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Synthesis and characterisation of novel heterobimetallic halide isopropoxides based on $M_2(OPr^i)_9^-$ (M = Sn, Zr or Ti) anions: crystal and molecular structures of $[CdI\{Sn_2(OPr^i)_9\}]$ and $[\{SnI[Zr_2(OPr^i)_9]\}_2]$†

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New heterobimetallic halide isopropoxides based on the interaction of $M_2(OPr^i)_9^-$ (M = Sn^{IV}, Zr^{IV} or Ti^{IV}) units with Cd^{II}, Sn^{II} and Pb^{II} have been prepared. These complexes have been characterised by multinuclear solution and solid-state cross polarisation magic angle spinning (CP MAS) NMR spectroscopy, elemental analyses and cryoscopy. Single-crystal X-ray diffraction studies have been performed for $[CdI\{Sn_2(OPr^i)_9\}]$ **1** and $[\{SnI[Zr_2(OPr^i)_9]\}_2]$ **2**. Compound **1** consists of a face-sharing bioctahedral $Sn_2(OPr^i)_9^-$ unit which interacts with the central metal atom, cadmium, using two μ- and two terminal OPr^i groups. The cadmium atom is within a distorted trigonal bipyramid of oxygen and iodine atoms. The ^{113}Cd chemical shifts in the solution and solid-state CP MAS NMR spectra of **1** are consistent with the retention of its heterometallic nature in solution. In contrast to the monomeric form of **1**, compound **2** exists as an iodo-bridged dimer in the solid state. Cryoscopic measurements for **2** indicate a monomer–dimer equilibrium (η = 1.6) in solution which has been confirmed by variable-temperature ^{119}Sn NMR studies. In the solid state the ligating mode of the $Zr_2(OPr^i)_9^-$ unit in **2** is different from isostructural $Sn_2(OPr^i)_9^-$ and it binds to tin *via* only three OPr^i groups, the fourth $M-OPr^i$ interaction being hindered by the stereochemically active lone pair of electrons present at Sn^{II}. The central SnI_2O_6 core in **2** can be viewed as two SnI_2O_3 octahedra fused along a common axial–equatorial edge where one of the axial co-ordination sites in each is occupied by the non-bonding electron pair of Sn^{II}.

Heterometallic alkoxides[1] have gained considerable attention as potential precursors to mixed-metal oxide materials mainly due to an anticipated structural and electronic relationship between metal oxides and metal alkoxides and the possible control over the desired metal stoichiometry at the molecular level. In view of the advanced ceramics generally being binary, ternary or higher mixed-metal oxides, the present synthetic challenge involves the synthesis of molecular species containing two, three or more different metals. Mehrotra *et al.*[1a] have systematically employed salt-elimination reactions to obtain heterometallic alkoxides of a large number of metals. We have recently synthesised[2] stoichiometrically precise heterotermetallic frameworks by the reactions of well characterised bimetallic alkoxide halides and co-ordinatively unsaturated species like $Ba(OPr^i)_3^-$. The high reproducibility of the results with halide precursors $[CdM_2I(OPr^i)_9]$ containing different metals (M = Ti, Zr or Hf) has two noteworthy features: (*i*) the utility of well characterised heterobimetallic alkoxide halides as building blocks and (*ii*) the importance of supporting units such as $M_2(OPr^i)_9$ in the precursor molecules with an extraordinary adaptability to bind different metals.

In view of the above, the stable bimetallic alkoxide halide systems which can be used as convenient intermediates for incorporating additional metals into molecular alkoxide assemblies are of considerable interest. We report here the first solid-state characterisation of a heterobimetallic alkoxide iodide based on the $Sn_2(OPr^i)_9$ fragment which is a novel example of the formation of a $M_2(OR)_9$ type cluster by a tetravalent main-group metal. Owing to its formulation, it is expected that the $Sn_2(OPr^i)_9$ unit may structurally resemble the well known M_2X_9 type confacial bioctahedral units commonly observed for early transition,[3,4] lanthanide[5] and actinide[6,7] metals. For comparison, we performed a single-crystal X-ray diffraction study on a heterobimetallic alkoxide iodide based on the $Zr_2(OPr^i)_9$ unit which however was found to exhibit an uncommon ligating mode which emphasises the versatility of $M_2(OR)_9$ groups in responding to the need of different metal atoms in order to build heterometallic alkoxide clusters.

Results and Discussion

Five new bimetallic halide isopropoxides of divalent Cd, Sn and Pb have been synthesised by the metathesis reactions of their iodides and alkali-metal salts of $M_2(OR)_9^-$ anions containing Sn, Zr and Ti atoms [equation (1) (M = Cd, M′ = Sn **1**, M =

$$MI_2 + K[M'_2(OPr^i)_9] \longrightarrow [MI\{M'_2(OPr^i)_9\}] + KI\downarrow \qquad (1)$$

