Novel double alkoxides of titanium(IV) and iron(II)/(III): synthetic, structural and spectroscopic studies

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The first structurally characterised titanium and iron polynuclear isopropoxides $[FeCl\{Ti_2(OPr^i)_9\}]$, 1, and $[Ti_3(OMe)_2(OPr^i)_9][Fe_4TiCl_4(O)(OPr^i)_9]$, 2, have been prepared from 2 : 1 : 1 mixtures of $[Ti(OPr^i)_4]$, $K(OPr^i)$ and $FeCl_2$. Their identity was confirmed by a number of chemical and physical methods including X-ray diffractometry. Semiempirical quantum mechanical calculations were consistent with an $S = 2$ ground state for 1. Structural and spectroscopic data support a mixed-valence formulation for the unique $\{Fe_4Ti\}$ anion in 2.

The elucidation of structural features and reactivity patterns of polymetallic alkoxides has aroused deep scientific interest, because the complexes have been used as precursors for super- or semi-conducting, ferroelectric, dielectric and even biocompatible oxide materials.[1,2] Many industrial applications have been developed in the past few years based on the preparation of films and powders from simple metallorganic compounds by sol–gel or chemical vapour deposition (CVD) technologies.[1–3] Expanding the possibilities of such processes, the use of well-characterised mixed-metal polynuclear precursors is expected to lead to a better stoichiometric control of final product composition than that from mixtures of homometallic alkoxides.[4] Our excursion into the chemistry of polynuclear $M^{II/III}$ species supported by O-donor ligands has also been motivated by their putative application in nitrogen-fixing systems, as shown by early reports of catalytic ammonia production from bimetallic oxide gels[5] and from iron–titania binary catalysts.[6]

This work adds to our previous reports on self-assembled early transition metal (TM) polynuclear systems relevant to bioinorganic processes.[7] It deals with the reactions of $M''Cl_x$ ($M'' = Fe$; $x = 2$ or 3) with potential chelating $[Ti_2(OR)_9]^-$ species generated from $[Ti(OR)_4]$. Trinuclear aggregates formulated as $[M''Cl_{(x-1)}\{Ti_2(OR)_9\}]$ can be isolated from the reaction mixtures following a two-step procedure based on a salt elimination reaction. Complexes where M'' is a main group or late transition metal have been described,[8] but species containing early TMs are particularly elusive. We report here the first examples of structurally characterised double alkoxides of iron and titanium. From these results and preliminary data gathered on iron(III)–titanium(IV) and –vanadium(IV) systems, we believe that a significant chemistry of first-row heterometallic alkoxides is now within reach.

The reaction of two molar equivalents of $[Ti(OPr^i)_4]$ with $K(OPr^i)$ in toluene, followed by the addition of one equivalent of $FeCl_2$ produced, after work-up, the light brown compound **1**, $[FeCl\{Ti_2(OPr^i)_9\}]$, and the deep brown compound **2**, $[Ti_3(OMe)_2(OPr^i)_9][Fe_4TiCl_4(O)(OPr^i)_9]$. Complex **1**, the main reaction product, has been reproducibly isolated as a first batch of pure crystalline solid. Complex **2** usually crystallises in mixtures with **1** following the addition of propan-2-ol to the reaction vessel. When allowed by suitable crystal sizes, the mixtures were hand-separated. Total yields (**1** + **2**), determined from the results of four different preparations, have been in the range of 40 to 60% based on total iron content. In one case, the estimation of the relative amounts of **1** and **2** in the mixture of crystals was made from the populations of the distinct iron sites in the Mössbauer spectrum.

Elemental analyses (C, H, Fe, Ti) and single crystal X-ray diffraction data for **1** were consistent with the expected formulation, $[FeCl\{Ti_2(OPr^i)_9\}]$ (Fig. 1). EPR and Mössbauer

