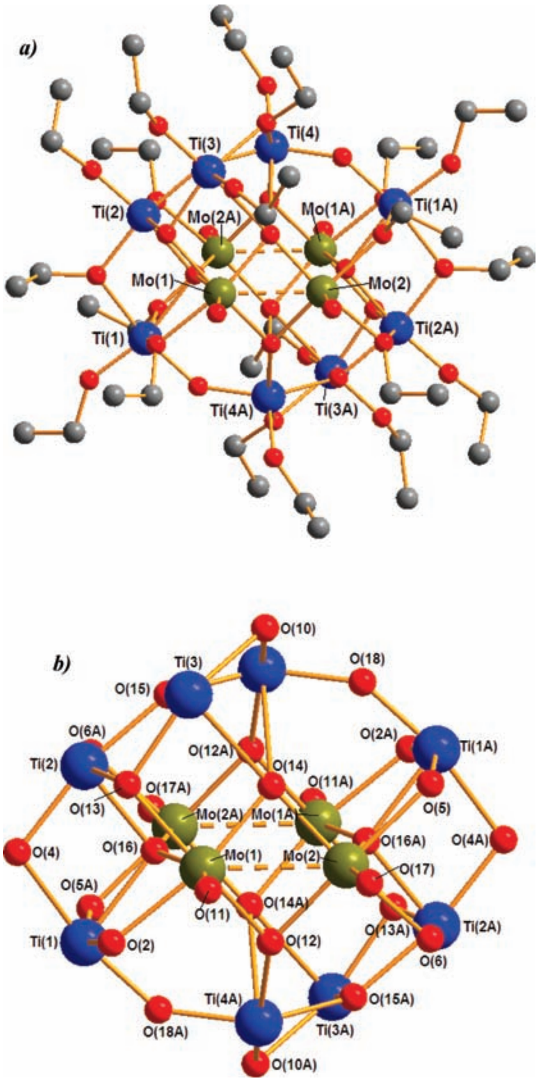


Figure 7. (**a**) Structure of the [{$Ti_4Mo^V{}_2O_8(OEt)_{10}$}$_2$] (**5**) (with H-atoms and disorder in the *Et*O groups removed for clarity), (**b**) the core of **5** (with terminal groups removed). Selected bond lengths (Å) and angles (deg): Ti−O*Et*(terminal) range 1.769(5)−1.802(7), Ti−(μ_2-O*Et*) range 1.973(6)−2.080(4), Ti−(μ_2-O) 1.820(6), Ti−(μ_3-O) 1.897(6)−2.029(5), Ti−(μ_4-O) 2.050(5)−2.8160(7), Mo(1)−O(11) 1.676(5), Mo(1)−O(12) 2.008(5), Mo(1)−O(13) 2.054(5), Mo(1)−O(14) 1.969(5), Mo(1)−O(16) 2.214(5), Mo(1)−O(2) 2.118(5), Mo(2)−O(17) 1.679(5), Mo(2)−O(12) 2.004(5), Mo(2)−O(14) 1.961(5), Mo(2)−O(16A) 2.114(5), Mo(2)−O(5) 2.116(5), Mo(2)−O(6) 2.102(4), Mo(1)···Mo(2) 2.6096(9), Ti−(μ_2-O*Et*)−(Ti,Mo) range 105.1(2)−107.0(3), Ti−(μ_2-O)−Ti 143.9(3), Ti−(μ_3-O)−(Ti,Mo) range 99.1(2)−146.0(4), Ti−(μ_4-O)−(Ti,Mo) range 71.0(2)−162.5(3), Mo(1)−O(12)−Mo(2) 81.1(2), Mo(1)−O(14)−Mo(2) 83.3(2), Mo(1)−O(16)−Mo(2) 147.1(2).