Sn, M′ = Zr **2**, M = Sn, M′ = Ti **3**, M = Pb, M′ = Zr **4** or M = Pb, M′ = Ti **5**)]. In contrast with the large amount of work on heterometallic alkoxides,[1] the developments in tin and lead alkoxide chemistry are rather limited.[1b] In spite of the interesting electrical and optical properties of tin(IV)-based oxide materials,[9] the use of tin(IV) alkoxides in chemical ceramics processing is in general prevented by the difficulties involved in the synthesis of simple tin(IV) alkoxides by conventional methods.[8,10] Attempts have been made to circumvent these limitations by synthesising tin(IV)-containing heterometallic alkoxides.[11] In this context, the alkali-metal alkoxide $Na[Sn_2(OPr^i)_9]$ obtained by Bradley *et al.*[12] during the attempted synthesis of $Sn(OPr^i)_4{\cdot}Pr^iOH$ appears to be an interesting precursor for obtaining heterometallic alkoxides of tin(IV).[13]

The reaction of freshly synthesised $K[Sn_2(OPr^i)_9]$ with CdI_2 in toluene according to equation (1) afforded $[CdI\{Sn_2(OPr^i)_9\}]$ **1** as a hydrocarbon-soluble white solid. Molecular-weight measurements in freezing (+5 °C) benzene indicate the monomeric nature of **1**. Attempted volatilisation of **1** (180 °C, 10^{-2} mmHg) resulted in its decomposition yielding $[\{Sn(OPr^i)_4\}_3]$ as the only volatile fragment (^1H NMR evidence).

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† *Non-SI unit employed:* mmHg ≈ 133 Pa.

The ^1H and ^{13}C NMR spectra of compound **1** at room temperature are too broad to be structurally diagnostic. On lowering the temperature resonances corresponding to different isopropyl environments separate and the best resolved spectra are obtained at −65 °C. The ^1H spectrum at −65 °C exhibits four distinct doublets which integrate as 2:2:1:4. The methine protons are observed as three overlapping septets which integrate approximately as 4:1:4. The pseudo C_{2v} molecular symmetry of **1** as indicated by the relative and total intensities of the signals in the ^1H and ^{13}C NMR spectra is corroborated by solid-state ^{13}C cross polarisation magic angle spinning (CP MAS) NMR studies [Fig. 1(*a*)]. The ^{119}Sn NMR data revealed a sharp resonance at δ −627.1 consistent with one type of six-co-ordinated tin atom.[14] Cadmium-113 NMR spectroscopy has proved to be a valuable tool in determining the co-ordination environment around Cd and the chemical shifts observed for **1** in both solution (δ 23.4) and in the solid state [δ 32.5, Fig. 1(*c*)] indicate retention of the structure of the heterometallic species in solution and are in agreement with those reported for other cadmium compounds with oxygen-containing ligands.[15] The integrated area of the satellites observed in the solution ^{113}Cd NMR spectrum is 26.8% of the total peak area and is consistent (calc. 27.7%) with a structure in which the cadmium atom is coupled through oxo-bridges to two equivalent tin atoms.[16]

Large transparent crystals of compound **1** obtained (50% yield) from toluene–hexane at −30 °C were cleaved to obtain crystals suitable for X-ray diffraction studies. In the solid-state structure (Fig. 2) the central cadmium atom bearing a terminal iodide ligand interacts with a face-shared bioctahedral $Sn_2(OPr^i)_9^-$ unit *via* two terminal and two bridging isopropoxo groups, a ligating mode of common occurrence for various $M_2X_9^-$ (X = OR, R = alkyl) units based on early transition,[3,4] lanthanide[5] and actinide[6,7] metals. Compound **1**, to the best of our knowledge, represents the first example of a structurally characterised bimetallic alkoxide halide based on a bioctahedral $M_2(OPr^i)_9$ substructure formed by a tetravalent main-group metal. The compound has a crystallographic C_2 symmetry and its deviation from the higher C_{2v} symmetry is only minor, the isopropyl group on O(2) being disordered (Fig. 2). Both tin atoms are six-co-ordinate with substantial deviation from an ideal octahedral geometry as can be deduced from the bond angles around tin (Tables 1 and 2). Cadmium with iodide as the only terminal ligand adopts a highly distorted trigonal-bipyramidal co-ordination [O(4)–Cd–O(4′) 134.5°] with O(4) and O(4′) occupying the axial sites.

