Structure/Volatility Correlation of Sodium and Zirconium Fluoroalkoxides

John A. Samuels, Kirsten Folting, John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405-4001

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The compounds $NaOR_f$ and $Zr(OR_f)_4$ ($R_f = CH(CF_3)_2$, $C(CF_3)_n(CH_3)_{3-n}$ with $n = 1-3$) have been studied in an attempt to establish a correlation between molecular weight, structure and volatility. The structure of $[NaOCCF_3(CH_3)_2]_4$ reveals a cubane form, with both intracube Na/F interactions and (even shorter) intercube Na/F interactions, the latter creating a polymeric structure. The structure of $[NaOC(CF_3)_3]_4$ is similar, but the greater steric bulk of the alkoxide prevents intercube Na/F interactions; all Na/F interactions are within a cube, and they are generally shorter than those in $[NaOCCF_3(CH_3)_2]_4$. Comparative volatilities, established using TGA, show the $[NaOR_f]_4$ species to have enhanced volatility as fluorine content increases. For $Zr(OR_f)_4$, all of which appear to be monomers, fluorination also increases volatility, but to a much smaller extent. It is suggested that intermolecular Na/F interactions in $[NaOR_f]_4$ do not decrease volatility because they can readily be replaced by intramolecular ones during volatilization. Crystal data for $[NaOCCF_3(CH_3)_2]_4$ at −168 °C: $a = 17.897(3)$Å with $Z = 8$ in space group $Pa\bar{3}$. For $[NaOC(CF_3)_3]_4$ at −172 °C: $a = 18.418(3)$Å with $Z = 8$ in space group $Pa\bar{3}$.

Introduction

Extensive research has been conducted on the modification of metal-organic species in order to make them more suitable as precursors to inorganic materials. Many of these modifications have been performed in the attempt to enhance precursor volatility, thus making them useful for chemical vapor deposition.[1] One method has been to incorporate partially or fully fluorinated ligands. This approach has been highly successful in increasing the volatility of many precursor species.[2] There are two rationales to account for the enhanced volatility of fluorinated species. One is that, with an increasing number of fluorines in the precursor (hence peripheral lone pairs), there is an *increasing* amount of intermolecular *repulsion*, causing enhanced volatility. A second is that the reduced polarizability of fluorine (as compared to hydrogen) causes fluorinated ligands to have *less* intermolecular *attractive* interactions.[3] To date there has been no systematic study of a series of fluorinated metal–organic species to study this question.

The situation is of course somewhat different for alkoxides vis-à-vis β-diketonates, due to the enhanced tendency of the former to serve as bridging ligands. Indeed, the following logic has been suggested to us recently by a reviewer of other work we submitted for publication: "the authors state that fluoro(alkoxide) derivatives are generally more volatile than their hydrocarbon analogs. Indeed this has been stated more than once in the alkoxide literature and is beginning to be accepted as fact. However, I believe the evidence for it in the form of careful comparative studies is actually quite weak. My incomplete analysis of this situation is as follows. The volatilities of β-diketonate complexes indeed increase upon fluorination, but that is thought to be due to the decrease in van der Waals interactions between monomers in the solid state (F is poorly polarizable, hence weak van der Waals interactions). However, alkoxides are more structurally complicated precursors in which volatilities are generally limited by molecularity rather than by intermolecular forces in the solid state. Fluorination should indeed decrease the basicity of alkoxide oxygen atoms and thereby their natural bridging tendencies. However, introduction of fluoroalkoxide ligands also increases the acidities of the metals to which they are attached, thereby increasing the desire of metal atoms for bridging ligands. It is not at all clear a priori which of these competing influences will dominate, and in the cases where we have made direct comparisons there are no significant differences between the volatilities of fluorinated and nonfluorinated compounds. By my model, differences should be expected for alkoxides that have naturally low molecularities (coordinative saturation without requiring bridging ligands)."

