Novel ionogenic heterometal alkoxide derivatives

Michael Veith,* Sanjay Mathur* and Volker Huch

Institute of Inorganic Chemistry, University of Saarland, D-66041 Saarbrücken, Germany

First examples of hydrocarbon soluble heterometal cation–anion systems containing metal alkoxide clusters as isolated ions, are reported.

Although a few cationic alkoxides of yttrium against non-metallic counter ion BPh_4^- have been reported,[1] the cation–anion systems based on different metals and discrete ions are unprecedented in heterometal alkoxide chemistry.[2] In view of the above, the title derivatives containing separated poly-metallic alkoxide ions, as solution and solid-state stable species, represent a new subset in alkoxide chemistry.

The equimolar interaction of SnI_4 with $KTi(OPr^i)_5$[2e] or $KTi_2(OPr^i)_9$[2c] in toluene–isopropyl alcohol, followed by removal of precipitated KI and leaving the deep orange solution at room temperature for a few hours, leads to crystallisation of the only isolable ionic complex $[\{Ti_3(OPr^i)_{11}\}^+][\{Sn_2I_6(OPr^i)_3\}^-]$ **1**, in both cases. **1** could be obtained in higher yield by the reaction of SnI_4, $KOPr^i$ and $Ti(OPr^i)_4$ in 2 : 2 : 3 molar ratio.†

The solid-state structure‡ of **1** consists of distinct $\{Ti_3(OPr^i)_{11}\}^+$ cations and $\{Sn_2I_6(OPr^i)_3\}^-$ anions (Fig. 1). The trinuclear cation, $Ti_3(OPr^i)_{11}^+$ is formed by three edge-sharing distorted octahedra, built about Ti(1), Ti(2) and Ti(3), which are also mutually confacial. The trimetallic Ti_3 core forms an equilateral triangle (non-bonding Ti···Ti distances = 3.082 Å) capped at both the faces by triply bridging μ_3-OPr^i ligands [O(8), O(9)], while the three doubly bridging μ-OPr^i ligands [O(6), O(7), O(12)] bridge the edges of the triangular frame. The cationic unit in **1** is a modification of the M_3X_{11} structure type, well known among trimetallic alkoxides of the general formula $M_3(O)(OR)_{10}$.[3,4] Whereas one of the eleven ligands in $M_3O(OR)_{10}$ derivatives is dianionic (O^{2-}), the presence of only univalent anions in Ti_3X_{11} unit produces a cationic species which acts as a stable entity due to the preferred six-coordination achieved by all the Ti atoms. The Ti–O bond lengths follow the trend μ_3-OPr^i (2.157 Å) > μ-OPr^i (2.044 Å) > terminal-OPr^i (1.753 Å) and are in harmony with Ti–O bond lengths observed in molecular titanium isopropoxide derivatives.[2c,5] The anionic part in **1** is a bioctahedron formed by the two octahedral tin atoms [Sn(1), Sn(2)] sharing a face defined by the oxygen atoms of μ-OPr^i groups [O(1), O(2), O(3)]. It can be visualised as a modification of cluster anion $M_2(OPr^i)_9^-$ (M = Sn,[6] Ti,[2c] Zr,[2a] Hf,[2e]) observed as a versatile chelating metallo-ligand in a variety of hetero bi- and tri-metallic alkoxides. The Sn–I distances (av. 2.765 Å) are comparable with the Sn–I contacts observed in the crystal structures[7] of non-ionic compounds $[I_2Sn\{Ti(OPr^i)_5\}_2]$ (2.778 Å), $[I_2Sn\{Al(OPr^i)_4\}_2]$ (2.736 Å) and $[I_3Sn\{Zr(OPr^i)_5(Pr^iOH)\}]$ (2.774 Å). It is noteworthy that bonding parameters of both the ions in **1** show no significant deviation when compared with analogous molecular compounds. The ambient-temperature ^1H NMR spectrum§ of **1** exhibits methyl resonances in the integrated ratio 6 : 3 : 3 : 2 which is consistent with the total number of alkoxide ligands observed in the solid-state structure; the methine protons are observed as several associated septets which overlap to give four multiplets in approximate intensity ratio 6 : 2 : 4 : 2. The solution ^{13}C NMR data corroborates the above observation. Although all the OPr^i ligands in the solid-state structure of **1** are unique, the solid-state ^{13}C CP MAS NMR spectrum reveals only six signals of relative intensities 6 : 3 : 2 : 1 : 1 : 1, which possibly occur from an accidental overlapping of some of the alkoxy ligands [*e.g.* 6 terminal, 3 μ- and 2 μ_3-OPr^i groups in $Ti_3(OPr^i)_{11}^+$], resonating at almost similar frequencies. The presence of a tin(IV)-based anionic species in the solution of **1** is evident in the significant lower frequency shift of the ^{119}Sn resonance (δ −1734.7) when compared with the ^{119}Sn NMR chemical shifts observed for neutral iodo-functionalised alkoxides $\{[I_2Sn\{Ti(OPr^i)_5\}_2]$, δ −1245.0; $[I_2Sn\{Al(OPr^i)_4\}_2]$, δ −1540.7} which also contain six-coordinate tin(IV) centers in an environment of terminal iodide and bridging isopropoxide ligands.[7] Various attempts to record a ^{119}Sn CP MAS NMR spectrum were thwarted by low signal to noise ratio which precluded an unambiguous assignment of anisotropic shifts.