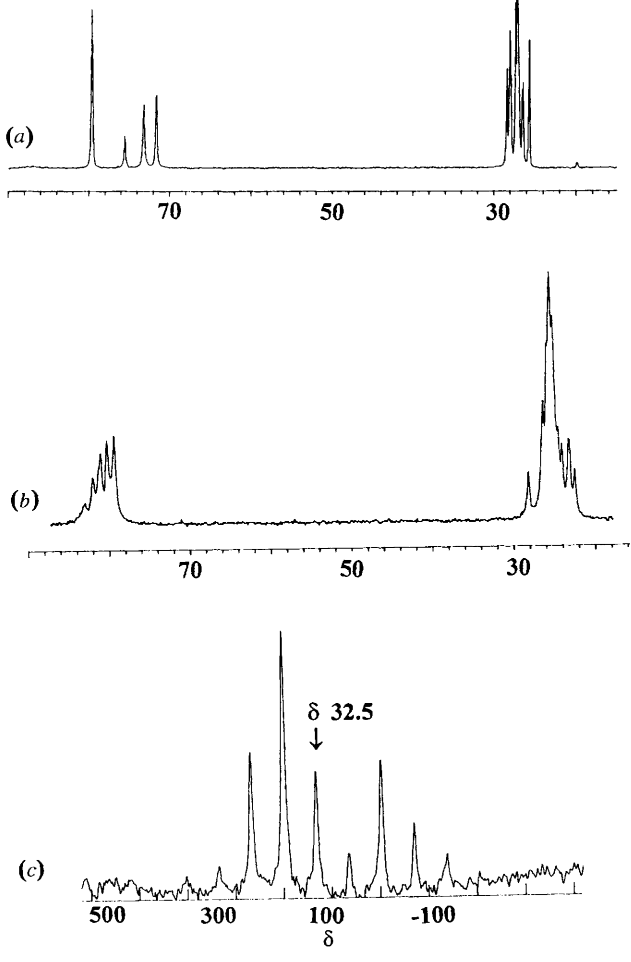

Fig. 1 Solid-state CP MAS ^{13}C NMR spectra of compounds **1**(*a*) and **2**(*b*) and the ^{113}Cd CP MAS NMR spectrum of **1**(*c*). The arrow indicates the isotropic shift for ^{113}Cd

Complex **1** is closely related to the recently described $[CdI\{Zr_2(OPr^i)_9\}]$[2a] and $[CdI\{Ti_2(OPr^i)_9\}]$[2b] based on confacial bioctahedral $M_2(OR)_9$ units, which interact with the central metal Cd^{II} in all three cases in a similar tetradentate manner. Table 1 shows the effect of inherent differences in the size and electrophilic behaviour of the different metals on the corresponding bond lengths, angles and geometry around the metal(IV) centres in the $M_2(OR)_9$ units. The Sn–OPr^i distances in **1** show a similar gradation (M–μ_3-OPr^i > M–μ-OPr^i > M–O-Pr^i) to those observed for the Ti- and Zr-containing $M_2(OPr^i)_9$ units which indicates the stability of the $Sn_2(OPr^i)_9$ unit as recently shown for the complexes of Ti and Zr.[2] In alkoxide derivatives of early transition metals, *e.g.* Ti and Zr (Table 1), short M–O bonds are always accompanied by large M–O–C angles and are considered as structural evidence for an O→M π donation from the alkoxide ligands.[5–7] Interestingly, in compound **1** the terminal M–O–C angles are 128.8(9) and 124.9(8)° as expected for an alkoxide ligand not involved in π donation to the metal, however the μ-OPr^i distances are comparable with that reported for the zirconium analogue which displays almost linear Zr–O–C angles showing an effective oxygen-to-metal π donation. The acute bond angles and comparatively short bond lengths in the case of Sn^{IV} with no accessible d orbitals indicate that shortening of M–O bond lengths does not always correlate to the extent of $O_\pi \rightarrow M$ donation and linearisation of M–O–C bond angles is not necessarily evidence for multiple p_π–d_π bond order. In comparison to covalent tin(IV), the more electropositive titanium and zirconium are expected to be more ionic in their highest oxidation states and short terminal M–O bonds can result from a high degree of ionic interaction. Therefore when account is taken of the inherent size effect and ionic behaviour of 'Sn^{4+}' and Zr^{4+} ions, the comparable terminal M–OPr^i

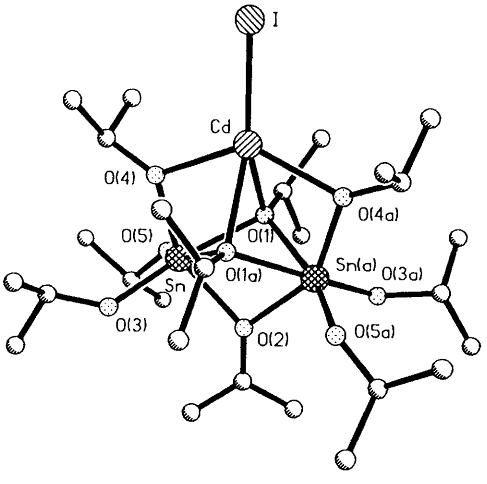

Fig. 2 Ball-and-stick drawing of the structure of $[CdI\{Sn_2(OPr^i)_9\}]$ **1**. Hydrogen atoms have been omitted for clarity

Table 1 Comparison of important crystallographic features (bond lengths in Å, angles in °) for a set of $M_2(OPr^i)_9^-$ (M = Sn, Zr or Ti) type tetradentate ligands in $[CdI\{M_2(OPr^i)_9\}]$ complexes

	M (ionic radius/Å)		
	Sn (0.71)	Zr (0.79)	Ti (0.68)
Crystal symmetry	Pseudo-C_{2v}	Pseudo-C_{2v}	C_s
Cd–I	2.642(4)	2.637(4)	2.619(6)
Cd–μ-OPr^i	2.297(8)	2.324(5)	2.342(7)
Cd–μ$_3$-OPr^i	2.370(7)	2.335(4)	2.280(5)
M–OPr^i	1.958(9)–1.972(9)	1.908(4)–1.920(5)	1.777(5)–1.779(5)
M–μ-OPr^i	2.048(8)–2.145(8)	2.052(5)–2.185(5)	2.040(7)–2.046(6)
M–μ$_3$-OPr^i	2.198(8)	2.262(4)–2.299(4)	2.158(5)–2.169(5)
Bite angle at Cd formed by			
(*i*) two μ-OPr^i	134.5(4)	136.7(2)	132.1(2)
(*ii*) two μ$_3$-OPr^i	63.1(3)	65.89(14)	65.6(2)
Pr^{i}O–Cd–I	112.8(2)–148.4(2)	110.47(14)–147.40(10)	112.5(2)–147.17(12)
M–O–C	124.9(8)–128.8(9)	169.9(7)–174.2(6)	160.4(7)–164.2(12)

