A mixed-valence (Ti^{III}Ti^{IV}) carboxylate complex: crystal structures and properties of [Ti$_2$OCl$_3$(O$_2$CPh)$_2$(thf)$_3$] and [NEt$_4$]$_3$[Ti$_2$Cl$_9$]

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The reaction of [TiCl$_3$(thf)$_3$] with 4 equiv. of PhCO$_2$H in refluxing thf or 3 equiv. of Cl$^-$ in CH$_2$Cl$_2$ gives [Ti$_2$OCl$_3$(O$_2$CPh)$_2$(thf)$_3$] **1** and [NEt$_4$]$_3$[Ti$_2$Cl$_9$] **2**, respectively: crystallography shows them to possess trapped-valence [Ti$_2$(μ-O)(μ-O$_2$CPh)$_2$]$^{3+}$ (Ti^{III}Ti^{IV}) and [Ti$_2$(μl)$_3$]$^{3+}$ cores, respectively, the former with an unusual asymmetrically bridging O^{2-} displaying triple/single bond distances to the metal ions.

We have a long-standing interest in the syntheses, structures and spectroscopic and physical properties of 3d metal carboxylate clusters, and this has recently been extended to titanium. In this report are described the preparation of two complexes, the mixed-valence species [Ti$_2$OCl$_3$(O$_2$CPh)$_2$(thf)$_3$] **1** and [NEt$_4$]$_3$[Ti$_2$Cl$_9$] **2**, from reactions of [TiCl$_3$(thf)$_3$]. The latter should prove a useful starting point for future studies, while the former is the first mixed-valence dinuclear Ti carboxylate. Crystallographically confirmed examples of mixed-valence Ti^{III}Ti^{IV} complexes with *any* ligation are extremely rare, and this is particularly true for dincuclear species. One previous example is the [Ti$_2$OCl$_4$(Me$_3$tacn)$_2$]$^+$ (Me$_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) cation,[1] which contains a linear [TiOTi]$^{5+}$ core. Unfortunately, this molecule lies on a crystallographic inversion centre, masking any possible differences between the two halves of the molecule, although the authors favour a trapped-valence description on the basis of spectroscopic data.[2] Complex **1** has no crystallographically imposed symmetry and this has allowed an unusual asymmetry to be observed in its [Ti$_2$(μ-O)]$^{5+}$ core.

[TiCl$_3$(thf)$_3$] (2 mmol) and PhCO$_2$H (8 mmol) were refluxed overnight in thf (40 ml) to form a green solution. Hexanes (40 ml) were added to the cooled solution, and after 3–5 days in the freezer, green–brown crystals of [Ti$_2$OCl$_3$(O$_2$CPh)$_2$(thf)$_3$]·thf (1·thf) were collected by filtration, washed with hexanes and dried *in vacuo*; the yield was 45%; the dried solid analysed as **1**.† The structure‡ of **1** (Fig. 1) consists of a triply bridged [Ti$_2$(μ-O)(μ-O$_2$CR)$_2$]$^{3+}$ core [Ti(1)···Ti(2) 3.370(2) Å] with terminal Cl$^-$ and thf groups. The complex is mixed valence (Ti^{III}Ti^{IV}), and the valences are trapped with Ti(1) being the Ti^{IV} centre; this description is clearly supported by an interesting asymmetry in the bridging oxide O(3) distances, with the Ti(1)–O(3) bond being much shorter than the Ti(2)–O(3) bond [1.706(6) *vs.* 1.964(6) Å, respectively]; the length of the former indicates considerable triple bond character (typical Ti^{IV}≡O 1.62–1.68 Å)[2,3] while that of the latter is consistent with a single bond. Thus, multiple bonding at one Ti occurs at the expense of multiple bonding at the other. The resulting structure is illustrated below. The Ti–O multiple bond has a significant *trans* influence on the Ti(1)–O(25) distance, which is *ca.* 0.1 Å longer than the Ti(2)–thf distances even though the latter

