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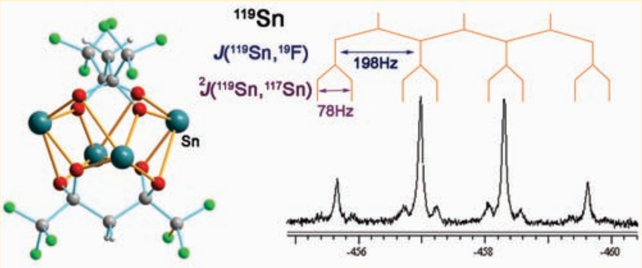
Homoleptic Tetranuclear Complexes of Divalent Tin and Lead Tetraolates

Zheng Wei, Jen-Hsien Yang, Volodimir D. Vreshch, Alexander V. Zabula, Alexander S. Filatov, and Evgeny V. Dikarev*

Department of Chemistry, University at Albany, SUNY, Albany, New York 12222, United States

S *Supporting Information*



ABSTRACT: Homoleptic tetranuclear complexes of divalent tin and lead tetraolates, $M_4(hfpt)_2$ [M = Sn (**1**) and Pb (**2**); $hfpt^{4-}$ is an anion of 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol], have been obtained in high yield from the corresponding (trimethylsilyl)amides. The solid-state structures of **1** and **2** contain discrete molecules in which a butterfly tetrahedron of metal atoms is sandwiched between two tetraolate ligands acting in tetradentate mode. The lone-pair Sn^{2+} and Pb^{2+} cations exhibit pyramidal coordination of four ligand oxygen atoms. A multinuclear NMR study unambiguously confirmed that metal tetraolates retain their polynuclear structure in solution of even coordinating solvents. An interesting example of the strong through-space coupling between ^{19}F of the tetraolate trifluoromethyl groups and $^{117/119}$Sn or ^{207}Pb nuclei was found. Both compounds were shown to have clean, low-temperature decomposition that results in crystalline oxides SnO_2 and PbO, respectively, for **1** and **2**. This work demonstrates the remarkable coordination properties of the tetraolate ligand that can be utilized for the preparation of a wide variety of poly- and heterometallic complexes. Decomposition studies revealed a great potential of metal tetraolate complexes as prospective molecular precursors for the soft chemistry approach to oxide materials.

INTRODUCTION

The interest in mixed-metal oxide materials has brought a great need for single-source precursors,[1] molecules that contain all of the necessary elements in the proper ratio and decompose in a controlled manner under mild conditions. The majority of single-source precursors known today are heterometallic and often heteroleptic alkoxides, carboxylates, and β-diketonates.[2] The search for new ligands[3] capable of bridging several metal atoms into a single molecule/cluster that has a clean, low-temperature decomposition pattern coupled with the ease of removing organic groups in the form of volatile nonreactive products represents an important direction in the development of single-source precursor chemistry.

Fluorinated bis(*gem*-diol), 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (H_4hfpt; Scheme 1B), has been initially detected[4] as a low-yield byproduct in the preparation of hexafluoroacetylacetone (Hhfac, **A**) and can be quantitatively obtained[5] by hydration of the latter. Deprotonation of tetraol in the presence of pyridine as a Lewis base that results in the corresponding tetraolate ($hfpt^{4-}$, **C**) was reported back in 1993.[5] The ligand was demonstrated to have interesting bridging properties in the complex $(pyH)_2[Mn_2(hfpt)(hfac)]$. Our group was working on thepreparation of metal tetraolate complexes using a variety of Lewis bases capable of taking the protons from tetraol. We have found that in most cases the presence of such bases results in the additional deprotonation of tetraolate, which, in turn, leads to an effective cleavage of two C−O bonds and the appearance of diketonate ($hfac^{-}$) and oxo ligands (Scheme 1, **C** → **D**). Therefore, it was proposed[6] to use tetraolate as a controlled source of both diketonate and oxo groups in the synthesis of metal oxodiketonates.