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Sn–O(5)	1.958(9)	Sn–O(3)	1.972(9)
Sn–O(4)	2.048(8)	Sn–O(2)	2.145(8)
Sn–O(1)	2.189(7)	Sn–O(1a)	2.198(8)
Cd–O(1)	2.370(7)	Cd–O(4)	2.297(8)
Cd–O(1a)	2.370(7)	Cd–O(4a)	2.297(8)
O(1)–C(1)	1.457(14)	Cd–I	2.642(4)
O(3)–C(6)	1.419(13)	O(2)–C(4)	1.32(2)
O(5)–C(12)	1.41(2)	O(4)–C(9)	1.453(13)
O(5)–Sn–O(3)	103.6(4)	O(5)–Sn–O(4)	98.9(4)
O(3)–Sn–O(4)	104.7(4)	O(5)–Sn–O(2)	102.2(3)
O(3)–Sn–O(2)	95.4(3)	O(4)–Sn–O(2)	146.5(3)
O(5)–Sn–O(1)	90.7(3)	O(3)–Sn–O(1)	163.7(3)
O(4)–Sn–O(1)	80.4(3)	O(2)–Sn–O(1)	73.6(3)
O(5)–Sn–O(1′)	159.6(3)	O(1′)–Cd–O(1)	63.1(3)
O(4)–Sn–O(1′)	77.7(3)	O(4′)–Cd–I	112.8(2)
O(1)–Sn–O(1′)	68.9(3)	O(1)–Cd–I	148.4(2)
O(4)–Cd–O(1′)	69.7(3)	Sn′–O(1)–Cd	91.8(3)
O(4)–Cd–O(1)	71.8(3)	O(3)–Sn–O(1′)	96.7(3)
O(2)–Cd–O(1)	73.4(3)	O(4)–Cd–O(4′)	134.5(4)
Sn–O(1)–Sn′	93.5(3)	Sn–O(1)–Cd	92.0(3)
Sn–O(2)–Sn′	96.2(4)	Sn–O(4)–Cd	98.0(3)

distances in the tin and zirconium derivatives despite very different M–O–C angles can be ascribed to a high degree of covalent π bonding in the former and a high degree of ionic character in the latter case.

The comparable reaction (1:1) between SnI_2 and freshly prepared $K[Zr_2(OPr^i)_9]$ afforded $[SnI\{Zr_2(OPr^i)_9\}]$ **2** in almost quantitative yield. The average molecular complexity (η = 1.6) determined at two different concentrations indicate the existence of an equilibrium between mono- and di-meric species. This observation of intermolecular dynamics is further supported by the room-temperature ^{119}Sn NMR spectrum in benzene which exhibits two sharp resonances at δ 160.50 and 275.42 assignable to four- and five-co-ordinated tin(II) species.[11a] Further evidence was obtained from variable-temperature ^{119}Sn NMR studies. The high-temperature (+50 °C) spectrum showed a decrease in intensity of the peak (δ 275.42) assigned to the dimer while the resonance due to the monomeric species showed a relative increase. An opposite effect was observed on lowering (−57 °C) the temperature and the relative intensities of the resonances indicate a predominance of the dimeric species at low temperature. However, the ^{1}H and ^{13}C NMR spectra at ambient temperature (20 °C) exhibit averaged signals for the different isopropoxide groups present. Owing to the presence of a monomer–dimer equilibrium, the ^{1}H NMR spectra above −30 °C were sufficiently complex to preclude the assignment of resonances to any limiting structure. However at much lower temperatures the peaks due to the monomer vanished and a prevalence of the dimeric species was observed, the spectrum at −60 °C showing five broad doublets which integrate approximately as 2:3:2:3:8 and can be assigned to the dimeric species as observed in the solid-state structure. Compound **2** could be sublimed (140 °C, 10^{-3} mmHg) without decomposition as a yellow solid.

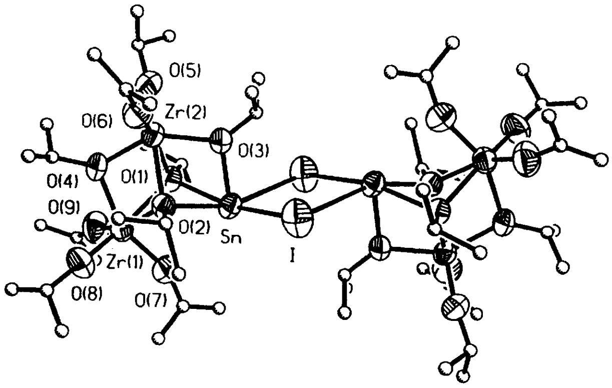

Fig. 3 An ORTEP[17] representation of the molecular structure of $[\{SnI[Zr_2(OPr^i)_9]\}_2]$ **2**, showing the atom labelling scheme