involve a lower oxidation state metal. The EPR spectrum of **1** in thf solution at 300 K shows a signal at g = 1.93, consistent with an S = 1/2 complex. Complex **1** is the first structural characterization of the [Ti$_2$O(O$_2$CR)$_2$]$^{3+}$ core, but it has been previously observed at both the Ti^{III}$_2$ and Ti^{IV}$_2$ levels, in [Ti$_2$O(O$_2$CPh)$_2$(tacn)$_2$]$^{2+4}$ (tacn = 1,4,7-triazacyclononane) and, for example, [Ti$_2$O(O$_2$CPh)$_2$Cl$_4$(EtOAc)$_2$],[5] respectively; as expected, these both have symmetric oxide bridges with average Ti–O^{2-} distances of 1.82(2) and 1.783(7) Å, respectively, indicating significant double bond character. The *average* Ti–O^{2-} length in **1** is 1.835(6) Å. Although unusual for Ti, asymmetrically bridged mixed-valence dinuclear species are known for V$_2$ species: for example, [V$_2$NBr$_3$(dmpe)$_3$] (dmpe = dimethylphosphinoethane) has an asymmetric [V$_2$(μ-N]$^{4+}$ core [V^{III}–N 1.972(14), V^{IV}–N 1.652(15) Å][6] and [V$_2$NCl$_5$(tmeda)$_2$] (tmeda = tetramethylethylenediamine) has an asymmetric [V$_2$(μ-N)]$^{5+}$ core [V^{III}–N 2.092(4), V^V–N 1.588(4) Å].[7] Attempts to prepare the V^{III}V^{IV} version of **1** are in progress.

[TiCl$_3$(thf)$_3$] (2 mmol) and NBu^n$_4$Cl (3 mmol) were dissolved in CH$_2$Cl$_2$ (20 ml) under nitrogen, and the resulting orange solution was layered with an equivolume solution of NEt$_4$Cl (3 mmol) in CH$_2$Cl$_2$. Well formed orange crystals of [NEt$_4$]$_3$-[Ti$_2$Cl$_9$]·5CH$_2$Cl$_2$ (2·5CH$_2$Cl$_2$) slowly grew as the solutions mixed, and these were collected by filtration, washed with Et$_2$O and dried *in vacuo*; the yield was 90%; the dried solid analyses as solvent-free.† The structure‡ of the anion of **2** (Fig. 2) is a
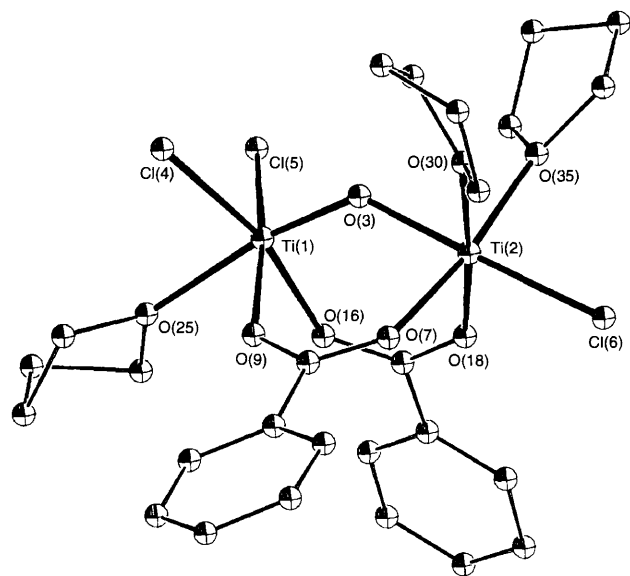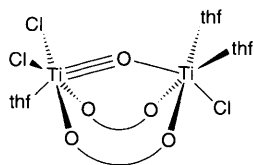

Fig. 1 ORTEP representation of [Ti$_2$OCl$_3$(O$_2$CPh)$_2$(thf)$_3$] **1**. Selected interatomic distances (Å) and angles (°): Ti(1)···Ti(2) 3.370(2), Ti(1)–O(3) 1.706(6), Ti(1)–Cl(4) 2.343(3), Ti(1)–Cl(5) 2.336(5), Ti(1)–O(9) 2.008(7), Ti(1)–O(16) 2.025(5), Ti(1)–O(25) 2.209(6), Ti(2)–O(3) 1.964(6), Ti(2)–Cl(6) 2.347(3), Ti(2)–O(7) 2.041(7), Ti(2)–O(18) 2.038(6), Ti(2)–O(30) 2.106(6), Ti(2)–O(35) 2.093(7); Ti(1)–O(3)–Ti(2), 133.20(8).