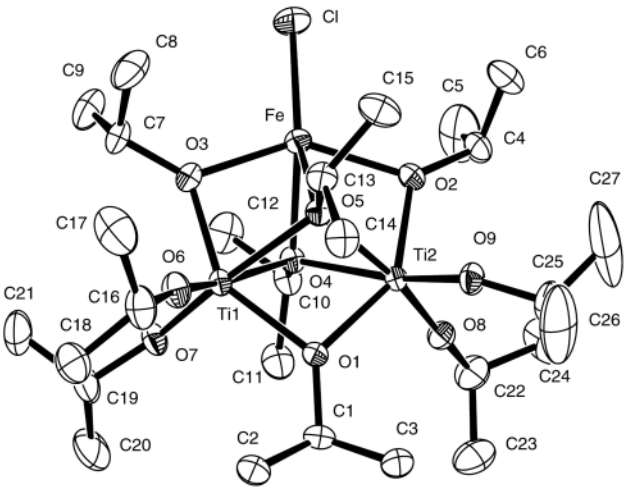

Fig. 1 ORTEP-3 plot of the molecular structure of $[FeCl\{Ti_2(OPr^i)_9\}]$, **1**, with the atom numbering scheme (50% ellipsoids). Average bond distances (Å) and angles (°) about the Fe centre: Fe–Cl 2.2491(6), Fe–O(2,3) 2.0879(15), Fe–O(4,5) 2.1502(14), O(2,3)–Fe–Cl 108.60(4); O(4,5)–Fe–Cl 145.25(4), O(2)–Fe–O(3) 142.81(6), O(4)–Fe–O(5) 69.46(5).

data (EPR-silent at 298 and 77 K; i.s. 1.05, q.s. 2.37, half-width at half-height, h.w., 0.13 mm s^{-1} at 77 K) indicate the presence of high-spin Fe^{II} in **1**. Infrared spectra are consistent with the presence of terminal and bridging Pr^iO^- groups.[9]

Both ions in **2** are new species and have striking structural features (Fig. 2 and 3). In the trinuclear $[Ti_3(OMe)_2(OPr^i)_9]^+$, the methoxide groups arise from traces of methanol in the solvent. The pentanuclear anion, $[Fe_4TiCl_4(O)(OPr^i)_9]^-$, shares an interesting parallel with square-pyramidal heterometallic molecules with $M_4M'O$ cores,[10] appearing in this group as a unique species because of its mixed-valence $M^{II/III}$ formulation (M = Fe; M′ = Ti). As a consequence of the partial Fe^{II} oxidation during the formation of **2**, the central μ_3-O(10) ligand (Fig. 3) replaces the μ_5-O feature common to the reported complexes. The Fe_4O moiety in **2** can be seen as a polymetallic ligand to a $[Ti(OPr^i)_5]^-$ unit formed from $[Ti(OPr^i)_4]$ in the reaction mixture; their aggregation leads to the self-assembly of the pentanuclear complex.

Two sets of bond dimensions about the iron centres can be distinguished in the anion (Fig. 3), in accordance with the observed geometries. Distances about the Fe(1) and Fe(3) sites compare well with data for iron(III) alkoxide centres in distorted trigonal-bipyramidal environments. As an example, the average Fe(1,3)–O(10) bond length in **2**, 2.049(3) Å, is shorter than the corresponding Fe–O(1) distance in $[Zr_3FeO(OPr^i)_{10}(acac)_3]$ [2.124(9) Å, complex **3**][11] and the mean Fe(1–4)–O(1) bond length in $[Fe_5O(OEt)_{13}]$ [2.189(3) Å, complex **4**].[12] Such variation is well accounted for by the gradual change from a μ_3- (in **2**) to a μ_5-coordination (in **4**) for the oxide ligand. The average Fe(1,3)–μ_2–O(1–4) distance in **2**, 1.905(4) Å, is also close to the similar dimensions in **3** and **4** [1.940(9) and 1.948(3) Å, respectively].[11,12] The Fe(2) and Fe(4) sites are distorted tetrahedral, with a mean distance of 2.356(3) Å to the central oxide ion and average Fe(2,4)–μ_2–O(1–4) distances of 2.028(4) Å. Angles about the four iron centres vary widely from values close to those expected for tetrahedral and trigonal-bipyramidal geometries [O(1)–Fe(2)–O(2), 109.99(16)° and O(1)–Fe(1)–O(5), 120.55(16)°, for example] to highly distorted figures probably imposed by the different electronic distributions around the iron sites and by the coordination to the titanium(IV) centre.