To gain more insight into the structural features of compound **2** a single crystal grown from a mixture of toluene–hexane was subjected to X-ray diffraction studies. Compound **2** crystallises in the monoclinic space group $P2_1/n$ with two molecules per unit cell which reside on centres of inversion (Fig. 3). The $Zr_2(OPr^i)_9$ unit interacts with Sn^{II} in a tridentate manner using two bridging and only one terminal OPr^i group which is different from the typical interaction of confacial bioctahedral $M_2(OR)_9$-type ligands. The ^{13}C CP MAS NMR spectrum [Fig. 1(*b*)] of **2** is consistent with the observed loss of symmetry within the bioctahedral $M_2(OR)_9$ framework due to its tridentate ligating mode and the total and relative intensities are consistent with the observed solid-state structure. This unusual ligating mode can be ascribed to the presence of a stereochemically active lone pair of electrons at Sn^{II} which inhibits the interaction of the oxygen on the terminal OPr^i groups of Zr(1) with tin. The presence of a stereochemically active lone pair on tin is indicated in the opening of the O(2)–Sn–I angle to 99.63(10)° (Table 3) along with an acute O(2)–Sn–O(3) angle, 74.3(2)°. The orientation of the isopropyl moiety at O(7) pointing away from tin in Fig. 3 further supports

Table 3 Selected interatomic distances (Å) and angles (°) in compound **2**

Sn–O(3)	2.196(4)	Sn–O(2)	2.367(4)
Sn–O(1)	2.404(4)	Zr(1)–O(9)	1.913(6)
Zr(1)–O(8)	1.948(6)	Zr(1)–O(7)	1.979(5)
Zr(1)–O(4)	2.246(5)	Zr(1)–O(1)	2.327(4)
Zr(1)–O(2)	2.333(4)	Zr(2)–O(6)	1.918(5)
Zr(2)–O(5)	1.933(5)	Zr(2)–O(4)	2.115(5)
Zr(2)–O(3)	2.130(4)	Zr(2)–O(1)	2.310(4)
Zr(2)–O(2)	2.337(4)	Sn–I′	3.3533(9)
Sn–I	3.2641(13)		
O(3)–Sn–O(2)	74.3(2)	O(6)–Zr(2)–O(5)	100.5(3)
O(2)–Sn–O(1)	62.66(14)	O(5)–Zr(2)–O(4)	102.4(2)
O(2)–Sn–I	99.63(10)	O(1)–Sn–I	155.38(10)
O(3)–Sn–I′	89.03(11)	O(2)–Sn–I′	159.91(10)
O(9)–Zr(1)–O(7)	101.8(3)	O(5)–Zr(2)–O(3)	99.9(2)
O(9)–Zr(1)–O(4)	95.7(2)	O(6)–Zr(2)–O(1)	161.6(2)
O(7)–Zr(1)–O(4)	153.6(2)	O(4)–Zr(2)–O(1)	74.1(2)
O(8)–Zr(1)–O(1)	160.0(2)	O(6)–Zr(2)–O(2)	97.0(2)
O(4)–Zr(1)–O(1)	71.5(2)	Zr(1)–O(1)–Sn	98.5(2)
O(8)–Zr(1)–O(2)	97.9(2)	Zr(2)–O(2)–Sn	91.39(13)
O(4)–Zr(1)–O(2)	71.8(2)	Zr(2)–O(4)–Zr(1)	102.0(2)
O(3)–Sn–O(1)	72.1(2)	O(9)–Zr(1)–O(8)	99.7(3)
O(8)–Zr(1)–O(7)	101.1(3)	O(8)–Zr(1)–O(4)	95.1(2)
O(9)–Zr(1)–O(1)	96.4(2)	O(7)–Zr(1)–O(1)	87.0(2)
O(9)–Zr(1)–O(2)	159.3(2)	O(7)–Zr(1)–O(2)	85.4(2)
O(1)–Zr(1)–O(2)	64.32(14)	O(6)–Zr(2)–O(4)	101.4(2)
O(6)–Zr(2)–O(3)	101.7(2)	O(4)–Zr(2)–O(3)	144.1(2)
O(5)–Zr(2)–O(1)	97.9(2)	O(3)–Zr(2)–O(1)	75.3(2)
O(5)–Zr(2)–O(2)	162.4(2)	O(3)–Zr(2)–O(2)	76.2(2)
Zr(2)–O(1)–Zr(1)	93.92(14)	Zr(2)–O(1)–Sn	91.12(14)
Zr(1)–O(2)–Sn	99.4(2)	Zr(2)–O(3)–Sn	102.2(2)
Sn–I–Sn′	89.52(2)	Sn′–I–I′	43.99(2)
Sn–I–I′	45.52(2)	I–Sn–I′	90.49(2)

the presence of a lone pair of electrons between the tin atom and the terminal OPr^i group on Zr(1). The only other example of tridentate co-ordination of a $Zr_2(OPr^i)_9$ moiety has been observed for the complex $Li[Zr_2(OPr^i)_9]$[18] and has been attributed to the smaller size of lithium which fails to span the distance between terminal OPr^i groups on two different Zr atoms and binds instead to one terminal and two bridging isopropoxo groups.