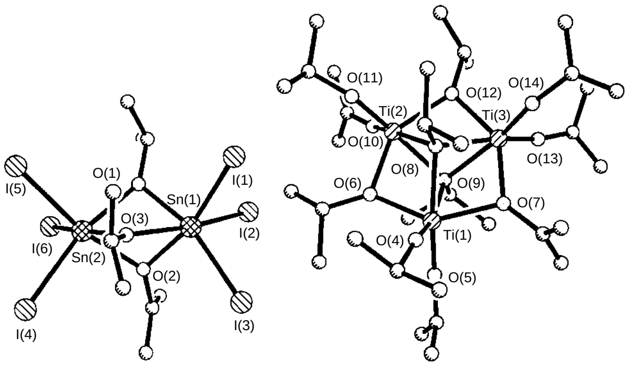

Fig. 1 Crystal structure of **1**. Hydrogen atoms of isopropyl moieties are not drawn. Representative bond lengths (Å) and angles (°): Sn(1)–O(2) 2.104(8), Sn(1)–O(1) 2.108(9), Sn(1)–O(3) 2.164(8), Sn(2)–O(1) 2.119(8), Sn(2)–O(2) 2.140(9), Sn(2)–O(3) 2.103(8), Sn–I(1) 2.779(2), Sn–I(2) 2.776(2), Sn–I(3) 2.742(2); O(1)–Sn(1)–I(3) 164.8(2), O(2)–Sn(1)–I(2) 97.0(2), O(3)–Sn(1)–I(1) 97.8(2), I(2)–Sn(1)–I(3) 95.45(6), I(1)–Sn(1)–I(2) 93.39(5), I(1)–Sn(1)–O(1) 95.4(2), O(6)–Ti(1)–O(7) 140.7(3), O(5)–Ti(1)–O(9) 98.3(4), O(4)–Ti(1)–O(9) 162.3(3), O(4)–Ti(1)–O(5) 99.2(4), O(4)–Ti(1)–O(6) 100.6(4), O(4)–Ti(1)–O(8) 93.7(3).

The unique arrangement of large bi- and tri-metallic alkoxide clusters as distinct ions in **1**, inspired us to explore similar systems. Ionogenic heterometal alkoxide derivatives could be rationally constructed by abstracting halide ligand from the well defined heteroleptic heterometal alkoxides [eqn. (1)].

$$[ClSn\{M_2(OPr^i)_9\}]_2 + 2\,SnCl_2 \xrightarrow{\text{toluene}} 2\,[\{SnM_2(OPr^i)_9\}^+][SnCl_3^-] \quad (1)$$

M = Ti **2** M = Ti **4**
M = Zr **3** M = Zr **5**

The halide heterobimetallic precursors, **2** and **3** are obtained in nearly quantitative yields on treating anhydrous $SnCl_2$ with stoichiometric amount of alkali metal reagent $KM_2(OPr^i)_9$ (M = Ti, Zr[8]). Both **2** and **3** react [eqn. (1)] with 1 equiv. of $SnCl_2$ to afford **4** and **5**, respectively. In contrast to the fluxional behaviour of **3**, which could not be frozen to a static structure at even −70 °C, the room. temp. spectral data of **5** are structurally diagnostic. Both ^1H and ^{13}C NMR spectra show 4 : 2 : 1 : 2 pattern of resonances, characteristically observed for hetero-bimetallic alkoxides based on tetradentate interaction of the