Despite the apparent difficulties in the preparation of metal tetraolates, we have recently managed[7] to isolate a heteroleptic bismuth(III) complex, $Bi_4(hfpt)_2(hfac)_4$, by a reaction that is virtually the reverse of **C** → **D** (Scheme 1). In this unusual tetranuclear molecule (Scheme 2A), two tetraolate ligands are bridging four bismuth atoms that also possess chelating diketonate ligands to maintain electroneutrality. The work on the bismuth complex revealed a great potential of tetraolate as a ligand in the preparation of polynuclear and heterometallic complexes and their application as single-source precursors for the synthesis of metal oxide materials. On the basis of the structure of $Bi^{III}{}_4(hfpt)_2(hfac)_4$, one can easily envisage a homoleptic neutral tetraolate complex, $M^{II}{}_4(hfpt)_2$ (Scheme 2B). While divalent transition metals in these types of molecules would likely require an additional coordination by donor solvents, the lone-pair Sn^{2+} and Pb^{2+} cations seem like ideal candidates for such a pyramidal coordination environment.

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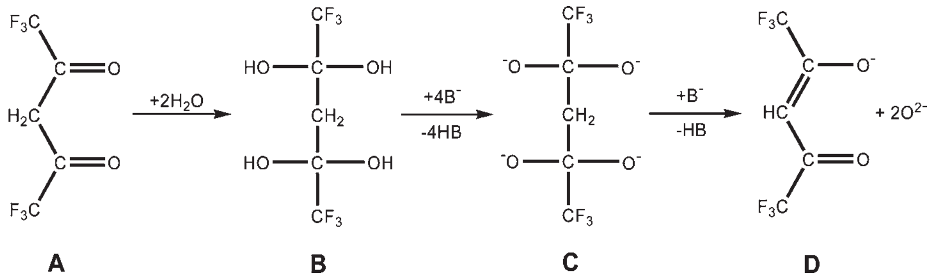
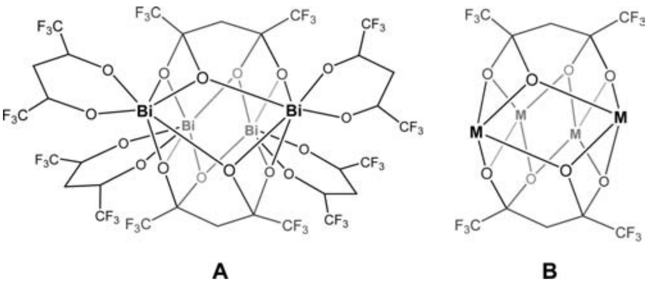
Scheme 1



Scheme 2



Herein we report the isolation and characterization of homoleptic polynuclear tetraolate complexes of divalent tin and lead.

RESULTS AND DISCUSSION

Synthesis and Properties. When describing the synthesis of a bismuth(III) tetraolate complex,[7] we noted the difficulties associated with retention of a deprotonated form of the ligand in solution. In an acidic medium, the ligand appears fully protonated and exists in equilibrium with a more reactive diketone, while moving to a basic solution results in the conversion of tetraol into oxo and diketonate species (Scheme 1). Taking these observations into account, we were looking for suitable starting materials having ligands that can assist in maintaining tetraolate species in solution.

The homoleptic tin(II) tetraolate $Sn_4(hfpt)_2$ (**1**) was initially obtained from the reaction between $Sn(OBu^t)_2$[8] and H_4hfpt in toluene or hexanes (eq 1). Despite a low yield (20%), the preparation of the tetraolate complex from *tert*-butoxide is important for future applications, taking into account the ubiquity of metal alkoxides, including heterometallic ones. Later on, an efficient synthetic route using tin(II) (trimethylsilyl)amide as a starting material (eq 2) was developed for near-quantitative isolation of tetraolate **1** in hexanes. The purity of the bulk product was confirmed by comparing the powder X-ray diffraction pattern for a bulk material with that calculated from single-crystal data (see the Supporting Information, Figure S1). The product was also characterized by elemental analysis, IR, and multinuclear NMR spectroscopy. Single crystals of compound **1** suitable for X-ray crystallographic studies can be instantly obtained by cooling its solution in hexanes.