The geometry around each tin, when the presence of a stereochemically active lone pair of electrons is taken in account, can be described as distorted octahedral in which one of the axial sites is occupied by a pair of non-bonding electrons and the central $Sn_2I_2O_6$ unit can be visualised as a fusion of two SnI_2O_3 octahedra with one of the axial sites in each being occupied by the non-bonding electron pair of tin. Alternatively, each tin(II) adopts a distorted trigonal-bipyramidal geometry and the $Sn_2I_2O_6$ core in compound **2** can be visualised as two SnI_2O_3 trigonal bipyramids joined along a common edge. All Zr atoms are six-co-ordinate but deviate from regular octahedral geometry mainly due to the constraints of the $M_2(OR)_9$ framework. Nevertheless, the $Zr_2(OPr^i)_9$ unit is distorted from a confacial bioctahedron and the steric demands of the bridging μ-OPr^i groups of the $M_2(OR)_9$ unit is clearly reflected in the *trans* O–Zr–O angles at two Zr atoms [O(7)–Zr–O(4) 153.6 and O(3)–Zr(2)–O(4) 144.1°]. The Zr–O distances involving the triply (μ_3) bridging oxygens of the OPr^i groups are longer than those for doubly (μ) bridging oxygen which as expected are longer than the terminal Zr–O distances. The central $(Pr^iO)_2Sn_2I_2$ unit of the iodide-bridged dimer is comparable with the $M_2(OBu^t)_2X_2$ (X = Cl or I, M = Sn^{II} or Ge^{II}) compounds synthesised by Veith *et al.*[18] in which alkoxy groups are in bridging positions with halogens *trans* to them. In comparison to the bridging Sn–I distances [2.862(1) and 3.545(1) Å] observed in the four-membered Sn_2-(μ-I)$_2$ ring of $[Ge_2(OBu^t)_4Na]_2[Sn_2I_6]$,[19] the Sn–I [3.2641(13) Å] and Sn–I′ [3.3533(9) Å] distances in **2** indicate a relatively stronger and symmetric bridging which corroborate its thermal stability and observed dimeric form in the solid state.

The ^1H and ^{13}C NMR spectra of $[SnI\{Ti_2(OPr^i)_9\}]$ **3** are uninformative of the structural pattern existing in solution and indicate a rapid alkoxide site exchange at room temperature. Analogous to **2**, the ^{119}Sn NMR solution spectrum at room temperature gave two resonances at δ −111.45 and −191.58 which in view of the expected similarity in the ligating behaviour of $Zr_2(OPr^i)_9$ and $Ti_2(OPr^i)_9$ units can be ascribed to the presence of four- and five-co-ordinate tin(II) species, respectively which along with the observed molecular complexity of 1.5 conforms to the proposed monomer–dimer equilibrium in solution. On heating (110 °C, 10^{-3} mmHg) **3** decomposed leaving an appreciable residue and a colourless oil which was identified as $Ti(OPr^i)_4$ by elemental analysis and ^1H NMR spectroscopy.

The compounds $[PbI\{Zr_2(OPr^i)_9\}]$ **4** and $[PbI\{Ti_2(OPr^i)_9\}]$ **5** obtained by equimolar reaction of PbI_2 with $K[Zr_2(OPr^i)_9]$ and $K[Ti_2(OPr^i)_9]$ respectively represent the first examples of bimetallic alkoxide halides of lead(II). Complex **4** is stereochemically rigid at ambient temperature and shows in the ^1H NMR spectrum four types of *gem*-dimethyl protons in a 1:3:4:1 integration ratio whereas methine protons are observed as three overlapping septets which integrate approximately as 2:4:3. In contrast to **4**, complex **5** shows fluxional behaviour as indicated in the room-temperature ^1H and ^{13}C NMR spectra (see Experimental section). The ^{207}Pb NMR spectra observed for **4** and **5** gave only single resonances in agreement with the values reported for other heterobimetallic alkoxides of Pb with Ti and Zr.[20]

Experimental

All manipulations were performed under a dry and deoxygenated dinitrogen atmosphere. All hydrocarbon solvents were distilled under an inert atmosphere from sodium–benzophenone. Isopropyl alcohol was dried by distillation from magnesium turnings and aluminium triisopropoxide. The compound $Ti(OPr^i)_4$ (Aldrich) was purified by distillation; $[Sn(OPr^i)_4{\cdot}Pr^iOH]_2$[21] and $[Zr(OPr^i)_4{\cdot}Pr^iOH]_2$[10] were synthesised according to the literature. Metal iodides were dried by heating *in vacuo*. The NMR spectra were recorded on a Bruker AC-200 NMR spectrometer by using protio impurities of the deuteriated solvents as reference for ^1H and the ^{13}C resonance of the solvents as reference for ^{13}C. The ^{113}Cd NMR chemical shifts in solution and the solid state were referenced externally to a 0.1 mol dm^{-3} solution of $Cd(NO_3)_2$ in D_2O and solid $Cd(NO_3)_2{\cdot}4H_2O$, respectively. The ^{119}Sn and ^{207}Pb NMR chemical shifts, recorded with $SnMe_4$ and $Pb(NO_3)_2$ in D_2O as an external reference, are quoted using the downfield positive sign convention. The ^{13}C, ^{113}Cd and ^{119}Sn CP MAS NMR spectra were recorded on a Bruker MSL 200S spectrometer. Elemental analyses (C and H) were performed using a LECO CHN 900 Elemental Analyser. Standard analytical procedures[22] were employed to estimate metal and iodine contents in the complexes. Molecular weights were determined cryoscopically by the freezing-point depression of benzene.