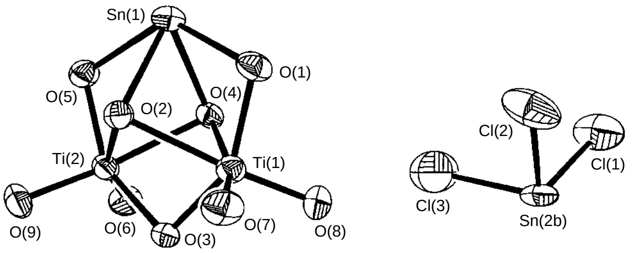

Fig. 2 An ORTEP diagram of **4**. Displacement ellipsoids are drawn at 30% probability levels. $SnCl_3^-$ unit shows only one of the partially occupied tin sites. All oxygen atoms bear isopropyl groups which are not drawn from clarity. Pertinent bond lengths (Å) and angles (°): Sn(1)–O(1) 2.321(4), Sn(1)–O(2) 2.214(4), Sn(1)–O(4) 2.164(4), Sn(1)–O(5) 2.422(4), Ti(1)–O(3) 2.014(4), Ti(2)–O(3) 2.027(3), Ti(1)–O(8) 1.755(4); O(5)–Sn(1)–O(1) 131.58(12), Sn(1)–O(4)–Ti(1) 94.19(13), Ti(1)–O(1)–Sn(1) 97.7(2), Sn(1)–O(2)–Ti(1) 92.54(14), Ti(1)–O(3)–Ti(2) 102.7(2). Sn–Cl bond lengths and Cl–Sn–Cl angles in the $SnCl_3^-$ unit are in the range 2.329–2.488 Å and 93.1–99.4°, respectively.

bioctahedral $M_2(OPr^i)_9^-$ alkoxide sub-structure with a cationic fragment and possessing molecular C_{2v} symmetry in solution.[2b,c] The ^{119}Sn NMR spectrum of **5** exhibits two resonances at δ −180.29 and −297.41 which according to the published data indicate the presence of two tin(II) species with coordination number at tin differing by one.[9] Ambient-temperature NMR data¶ of compound **4** shows a non-rigid behaviour, however, cooling a [$^2H_8$]toluene solution to −40 °C results in a static structure with spectral features essentially similar to that of **5**. The ^{119}Sn NMR chemical shifts (δ −147.2 and −281.3), similar to that observed for **5**, indicate a compositional similarity among the tin(II) species present in the solutions of both **4** and **5**.

The formulation of **4** and **5** suggested on the basis of spectroscopic and analytical data was established for **4**, by X-ray crystallography.‡ The crystal structure consists of discrete $\{SnTi_2(OPr^i)_9\}^+$ cation and $SnCl_3^-$ anion (Fig. 2). The heterobimetallic fragment based on the interaction of mono-anionic $\{Ti_2(OPr^i)_9\}^-$ unit to Sn^{2+}, is of special interest as no $Sn^{II}Ti^{IV}$ mixed-metal species is formed in the reaction of neutral constituent alkoxides.[9b] Curiously, all the four alkoxide arms of $Ti_2(OPr^i)_9^-$ unit are used to cradle Sn^{2+} in the $Sn\{Ti_2(OPr^i)_9\}^+$ unit, whereas only bidentate interaction of $\{M_2(OPr^i)_9\}^-$ moieties toward an $SnCl^+$ fragment is observed in $[ClSn\{M_2(OPr^i)_9\}]_2$ (M = Zr, Hf) derivatives.[8] The tin atom, in both cases, is present in a pseudotrigonal bipyramidal geometry. Whereas the lone pair of electrons occupies an equatorial position in the $SnTi_2(OPr^i)_9^+$ unit, the presence of a terminal halide ligand at tin in $[XSn\{M_2(OPr^i)_9\}]_2$ compounds[8] directs the lone pair of electrons to an axial position which inhibits the coordination of remaining isopropoxy ligands to tin(II).[6,8]

The 'bare' coordination hemisphere of tin(II) atom (no terminal ligands) makes the $Sn\{Ti_2(OPr^i)_9\}^+$ unit comparable, in a structural sense, with the molecular derivatives $K\{U_2(OBu^t)_9\}$[10] and $Na\{Th_2(OBu^t)_9\}$,[4] in which the alkali metals are devoid of any terminal ligands. Further, the Sn–μ_3-OR (av. 2.189 Å) distances are significantly shorter than Sn–μ-OR contacts which contrasts the usual trend (μ_3-OR > μ-OR > terminal OR) observed among M′M_2 heterobimetallic alkoxides containing a $M_2X_9^-$ unit. The repulsive forces between the Sn–O bonding electrons and the tin(II) electron lone pair along with the geometric constraints of the bioctahedral $Ti_2(OPr^i)_9^-$ unit result in a strained pseudotrigonal bipyramidal geometry at the tin center [O(2)–Sn(1)–O(4) 67.44(12)°, O(1)–Sn(1)–O(5) 131.58(12)°]. The ligand geometry about tin in $SnCl_3^-$ anion is trigonal pyramidal implying a stereochemically active lone pair; the tin atom, in the crystal structure, is disordered at two sites with partial site occupancy factors 0.66 : 0.34 [Sn(2A): Sn(2B)]. The Sn–Cl distances (av. 2.427 Å) fall in the range typically observed for $SnCl_3^-$ species.