face-sharing bioctahedron with a Ti···Ti distance [3.216(5) Å] ruling out a Ti–Ti bond. The anion has virtual D_{3h} symmetry and crystallographic C_2 symmetry, the rotation axis passing through Cl(6) and the midpoint of the Ti(1)–Ti(1') vector. Previous reports of the $[Ti_2Cl_9]^{3-}$ ion are few,[8] and crystallographic data have been lacking; recently, however, the $[Ti_2Br_9]^{3-}$ anion was structurally characterized for the first time in the solid-state material, $In_3[Ti_2Br_9]$ (Ti···Ti 3.144 Å).[9] The $[Ti_2Cl_9]^-$ ion (i.e., 2 Ti^{IV}) is known in the $[PCl_4]^+$ and $[(C_6Me_6)TiCl_3]^+$ salts;[10] the Ti···Ti distance in the former is 3.439(6) Å.

The effective magnetic moment (μ_{eff}/Ti$_2$) of 2 decreases from 2.10 μ_B at 360 K to 0.96 μ_B at 100 K and then to 0.58 μ_B at 5.0 K. The data support the presence of antiferromagnetic exchange interactions between the Ti^{III} ions to give an $S = 0$ ground state and $S = 1$ excited state. The fitting of magnetic data for octahedral Ti^{III} has long been recognized to be particularly challenging owing to its orbitally triply degenerate ground state and the resulting presence of unquenched orbital angular momentum that makes inapplicable the Heisenberg Hamiltonian, which assumes only spin angular momentum is present. This problem has been addressed at various levels[11] with varying degrees of success. The Bleaney–Bowers (spin-only) equation for a d^1–d^1 dimer is thus, strictly speaking, a poor model for the interactions in 2 but, in line with other Ti^{III}_2 studies,[9] has been applied to 2 to gain some insight into the coupling. Only data at >100 K were employed, where the changing singlet–triplet populations should dominate the observed temperature dependence, and the fitting parameters were $J = -171(10)$ cm^{-1} and $g = 1.61(10)$, with a temperature independent paramagnetism term held constant at 800 × 10^{-6} cm^3 mol^{-1} and a paramagnetic impurity term of 3.8%. The latter is likely an artifact of the spin-only model employed; similar fitting[9] of the data for $In_3[Ti_2Br_9]$ to the Bleaney–Bowers equation required a 7% impurity term. The singlet–triplet gap in 1 is thus $|2J| = 342$ cm^{-1}; a value of ca. 500 to 525 cm^{-1} has been reported for $Cs_3[Ti_2Cl_9]$,[8a] and 430 cm^{-1} and ca. 350 cm^{-1} for $In_3[Ti_2Br_9]$ and $Rb_3[Ti_2Br_9]$,[11f] respectively.

This work was supported by the US Department of Energy.
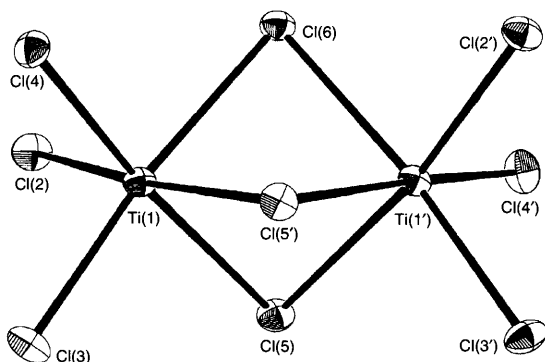
Fig. 2 ORTEP representation of the $[Ti_2Cl_9]^{3-}$ anion of 2. Selected interatomic distances (Å) and angles (°): Ti(1)···Ti(1') 3.216(5), Ti(1)–Cl(2) 2.364(4), Ti(1)–Cl(3) 2.363(5), Ti(1)–Cl(4) 2.365(4), Ti(1)–Cl(5) 2.482(4), Ti(1)–Cl(5') 2.507(4), Ti(1)–Cl(6) 2.511(5); Ti(1)–Cl(5)–Ti(1') 80.26(14), Ti(1)–Cl(6)–Ti(1') 79.65(18).

Footnotes

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