Syntheses

$[CdI\{Sn_2(OPr^i)_9\}]$ 1. *Method 1.* A benzene (25 cm^3) solution of $K[Sn_2(OPr^i)_9]$ [obtained by treating potassium (0.15 g, 3.84 mmol) with $Sn(OPr^i)_4{\cdot}Pr^iOH$ (3.16 g, 7.61 mmol) in a mixture of isopropyl alcohol (5 cm^3) and benzene (20 cm^3) at 70 °C, followed by the removal of volatiles] was added to a suspension of CdI_2 (1.39 g, 3.80 mmol) in benzene (20 cm^3). After stirring the reaction mixture for ≈4 h at 50 °C the precipitated KI was filtered off. Removal of volatiles from the filtrate under reduced

Table 4 Crystal data and details of measurements for compounds **1** and **2** *

	1	**2**
Formula	$C_{27}H_{63}CdIO_9Sn_2$	$C_{54}H_{126}I_2O_{18}Sn_2Zr_4$
M	1008.45	1919.61
Space group	*C*2/*c*	*P*2$_1$/*n*
a/Å	15.22(2)	13.516(3)
b/Å	12.92(2)	16.916(3)
c/Å	24.45(5)	18.974(4)
β/°	103.66(14)	102.31(3)
U/Å^3	4672(13)	4238(2)
Z	4	2
F(000)	1992	1920
D_c/g cm^{-3}	1.434	1.504
Crystal size/mm	0.5 × 0.4 × 0.3	0.5 × 0.3 × 0.2
Diffractometer	Siemens Stoe AED 2	Stoe IPDS
Scan type	ω–θ	
Standard reflections	3	200 [$I > 6\sigma(I)$]
θ range/°	1.71–23.99	2.51–26.13
Reflections collected	4244	32 579
Independent reflections	3666	8216
Observed reflections [$I > 2\sigma(I)$]	2763	6545
Goodness of fit on F^2	1.119	1.089
Final *R* [$I > 2\sigma(I)$] (all data)	0.0576 0.0808	0.0636 0.0755

* Details in common: monoclinic; 293(2) K; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); programs SHELXL 93[24] and SHELXS 86.[25]

pressure yielded a sticky solid (2.92 g, 95%) which analysed to [CdI{$Sn_2(OPr^i)_9$}] **1**. The solid was redissolved in a mixture of toluene–hexane and the solution left to stand at −30 °C to yield large colourless crystals (37% isolated yield). Another 15% of the compound was recovered by recooling the concentrated mother-liquor (Found: C, 32.10; H, 6.30; Cd, 11.20; Sn, 23.45. Calc. for $C_{27}H_{63}CdIO_9Sn_2$: C, 32.15; H, 6.25; Cd, 11.15; Sn, 23.55%). NMR: ^{1}H ($C_6D_5CD_3$, −65 °C), δ 4.77, 4.60, 4.44 (spt, CH, *J* 6, 4:1:4, 9 H); 1.72, 1.60, 1.54, 1.36 (d, CH_3, *J* 6 Hz, 2:2:1:4, 54 H); ^{13}C-{^{1}H}, δ 71.61, 70.24, 69.94, 67.76, 67.23 (CH); 27.59, 27.14, 26.88, 26.75, 26.50, 26.13, 24.83 (CH_3); ^{13}C CP MAS, δ 72.33, 71.56, 70.39, 69.54, 68.67, 68.15, 66.72, 64.63 (CH); 28.52, 27.50, 26.64, 25.36, 24.72 (CH_3).

Method 2. In a direct synthesis, complex **1** was also obtained by the equimolar reaction of CdI_2 and a fresh sample of K[$Sn_2(OPr^i)_9$] prepared from the reaction of $SnCl_4$ and KOPr^i in 2:9 molar ratio in benzene at 0 °C. The synthesis of K[$Sn_2(OPr^i)_9$] is sensitive to the reaction conditions and addition of $SnCl_4$ to a cooled (0 °C) solution of KOPr^i must be carefully controlled otherwise it results in the formation of chlorine-containing products of different compositions.

[{SnI[$Zr_2(OPr^i)_9$]}$_2$] 2. To a pre-stirred suspension of SnI_2 (2.31 g, 6.20 mmol) in benzene (20 cm^3) was added freshly synthesised K[$Zr_2(OPr^i)_9$] (4.65 g, 6.18 mmol) {preparation using Zr(OPr^i)$_4$·Pr^{i}OH is analogous to that of K[$Sn_2(OPr^i)_9$]} in a benzene (25 cm^3) solution. The reaction mixture was stirred at room temperature for ≈6 h followed by stirring at 50 °C for ≈1 h. After the work-up a yellow solid was obtained which could be recrystallised (−8 °C) from toluene as yellow prismatic crystals **2** in 40% yield (Found: C, 33.35; H, 6.50; Zr, 19.00. Calc. for $C_{54}H_{126}I_2O_{18}Sn_2Zr_4$: C, 33.80; H, 6.60; Zr, 19.00%). NMR ($C_6D_5CD_3$, 20 °C): δ 4.54 (spt, CH, *J* 6 Hz, 18 H) and 1.33 (d, CH_3, *J* 6 Hz, 108 H); (−60 °C) δ 4.66, 4.48, 4.22 (spt, CH, 4:4:10, 18 H); 1.73, 1.49, 1.42, 1.32, 1.19 (d, CH_3, 2:3:2:3:8, 108 H). ^{13}C-{^{1}H}, δ 70.11 (CH) and 25.80 (CH_3). ^{13}C CP MAS, δ 73.90, 73.15, 72.33, 71.69, 70.99 (CH); 29.55, 26.23, 25.53, 24.95 (CH_3).