Microanalytical and spectroscopic data for **2** are consistent with the remarkable structure revealed by X-ray diffraction analysis and give support to the proposed mixed-valence

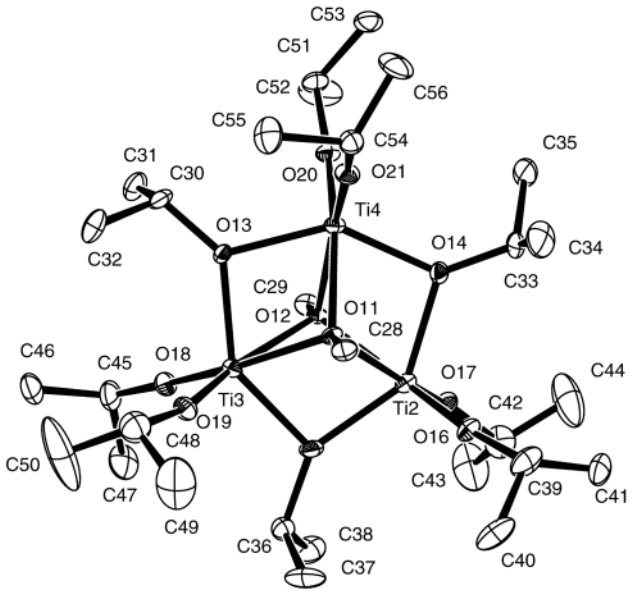

Fig. 2 ORTEP-3 plot of the $[Ti_3(OMe)_2(OPr^i)_9]^+$ cation in **2**, with the atom labelling scheme (20% ellipsoids).

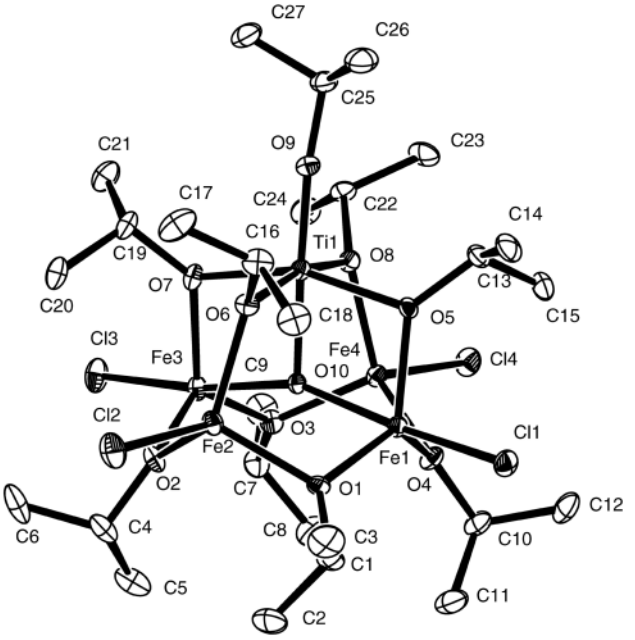

Fig. 3 ORTEP-3 plot of the $[Fe_4TiCl_4(O)(OPr^i)_9]^-$ anion in **2**, with the atom labelling scheme (20% ellipsoids). Selected bond distances (Å) and angles (°) about the iron centres: Fe(1)–O(4) 1.889(4), Fe(1)–O(1) 1.917(4), Fe(1)–O(5) 1.986(4), Fe(1)–O(10) 2.054(3), Fe(1)–Cl(1) 2.2982(14), Fe(2)–O(1) 2.033(3), Fe(2)–O(2) 2.025(4), Fe(2)–O(6) 2.057(4). Fe(2)···O(10) 2.371(3), Fe(2)–Cl(2) 2.3201(17), O(1)–Fe(1)–O(4) 123.49(17), O(1)–Fe(1)–O(5) 120.55(16), O(4)–Fe(1)–O(5) 110.13(16), O(10)–Fe(1)–Cl(1) 171.59(12), O(1)–Fe(2)–O(2) 109.99(16), O(2)–Fe(2)–O(6) 123.42(15), O(1)–Fe(2)–O(6) 103.12(14), O(1)–Fe(2)–Cl(2) 115.72(11), O(2)–Fe(2)–Cl(2) 100.13(11), O(6)–Fe(2)–Cl(2) 105.09, Fe(1)–O(10)–Fe(3) 156.9(2). Dimensions about Fe(3) and Fe(4) are very similar to the ones around Fe(1) and Fe(2), respectively.

formulation for the anion. High-spin iron(II) and iron(III) in *ca.* 1 : 1 proportion appear in the Mössbauer spectrum at 77 K [i.s. 1.13, q.s. 2.03, h.w. 0.16 mm s^{-1} for iron(II); i.s. 0.23, q.s. 1.12 and h.w. 0.15 mm s^{-1}, for iron(III)]. The presence of high-spin iron(III) is also supported by the typical EPR spectra recorded at 293 and 77 K for **2** in the solid state and in toluene solution. A representative spectrum is shown in Fig. 4. The resonances at $g = 2$ and $g = 6$ are assigned to iron(III) sites in axial EPR symmetry, with the greater intensity of the signal at $g = 2$ indicating an exchange interaction between the d^5 ions across the oxide bridge.[13] The signal at $g = 4.3$ suggests the formation of a rhombic species from **2**, following what appears to be a slow decomposition process. Accordingly, in toluene solution kept at room temperature for 24 h, the signals with $g = 2$ and 6 gradually disappear, leaving only the isotropic line at $g = 4.3$.