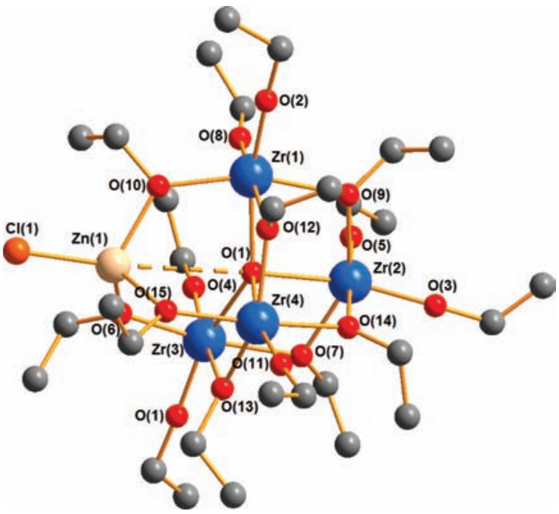


Figure 8. Proposed model for the structure of the heterometallic complex $[Zr_4ZnO(OEt)_{15}Cl]$ (**6**). H-atoms and the minor disorder components in some of the *Et*O groups are omitted.

diamagnetic in solution (as indicated by the presence of sharp resonances in the ^1H and ^{13}C NMR spectra) it is likely that the relatively short Mo···Mo contacts [Mo(1)···Mo(2) 2.6096(9)Å] represent a (d^1-d^1) single bond. Other complexes containing $[Mo(=O)(\mu\text{-}O)]_2^{2+}$ ring units have been structurally characterized previously, in which the short Mo···Mo distance has also been interpreted as arising from a single Mo−Mo bond (normally in the range 2.54−2.58 Å).[50]

Despite repeated attempts the X-ray data collected on $[Zr_4ZnO(OEt)_{15}Cl]$ (**6**) was of poor quality (R_1 = 15.7%), owing to weak diffraction at wide angle, and the refinement did not converge (more details are to be found inside the CIF file in the Supporting Information).[42] Readers should then consider the X-ray data as preliminary and the proposed structure of **6** shown in Figure 8 as a model. That structure is isostructural with the previously reported compounds $[Ti_4MO(OEt)_{15}Cl]$ (M = Co, Fe, Zn, Cu).[31] Similarly to the latter, the core has a trigonal bipyramidal Zr_4Zn arrangement, where a $Zr_4(\mu_4\text{-}O)$ fragment is capped at one of the faces by the Zn^{II} center. Three μ_2-bridging *Et*O ligands bind the Zn^{II} to the cage [Zn−O range 1.992(13)−2.005(13) Å], with the Cl ion completing the pseudo-tetrahedral geometry of Zn^{II}.

CONCLUSIONS

The studies described in this paper demonstrate that the initial nuclearity of the precursors can help in finding the path to obtain thermodynamically stable heterometallic cages with higher nuclearity. This is seen in the syntheses of the octanuclear cages **1**, **2**, and **3** in the reactions of the heptanuclear cage **A** with $[FeCl_2]$ and $[CoCl_2]$. Although the formation of clusters does not seem to be affected by the chemical nature of the metals and ligands in **1**−**3**, we observe how the same procedure with different metals can lead to the formation of completely different structures in **4** and **5** because of geometrical constraints and the formation of metal−metal bonds (Mo−Mo). Thus in the cases of reactions of $[TmCl_2]$ (Tm = Co, Zn, Fe, Cu) with $[Ti(OEt)_4]$ the series of similar pentanuclear cages $[Ti_4TmO(OEt)_{15}Cl]$ are produced, whereas reactions of $[CrCl_2]$ and $[MoCl_5]$ with $[Ti(OEt)_4]$ show completely different cage arrangements in the new tetranuclear and dodecanuclear cages **4** and **5**, respectively (both containing Tm^V centers).

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic data of clusters **1**−**6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: se296@cam.ac.uk.

ACKNOWLEDGMENT

We thank the EPSRC for funding this work (D.S.W. and PDRA for S.E., Grant EP/F00253X/1); Dr J. E. Davies (Cambridge) for collecting crystallographic data.

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