[{SnI[$Ti_2(OPr^i)_9$]}$_2$] 3. In a similar procedure to that described for complex **2**, a benzene solution of K[$Ti_2(OPr^i)_9$] [obtained by reaction (2:1) of Ti(OPr^i)$_4$ (4.81 g, 16.91 mmol) and KOPr^i (0.83 g, 8.44 mmol) in refluxing benzene] reacted with SnI_2 (3.14 g, 8.44 mmol) to give after work-up **3** in 97% yield which could be recrystallised from toluene as yellow flakes (Found: I, 14.35; Sn, 13.40; Ti, 10.85. Calc. for $C_{27}H_{63}IO_9SnTi_2$: I, 14.55; Sn, 13.60; Ti, 10.95%). NMR: (^{1}H C_6D_6, 20 °C), δ 4.63 (spt, CH, *J* 6, 9 H) and 1.25 (d, CH_3, *J* 6 Hz, 54 H); ^{13}C-{^{1}H}, δ 75.63 (CH) and 26.26 (CH_3); ^{119}Sn-{^{1}H}, δ −111.45 and −191.58.

[PbI{$Zr_2(OPr^i)_9$}] 4 and [PbI{$Ti_2(OPr^i)_9$}] 5. Analogous to the preparations of complexes **2** and **3**, the reaction of K[$Zr_2(OPr^i)_9$] or K[$Ti_2(OPr^i)_9$] with a pre-stirred (≈24 h) suspension of anhydrous PbI_2 in benzene gave compound **4** or **5** as waxy solids in 90 and 80% yield, respectively, which could be recrystallised from toluene–hexane (**4**) or toluene–isopropyl alcohol (**5**).

[PbI{$Zr_2(OPr^i)_9$}] (Found: I, 12.10; Pb, 19.80; Zr, 17.35. Calc. for $C_{27}H_{63}IO_9PbZr_2$: I, 12.10; Pb, 19.75; Zr, 17.40%): ^{1}H NMR (C_6D_6, 20 °C) δ 4.79, 4.59, 4.45 (spt, CH, *J* 6, 2:4:3, 9 H); 1.52, 1.42, 1.34, 1.24 (d, CH_3, *J* 6 Hz, 1:3:4:1, 54 H); ^{13}C-{^{1}H} δ 70.01, 67.66 (CH); 29.59, 26.50 (CH_3); ^{207}Pb-{^{1}H} δ 3626.79.

[PbI{$Ti_2(OPr^i)_9$}] (Found: I, 13.10; Pb, 21.70; Ti, 9.90. Calc. for $C_{27}H_{63}IO_9PbTi_2$: I, 13.20; Pb, 21.55; Ti, 9.95%): ^{1}H NMR (C_6D_6, 20 °C) δ 4.48 (spt, CH, *J* 6, 9 H) and 1.21 (d, CH_3, *J* 6 Hz, 54 H); ^{13}C-{^{1}H} δ 75.77 (CH) and 26.83 (CH_3); ^{207}Pb-{^{1}H} δ 2508.32.

X-Ray crystallography

A summary of the fundamental crystal data and data collection parameters is given in Table 4. The structures were solved by direct methods[24] and refined by full-matrix least squares on F^2. Corrections were applied to the data for decay during the collection and for non-uniform absorption of X-rays. All non-hydrogen atoms in compounds **1** and **2** were refined anisotropically; hydrogen atoms in **1** were geometrically fixed to the carbon atoms and were not included in idealized positions in **2**.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/61.

Conclusion

The reactions of confacial bioctahedral alkoxometalate units $M_2(OPr^i)_9^-$ ($M = Sn^{IV}, Zr^{IV}$ or Ti^{IV}) with bivalent metals are described. The present work has provided the first structural evidence for the existence of the $Sn_2(OPr^i)_9$ unit in the solid state and a convenient route to hitherto scarce tin(IV)-containing heterometallic alkoxides. Attempts made to synthesise heteroleptic alkoxides of lead by using $PbCl_2$ were unfruitful, which in view of the formation of the desired product with PbI_2 shows the importance of employing metal iodides in salt-elimination reactions. Complex **1** is an interesting precursor for obtaining novel tin(IV)-containing heterotermetallic alkoxides by the further metathesis of the Cd–I bond. In **2** the typical interaction of the $Zr_2(OPr^i)_9^-$ unit is inhibited due to the presence of the non-bonding electron pair at Sn^{II} which in view of the thermal stability of **2** shows the significance of multidentate alkoxometallate units in constituting molecular heterometallic alkoxide assemblies. A similar flexibility in the ligating behaviour of the $Zr_2(OPr^i)_9$ moiety has also been observed in $[Pb_2Zr_4(OPr^i)_{20}]$ where it binds to Pb using only one terminal and one bridging OPr^i group.[23]

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