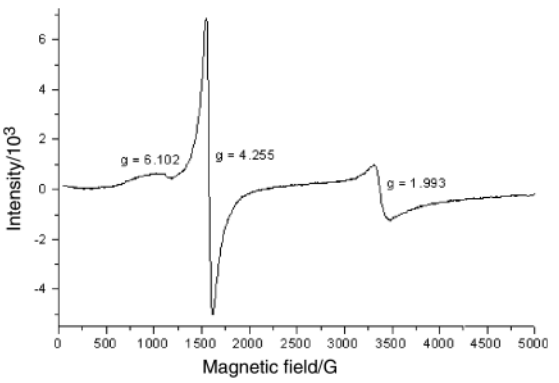

Fig. 4 X-Band EPR spectrum at 77 K of **2** in the solid state.

Semi-empirical quantum mechanical calculations on the electronic structure of **1** employed the INDO/S code and were based on the molecular geometry determined by X-ray diffractometry. The ground state was calculated to be a quintet, 92.5 kJ mol^{-1} below a triplet and 190.8 kJ mol^{-1} below a singlet. This is compatible with the presence of a high-spin Fe^{II} centre with C_{2v} microsymmetry in **1**, consistent with a detailed analysis of the bond dimensions around the Fe (Fig. 1). By comparison between the experimental UV-vis and the calculated INDO/S spectra, a masked, weak absorption at *ca.* 500 nm has been assigned to a spin-allowed d–d transition within the iron 3d manifold. This is probably responsible for the observed colour of **1**.

Room-temperature magnetic-susceptibility measurements by a modified Gouy method[14] have been carried out for **1** in the solid state and in toluene solution. This gave effective magnetic moments of 5.04 and 3.85 μ_B, respectively. The second value, significantly lower than the expected "spin-only" value for high-spin iron(II), can be reasonably ascribed to the formation of $Fe(\mu\text{-}Cl)_2Fe$ bridges between the iron centres with consequent dimerization of **1** in solution. This has been suggested earlier by Mehrotra and Singh for related zirconium(IV) alkoxides.[8a] Similar magnetochemical analyses are to be carried out with **2**.

Neutral complex **1** can be seen as a potential molecular precursor for industrially relevant heterometallic oxides. The chloride is a potentially significant problem, as halides often remain as contaminants in such systems, but halide substitution may help in this respect.[15] These synthetic studies, which can generate a number of interesting new materials, are under way in our laboratory. Additionally, a rational synthesis for **2** is currently under investigation.

Experimental

All operations were carried out under an inert dinitrogen atmosphere with the use of standard Schlenk and glove-box techniques. Solvents were dried and distilled under N_2 prior to use. Commercial reagents were supplied by Aldrich. Research grade liquefied ammonia (99.99%, moisture <33 ppm) was supplied by Praxair. $KOPr^i$ was prepared in quantitative yield by a published method.[16] $[Ti(OPr^i)_4]$ was prepared according to Bradley and co-workers.[17] Typical yields were *ca.* 50%. Titanium content, found (calcd): 16.8 (16.8%) δ_H (400 MHz, C_6D_6, 20 °C) 1.26 (6H, d) and 4.54 (1H, sept). δ_C (400 MHz, C_6D_6, 20 °C) 26.75, $-CH_3$, and 76.36, –CH–. IR (cm^{-1}) 1124vs, 1006vs, ν(C–O); 621s, ν(Ti–O).

Microanalyses were carried out under argon by Medac Laboratories Ltd. (Surrey, UK). Metal analyses were performed by ICP-OES at the Institute of Chemistry, University of São Paulo, Brazil, using Spectroflame Sequential equipment from Spectro Co. IR (Nujol mulls) and X-band EPR data were recorded on Bomem Hartmann Braun (MB series) and Bruker ESP-300E instruments, respectively. Magnetic susceptibility measurements were carried out at room temperature using a MKII magnetic susceptibility balance from Johnson-Matthey. Corrections for the diamagnetism of the ligands were applied.[18] Mössbauer data were recorded at 77 K on an ES-Technology MS105 spectrometer with a ^{57}Co source in a rhodium matrix. Spectra were referenced against iron foil at 298 K.