Lead(II) tetraolate (**2**) was prepared by a procedure similar to that described by eq 2 but using chlorobenzene as a solvent. The purity of the bulk product that appeared to contain interstitial solvent molecules was confirmed by powder X-ray diffraction. Single crystals of $\mathbf{2}\cdot 0.5C_6H_5Cl$ can be grown by layering a chlorobenzene solution of **2** with hexanes at room temperature.

$$4Sn(OBu^t)_2 + 2H_4hfpt \rightarrow Sn_4(hfpt)_2 + 8Bu^tOH \qquad (1)$$

$$4Sn[N(SiMe_3)_2]_2 + 2H_4hfpt \rightarrow Sn_4(hfpt)_2 + 8HN(SiMe_3)_2 \qquad (2)$$

Tin(II) tetraolate **1** exhibits good solubility in both coordinating [tetrahydrofuran (THF), acetone, and acetonitrile] and noncoordinating (hexanes, benzene, chloroform, and dichloromethane) solvents. Analogous lead(II) complex **2** is soluble in coordinating and aromatic solvents, while its solubility in $CHCl_3$ and CH_2Cl_2 is very limited. Both compounds **1** and **2** are not volatile. Homoleptic tetraolates are stable in open air, as evidenced by the continuous re-collection of their powder X-ray diffraction patterns, and can be handled outside the glovebox. Interstitial chlorobenzene molecules can be readily removed from the structure of $\mathbf{2}\cdot 0.5C_6H_5Cl$ by keeping the sample overnight under a vacuum at 80 °C. The latter was confirmed by measuring the total weight loss and recording the ^{1}H NMR spectrum, which shows the absence of aromatic proton signals. The powder X-ray diffraction pattern indicates that **2** retains both its crystallinity and structural motif upon solvent removal (see the Supporting Information, Figures S11−S13).

Solid-State and Solution Structures. Single-crystal X-ray investigation revealed that the solid-state structures of both **1** and **2** contain tetranuclear molecules $M_4(hfpt)_2$, in which four metal

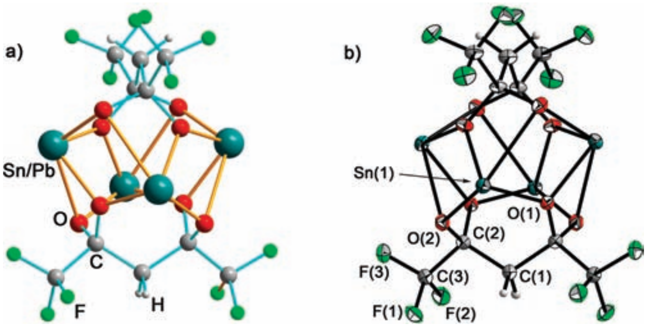


Figure 1. Molecular structure of $M_4(hfpt)_2$ [M = Sn (**1**) and Pb (**2**)]. (a) Ball-and-stick presentation. The bonds in the hfpt ligands are highlighted with different colors. (b) Perspective drawing of **1**. Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Only crystallographically independent atoms are labeled.

atoms are bridged by two tetradentate tetraolate ligands (Figure 1). The structure of **1** is highly symmetrical, with only one crystallographically independent tin atom. The symmetry of complex **2** is reduced by the presence of interstitial chlorobenzene molecules. There are two crystallographically independent $[Pb_4]$ molecules; however, each lead atom exhibits a geometry similar to that of tin. As we have previously observed in the case of the bismuth(III) tetraolate complex,[7] four metal atoms form a butterfly tetrahedron. Despite the differences in atomic radii, all hfpt-bridged tetrahedra have similar dimensions, with four short and two long M···M distances being respectively 3.72/4.97 (Sn), 3.82/5.21 (Pb), and 3.88/5.16 Å (Bi). Metal atoms in **1** and **2** exhibit a pyramidal coordination of four ligand oxygen atoms, as can be expected for the lone-pair Sn^{2+} and Pb^{2+} ions. Each oxygen atom links a pair of metal atoms with Sn−O distances of 2.13−2.75 Å (Table 1). The corresponding Pb−O interactions span an even more narrow range of 2.27−2.68 Å. The structure of **2** features some contacts between lead and carbon atoms of chlorobenzene (3.51−3.54 Å) that are shorter than the sum of the corresponding van der Waals radii (3.72 Å). The crystal structures of **1** and **2** demonstrate remarkable coordination properties of a tetraolate ligand that can hold four metal atoms together, forming a discrete molecule rather than a coordination polymer. Such coordination preferences can be broadly utilized in the formation of polynuclear and heterometallic complexes.