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Footnotes and References

* E-mail: veith@rz.uni-sb.de

† Satisfactory elemental analyses were obtained for the new compounds **1** and **3**–**5**.

‡ *Crystallography* Both structures were solved by direct methods and refined on all F^2 data using the SHELX-97 suite of programs.[11]

Crystal data: **1**: $C_{56}H_{114}I_6O_{14}Sn_2Ti_3$, M = 2152.98, orange bars, crystal size 0.60 × 0.45 × 0.50 mm, triclinic, space group $P\bar{1}$, a = 15.867(3), b = 15.970(3), c = 16.684(3) Å, α = 80.60(3), β = 79.56(3), γ = 86.75(3)°, U = 4100.2(13) Å^3, Z = 2, D_c = 1.732 g cm^{-3}, T = 293(2) K, 26 338 reflections total, 12 179 unique (R_{int} = 0.0756), 6474 observed [$I > 2\sigma(I)$], $R(wR_2)$ = 0.081(0.198).

4: $C_{27}H_{63}Cl_3O_9Sn_2Ti_2$, M = 971.30, colourless cubes, crystal size 0.50 × 0.40 × 0.25 mm, triclinic, space group $P\bar{1}$, a = 12.200(11), b = 12.849(12), c = 14.465(12) Å, α = 91.06(8), β = 91.43(8), γ = 107.95(7)°, U = 2156(3) Å^3, Z = 2, D_c = 1.496 g cm^{-3}, T = 293(2) K, 7249 reflections total, 5917 unique (R_{int} = 0.0091), 5566 observed [$I > 2\sigma(I)$], $R(wR_2)$ = 0.0469(0.1308). CCDC 182/613.

§ *Spectral data*: **1**: ^1H NMR ($CDCl_3$, 20 °C, 200.13 MHz) δ 1.24 (d, 36 H), 1.31 (d, 18 H), 1.40 (d, 18 H), 1.63 (d, 12 H) (CH_3); 4.41 (m, 6 H), 4.58 (m, 2 H), 4.74 (m, 4 H), 5.02 (m, 2 H) (CH). ^{13}C NMR ($CDCl_3$, 20 °C, 50.3 MHz) δ 25.73, 25.93, 26.55, 29.86 (CH_3); 68.27, 69.57, 70.94, 74.15, 75.42 (CH). ^{13}C CP MAS NMR δ 24.89, 25.30, 25.65, 26.29, 27.04, 27.80 (CH_3); 71.63, 77.24, 77.98, 79.61, 84.15, 85.20 (CH). ^{119}Sn NMR (C_6D_6, 20 °C, 74.13 MHz) δ −1734.7.

5: ^1H NMR (C_6D_6, 20 °C, 200.13 MHz) δ 1.19 (d, 24 H), 1.29 (d, 12 H), 1.34 (d, 6 H), 1.42 (d, 12 H) (CH_3); 4.22, 4.29, 4.65 and 4.87 (spt, 9 H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 50.3 MHz) δ 25.92, 25.99, 26.21, 26.74 (CH_3, intensity ratio = 4 : 2 : 1 : 2); 72.93, 73.45, 74.37, 74.89 (CH, intensity ratio = 2 : 1 : 4 : 2). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 20 °C, 74.6 MHz): δ −180.3, −297.4.

¶ **4**: ^1H NMR ($CDCl_3$, 20 °C, 200.13 MHz) δ 1.25 (d, 54 H, CH_3), 4.61 (m, 9 H, CH). ^{13}C NMR ($CDCl_3$, 20 °C, 50.13 MHz) δ 26.21 (CH_3); 75.68 (CH). ^1H NMR ($CDCl_3$, −40 °C, 200.13 MHz) δ 1.34 (d, 24 H), 1.38 (d, 12 H), 1.41 (d, 6 H), 1.52 (d, 12 H) (CH_3); 4.53 (spt, 2 H), 4.65 (spt, 1 H), 4.82 (spt, 4 H), 4.99 (spt, 2 H). ^{13}C NMR ($CDCl_3$, −40 °C, 50.3 MHz) δ 24.74, 25.41, 25.87, 26.29 (CH_3, intensity ratio = 1 : 2 : 4 : 2); δ 72.49, 74.80, 76.06, 76.37, 76.69, 77.00, 77.33, 82.84 (CH, intensity ratio = 1 : 1 : 1 : 1 : 1 : 1 : 1 : 2). ^{119}Sn NMR ($CDCl_3$, 20 °C, 74.6 MHz) δ −147.2, −281.3.

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