Preparation of $[FeCl\{Ti_2(OPr^i)_9\}]$, complex 1, and $[Ti_3(OMe)_2(OPr^i)_9][Fe_4TiCl_4(O)(OPr^i)_9]$, complex 2

A mixture of $KOPr^i$ (0.68 g, 6.9 mmol) and $[Ti(OPr^i)_4]$ (4.1 mL, 3.95 g, 13.9 mmol) in 50 mL of toluene was heated at 70 °C for 5 h to give a pale yellow solution. A suspension of $FeCl_2$ (0.93 g, 7.3 mmol) in toluene–propan-2-ol (10 : 1) was then added to the mixture, which was kept at 40 °C for 18 h. The resulting brown suspension was filtered to give an off-white solid (0.57 g, probably KCl), which was washed with 20 mL of toluene and dried under vacuum. The brown filtrate was taken to dryness under vacuum, giving a greenish-brown solid that was dissolved in toluene–propan-2-ol (1 : 1) and cooled down to −20 °C. Light brown diamond-shaped crystals of **1** (0.23 g) were isolated by filtration, washed with propan-2-ol and dried under vacuum. From the mother liquor, which received an addition of 30 mL of propan-2-ol, 2.39 g of a mixture of light and deep brown crystals (complexes **1** and **2**, respectively) were filtered off, washed with propan-2-ol and dried under vacuum. The relative amounts of **1** and **2** in this mixture (69% and 31% of the iron content, respectively) were determined by Mössbauer spectroscopy analysis. Crystals were hand-separated for further studies.

1: FTIR (cm^{-1}) 480 ν(Fe–O); 617 ν(Ti–O); 945, 1004, 1124, 1149 ν(C–O).

Found for **1** (%): C, 44.2; H, 8.3; Ti, 13.3; Fe, 7.6. $C_{27}H_{63}ClFeO_9Ti_2$ requires (%): C, 45.1; H, 8.8; Ti, 13.3, Fe, 7.8.

2: EPR (X-band, solid state) 293 K: $g_{eff} = 1.999$, 4.240, 6.105. 77 K: $g_{eff} = 1.993$, 4.255, 6.102.

Found for **2**: C, 39.5; H, 7.4. $C_{56}H_{132}Cl_4Fe_4O_{21}Ti_4$ requires (%): C, 39.6; H, 7.2.

Single-crystal X-ray diffraction analyses of complexes 1 and 2

Data were collected on a Nonius Kappa CCD area detector diffractometer at CPES (Brighton, UK). Suitable crystals were mounted on glass fibres and cooled to 173(2) K. Cell dimensions were based on all observed reflections ($I > 2\sigma_I$). Structures were solved by direct methods using the program package WinGX[19] and refined by full-matrix least-squares on F^2 with SHELXL-97.[20] Absorption corrections were carried out with MULTISCAN. Drawings were made with ORTEP3 for Windows.[21]

Crystal data for 1: $C_{27}H_{63}ClFeO_9Ti_2$, $M = 718.87$, triclinic, $a = 9.8982(1)$, $b = 10.1089(2)$, $c = 21.5841(3)$ Å, $\alpha = 84.213(1)$, $\beta = 83.627(1)$, $\gamma = 60.722(1)°$, $U = 1869.47(5)$ $Å^3$, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 0.91 mm^{-1}, 27583 reflections measured, 6542 unique ($R_{int} = 0.0330$) which were used in all calculations. Final R indices: $R_1 = 0.033$, $wR_2 = 0.083$ ($I > 2\sigma_I$); $R_1 = 0.037$, $wR_2 = 0.086$ (all data).

Crystal data for 2: $C_{56}H_{132}Cl_4Fe_4O_{21}Ti_4$, $M = 1698.42$, monoclinic, $a = 13.9455(3)$, $b = 38.1289(12)$, $c = 16.0638(5)$ Å, $\beta = 96.312(2)°$, $U = 8489.8(4)$ $Å^3$, space group $P2_1/c$ (no. 14), $Z = 4$, μ(Mo-Kα) = 1.20 mm^{-1}, 35844 reflections measured, 14781 unique ($R_{int} = 0.0962$) which were used in all calculations. Final R indices: $R_1 = 0.062$, $wR_2 = 0.117$ ($I > 2\sigma_I$); $R_1 = 0.145$, $wR_2 = 0.142$ (all data).

CCDC reference numbers 171715 and 171716. See http://www.rsc.org/suppdata/b1/b111517k/ for crystallographic data in CIF or other electronic format.

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