Table 1. Selected Bond Distances (Å) and Angles (deg) in the Structures of $M_4(hfpt)_2$ [M = Sn (1) and Pb (2)]

	M−O	O−M−O	M−O−M
$Sn_4(hfpt)_2$	2.13, 2.16, 2.20, 2.75	53.3−121.7	98.6, 117.0
$Pb_4(hfpt)_2$	2.27−2.68	53.6−113.8	102.6−111.7

In order to investigate the behavior of $Sn_4(hfpt)_2$ **1** and $Pb_4(hfpt)_2$ (**2**) in solution, we recorded their multinuclear NMR spectra in noncoordinating ($CDCl_3$), weakly coordinating (C_6D_6), and coordinating (THF-d_8) solvents. In all three solvents, ^1H and ^{19}F NMR spectra show almost identical chemical shifts of the hfpt resonances for **1**. The ^{13}C NMR spectrum for **1** revealed two sets of quartet resonances (**B**, OCO; **C**, CF_3) and one singlet peak (**A**, CH_2) that were assigned to three nonequivalent carbon atoms of the hfpt ligand (Figure 2a). Interestingly, the ^{19}F resonance signals in the NMR spectra of **1** and **2** appear as singlets with

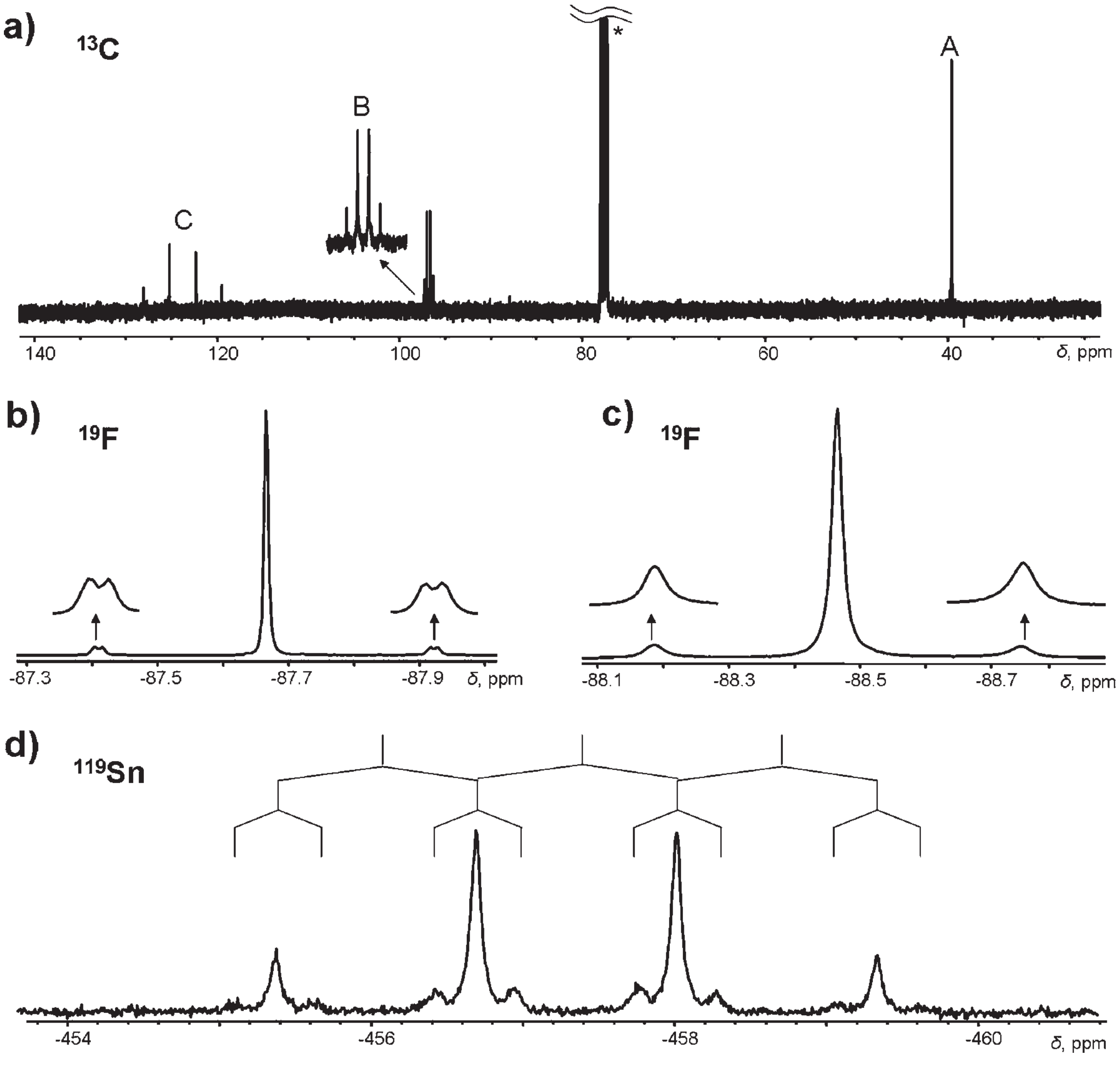


Figure 2. NMR spectra of **1** and **2** at room temperature: (a) ^{13}C NMR spectrum of **1** in $CDCl_3$ (*, solvent peak); (b) ^{19}F NMR spectrum of **1** in C_6D_6; (c) ^{19}F NMR spectrum of **2** in C_6D_6; (d) ^{119}Sn NMR spectrum of **1** in C_6D_6.

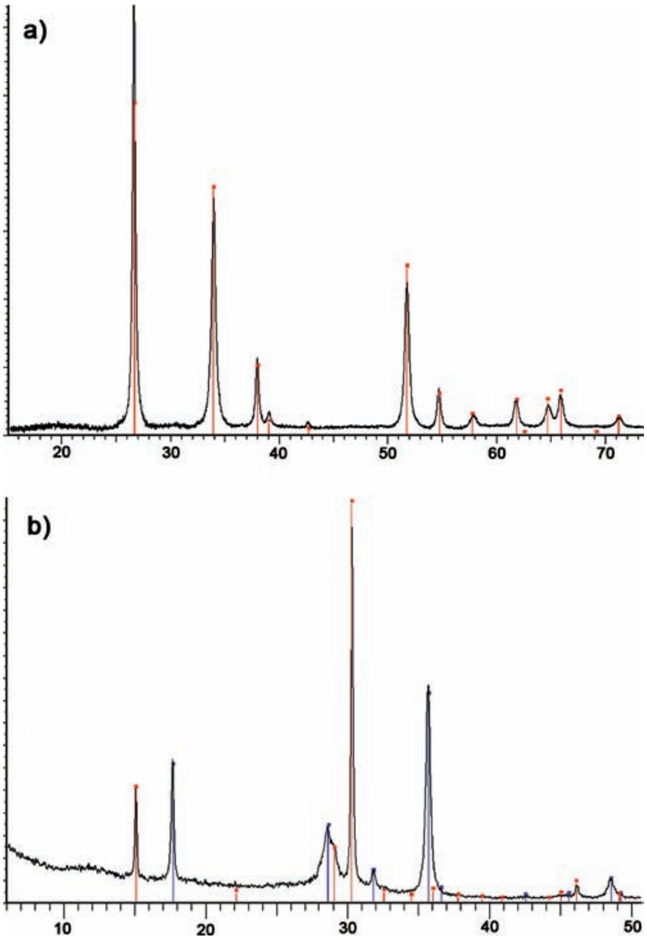


Figure 3. Phase identification of the samples obtained by thermal decomposition of $M_4(hfpt)_2$ [M = Sn (**1**) and Pb (**2**)]. The powder X-ray diffraction pattern (a) corresponds to SnO_2, which is shown as a peak diagram. Two modifications of lead monoxide in part b are highlighted with different colors.

several satellites owing to coupling with $^{117/119}Sn$ or ^{207}Pb nuclei, respectively (Figure 2b,c). The signal at $\delta = -87.7$ ppm in the ^{19}F NMR spectrum of **1** (C_6D_6) shows coupling constants between ^{19}F and ^{117}Sn or ^{119}Sn nuclei of 189 and 198 Hz, respectively. The lead analogue **2** exhibits only two satellites for the ^{19}F resonance signal ($\delta = -88.5$ ppm) with a related $J(^{19}F,^{207}Pb)$ coupling constant of 211 Hz. The relative intensities of the ^{19}F resonance signals and their satellites in the spectra of **1** and **2** correspond well with the natural abundances of $^{117/119}Sn$ (total 16%) and ^{207}Pb (22%) nuclei. Moreover, the ratio of $J(^{19}F,^{119}Sn)$ and $J(^{19}F,^{117}Sn)$ coupling constants, measured in all three solvents (av. 1.040), is in good agreement with the relative frequency ratios for the ^{119}Sn and ^{117}Sn nuclei (1.048). The strong F,Sn(Pb) coupling can be explained by taking into account through-space interactions between the fluorine atoms of the CF_3 group and the tin (lead) atoms. The interatomic F···Sn(Pb) separations in the solid-state structures of **1** (3.22 Å) and **2** (3.15−3.27 Å) are indicative of the proposed intramolecular interaction. The unhindered rotation of the CF_3 moiety about the C−CF_3 bond in solution makes all three fluorine atoms equivalent on the NMR time scale. It should be noted that such satellites were not observed in the ^{19}F NMR spectra of H_4hfpt or the tetranuclear Bi-hfpt complex. The ^{119}Sn NMR spectrum for **1** in benzene shows one signal at $\delta = -457$ ppm corresponding to the four-coordinated tin(II) atom (Figure 2d).[9] The splitting of the ^{119}Sn resonance into a quartet is attributed to coupling with the ^{19}F atom [$J(^{119}Sn,^{19}F) = 198$ Hz in C_6D_6]. The observation of identical long-range coupling[10] in THF-d_8 [$J(^{119}Sn,^{19}F) = 203$ Hz] indicates the persistence of the above-mentioned Sn···F interaction in the presence of even a coordinating solvent. The ^{119}Sn resonance peak in THF-d_8 is shifted to high field by 36 ppm compared to the resonance in weakly coordinating C_6D_6. Coordination of THF molecules to the divalent tin center explains the observed high-field shift of the tin resonance for **1** in THF compared to the low-field value found in benzene.[11] Observation of the $^2J(^{119}Sn,^{117}Sn)$ coupling constant (78 Hz in C_6D_6 and 73 Hz in THF-d_8) along with the presence of a single tin resonance in the ^{119}Sn NMR spectra is indicative of the Sn−O−Sn linkages between equivalent tin atoms.[12] Thus, the NMR data unambiguously confirm that **1** retains its polynuclear structure in solution.

Thermal Decomposition. Thermogravimetric analysis (TGA) of **1** revealed that decomposition of **1** in air proceeds in one step between 150 and 230 °C and results in pure tin(IV) oxide[13] (Figure 3a) with ca. 98% yield calculated based on the tin content. Thermal decomposition of **2** proceeds in two steps between 175 and 300 °C, with the mass loss in the initial step well exceeding the content of interstitial chlorobenzene. The decomposition residue in this case was found to contain two different forms of lead(II) oxide (Figure 3b). Clean, low-temperature decomposition of **1** and **2** is pointing to the suitability of metal tetraolate complexes as precursors for the synthesis of oxide materials. In particular, the thermal behavior of **1** coupled with its solubility in a variety of solvents can be utilized for the liquid-injection chemical vapor deposition preparation of thin films of SnO_2 that is well-known for applications in gas (NO_x, CO_x, HOR, and CH_4) sensing,[14] light-emitting diode (LED) devices,[15] and anodes of lithium-ion batteries.[16]

■ CONCLUSIONS

This work reveals interesting coordination properties of fluorinated tetraolate as a new ligand for the synthesis of polymetallic complexes. It has been found that metal alkoxides and amides are suitable starting materials for the formation of tetraolate compounds. The $M_4(hfpt)_2$ [M = Sn (**1**) and Pb (**2**)] complexes were shown to exhibit clean thermal decomposition, yielding pure crystalline metal oxides. These observations should help in the design of the future applications of this attractive tetraolate ligand for the preparation of a variety of homo- and heterometallic complexes that can be used as precursors in the low-temperature synthesis of oxide materials. One can envision a great variety of similar poly- and heterometallic tetraolate complexes of divalent and trivalent cations as well as of mixed-valent $M_2{}^{I}/M'_2{}^{III}$ combinations that can be obtained by the approach described upon careful selection of starting materials and solvents.

■ EXPERIMENTAL SECTION

General Procedures. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk-line and glovebox techniques. Bis(*gem*-diol), 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (H_4hfpt),[5] $Sn\{N(SiMe_3)_2\}_2$,[17] $Pb\{N(SiMe_3)_2\}_2$,[17] and $Sn(OBu^t)_2$[8] were prepared according to literature procedures. Hexafluoroacetylacetone (Hhfac), $Li\{N(SiMe_3)_2\}$, lead(II) chloride, and tin(II) chloride were purchased from Aldrich and used as

Table 2. Crystallographic Data and Structure Refinement Parameters for 1 and $2\cdot0.5C_6H_5Cl$

	1	$2\cdot0.5C_6H_5Cl$
formula	$Sn_4O_8C_{10}H_4F_{12}$	$Pb_4Cl_{0.5}O_8C_{13}H_{6.5}F_{12}$
fw	954.97	1365.17
cryst syst	tetragonal	monoclinic
space group	$I4_1/a$	$P2_1/n$
a (Å)	14.7107(14)	10.8813(6)
b (Å)	14.7107(14)	27.3449(16)
c (Å)	9.6386(17)	15.7652(9)
β (deg)		93.3870(10)
V (Å^3)	2085.8(5)	4682.7(5)
Z	4	8
ρ_{calcd} (g·cm^{-3})	3.041	3.873
μ (mm^{-1})	4.878	28.867
transm factors	0.3526−0.5484	0.0521−0.1604
temp (K)	173(2)	100(2)
data/restraints/param	1256/0/78	10973/0/676
R1,[a] wR2[b]		
$I > 2\sigma(I)$	0.0187, 0.0510	0.0299, 0.0670
all data	0.0197, 0.0520	0.0396, 0.0706
GOF[c]	1.046	1.030

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

received; Bu^{t}OH was purchased from Acros Organics and purified by distillation. The attenuated total reflectance (ATR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained using a Bruker Avance 400 spectrometer at 400 MHz for ^{1}H, 100.54 MHz for ^{13}C, 376.47 MHz for ^{19}F, and 149.12 MHz for ^{119}Sn. Chemical shifts (δ) are given in ppm relative to the residual solvent peaks for ^{1}H and ^{13}C, to the $CFCl_3$ peak for ^{19}F, and to the ^{119}Sn peak of the external standard $(CH_3)_4Sn$ (δ = 0.00 ppm). TGA measurements were carried out under nitrogen or air at a heating rate of 5 °C·min^{-1} using a TGA 2050 thermogravimetric analyzer (TA Instruments, Inc.). Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer (Cu Kα radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, 2θ step of 0.02°, 20 °C). The crystalline samples under investigation were grounded and placed in the domelike airtight holders inside a glovebox.

*$Sn_4(hfpt)_2$ (**1**).* An orange solution of $Sn\{N(SiMe_3)_2\}_2$ (3.15 g, 7.17 mmol) in 20 mL of hexanes was added dropwise to a suspension of H_4hfpt (0.96 g, 3.93 mmol) in 20 mL of hexanes. After stirring for 30 min, the reaction mixture was filtered and concentrated to about 2 mL, resulting in the precipitation of a white powder. The remaining solvent was removed by a cannula, and the white powder was washed three times with 5 mL of cold hexanes. The product was dried under a vacuum at room temperature for 2 h. The yield is ca. 82% (1.40 g). The purity of the bulk product has been confirmed by a comparison of the powder X-ray diffraction pattern with the theoretical one calculated on the basis of single-crystal data. Elem anal. Calcd for $Sn_4O_8C_{10}F_{12}H_4$: C, 12.58; F, 23.88; O, 13.40. Found: C, 12.74; F, 24.15; O, 13.21. ^{1}H NMR (C_6D_6, 22 °C): δ 1.97 (s). ^{1}H NMR (THF-d_8, 22 °C): δ 2.13 (s). ^{1}H NMR ($CDCl_3$, 22 °C): δ 2.20 (s). ^{13}C NMR (C_6D_6, 22 °C): δ 39.5 (s, CH_2), 96.4 [q, $^2J(^{13}C,^{19}F)$ = 32 Hz, OCO], 124.1 [q, $^1J(^{13}C,^{19}F)$ = 289 Hz, CF_3]. ^{13}C NMR (THF-d_8, 22 °C): δ 39.9 (s, CH_2), 96.4 [q, $^2J(^{13}C,^{19}F)$ = 31 Hz, OCO], 124.8 [q, $^1J(^{13}C,^{19}F)$ = 291 Hz, CF_3]. ^{13}C NMR ($CDCl_3$, 22 °C): δ 39.1 (s, CH_2), 96.4 [q, $^2J(^{13}C,^{19}F)$ = 32 Hz, OCO], 123.1 [q, $^1J(^{13}C,^{19}F)$ = 289 Hz, CF_3]. ^{19}F NMR (C_6D_6, 22 °C): δ −87.7 q[s, $J(^{19}F,^{117}Sn)$ = 189 Hz, $J(^{19}F,^{119}Sn)$ = 198 Hz]. ^{19}F NMR (THF-d_8, 22 °C): δ −88.3 [s, $J(^{19}F,^{117}Sn)$ = 196 Hz, $J(^{19}F,^{119}Sn)$ = 203 Hz]. ^{19}F NMR ($CDCl_3$, 22 °C): δ −88.4 [s, $J(^{19}F,^{117}Sn)$ = 188 Hz, $J(^{19}F,^{119}Sn)$ = 195 Hz]. ^{119}Sn NMR (C_6D_6, 22 °C): δ −457 [q, $J(^{119}Sn,^{19}F)$ = 198 Hz, $^2J(^{119}Sn,^{117}Sn)$ = 78 Hz]. ^{119}Sn NMR (THF-d_8, 22 °C): δ −493 [q, $J(^{119}Sn,^{19}F)$ = 203 Hz, $^2J(^{119}Sn,^{117}Sn)$ = 73 Hz]. ATR-IR (cm^{-1}): 3201w, 2160w, 1438m, 1407w, 1330w, 1272s, 1220w, 1171s, 1145s, 1111s, 1021s, 969s, 897s, 844m, 795m, 700s, 674s, 661s, 604m. Crystals of complex **1** suitable for X-ray crystallographic studies (Table 2) were obtained by keeping the hexanes solution at −30 °C for 3 days.

*$Pb_4(hfpt)_2$ (**2**).* A solution of $Pb\{N(SiMe_3)_2\}_2$ (3.20 g, 6.07 mmol) in 15 mL of chlorobenzene was added dropwise for 30 min to a suspension of H_4hfpt (0.89 g, 3.64 mmol) in 20 mL of chlorobenzene. After stirring for 1 h, the reaction mixture was filtered and 20 mL of cold hexanes was added to force product precipitation. The solvents were removed by a cannula, and the product was washed three times with 10 mL of cold hexanes and dried under a vacuum. The yield was ca. 87% (1.80 g). The powder X-ray diffraction pattern of the bulk product matched well with the one calculated from single-crystal data. ^{1}H NMR (C_6D_6, 22 °C): δ 1.52 (s). ^{1}H NMR (THF-d_8, 22 °C): δ 1.46 (s). ^{19}F NMR (C_6D_6, 22 °C): δ −88.5 [s, $J(^{19}F,^{207}Pb)$ = 211 Hz]. ^{19}F NMR (THF-d_8, 22 °C): δ −89.1 [s, $J(^{19}F,^{207}Pb)$ = 222 Hz]. ATR-IR (cm^{-1}): 2968w, 1434w, 1375w, 1310w, 1263s, 1134s, 1095s, 1003s, 975s, 873s, 834w, 794w, 736w, 695m, 676s, 636s. Crystals of this complex suitable for X-ray crystallographic studies (Table 2) were obtained by layering its solution in chlorobenzene with hexanes at room temperature for 3 days. The crystals grown in this way were shown to contain interstitial chlorobenzene molecules. The complete removal of C_6H_5Cl can be achieved by heating the product at 80 °C under a vacuum for 14 h.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full synthetic details, TGA plots and traces of thermal decomposition, IR and NMR spectra, powder X-ray diffraction patterns for **1** and **2**, additional details on interatomic distances and angles in the structures of **1** and **2**, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dikarev@albany.edu. Phone: (518)442-4401. Fax: (518)442-3462.

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