It is to this authoritative description of the current state of our knowledge/ignorance that the present paper is addressed. In this report, we examine a series of sodium and zirconium fluoroalkoxides with increasing degrees of ligand fluorination in order to observe the effects of this modification on structure and volatility. From the comparison of sodium and zirconium species, we find that the degree of volatility enhancement is not

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(1) (a) Schulz, D. L.; Hinds, B. J.; Stera, C. L.; Morris, T. J. *Inorg. Chem.* **1993**, *32*, 249. (b) Gross, M. E. *J. Electrochem. Soc.* **1991**, *138*, 2422. (c) Hubert-Pfalzgraf, L. G. *Appl. Organomet. Chem.* **1992**, *6*, 627.

(2) (a) Purdy, A. P.; Berry, A. D.; Holm, R. T.; Fatemi, M.; Gaskill, D. K. *Inorg. Chem.* **1989**, *28*, 2799. (b) Bradley, D. C.; Chudzynska, H.; Hammond, M. E.; Hursthouse, M. B.; Motevalli, M.; Ruowen, W. *Polyhedron* **1992**, *11*, 375. (c) Jefferies, P. M.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1992**, *31*, 4503.

(3) Reed, T. M., III In *Fluorine Chemistry*. Simons, J. H., Ed.; Academic Press: New York, 1964; Vol. 5, p 133.

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Table 1. Characterization Data

	sublimation temp (10^{-2} Torr)	NMR (ppm)	
		$^1H^a$	$^{19}F^b$
Na(HFIP) (**1a**)	80	4.12^c (sept, $^3J_{H-F} = 6.5$ Hz)	-83.4^c (d, $^3J_{H-F} = 6.5$ Hz)
Na(TFTB) (**1b**)	120	$1.05(5)^d$	$-85.9(5)^d$
Na(HFTB) (**1c**)	100	$1.41(5)^c$	$-85.1(5)^c$
Na(PFTB) (**1d**)	30		$-81.1(5)^c$
$Zr(HFIP)_4$ (**2a**)	70	4.79^c (br, sept, $^3J_{H-F} = 5.4$ Hz)	-77.3 (br,s)^c
$Zr(TFTB)_4$ (**2b**)	*e*	$1.25(5)^d$	$-84.9(5)^d$
$Zr(HFTB)_4$ (**2c**)	40	$1.54(5)^c$	$-82.9(5)^c$
$Zr(PFTB)_4$ (**2d**)	35		$-77.9(5)^c$

[a] Internal reference to residual protons in $C_6D_6 = 7.15$ ppm. J_{HF} in parentheses. [b] External reference F_3CCOOH (neat) = -78.45 ppm. [c] Solvent = C_6F_6. [d] Solvent = C_6D_6. [e] Liquid at room temperature; distilled at 60 °C and 10^{-2} Torr.

merely a function of the degree of ligand fluorination. In this study, we present evidence for a structural explanation for the observed volatility enhancement.

Experimental Section

General Techniques. All manipulations were carried out under dry nitrogen atmosphere using oven-dried glassware. Solvents were freshly distilled over Na/benzophenone. Reagents were purchased from Aldrich with the exception of fluorinated alcohols which were purchased from PCR. Tetraneopentylzirconium was prepared by literature methods.[4] Temperature of sublimation of bulk material was that which gave a convenient transport rate onto a water-cooled coldfinger. NMR spectra were recorded on a Nicolet NT-360 spectrometer (^{19}F and ^1H NMR at 340 and 361 MHz, respectively). Samples were run in C_6D_6 and C_6F_6 with external references when necessary ($^{19}F_3CCOOH$ (neat) = -78.45 ppm, ^1H residual protons in $C_6D_6 = 7.15$ ppm). Abbreviations: OR_f = general fluorinated alkoxide, HFIP = hexafluoroisopropoxide ($OCH(CF_3)_2$), TFTB = trifluoro-*tert*-butoxide ($OCMe_2(CF_3)$), HFTB = hexafluoro-*tert*-butoxide ($OCMe(CF_3)_2$), PFTB = perfluoro-*tert*-butoxide ($OC(CF_3)_3$). TGA studies were performed on a DuPont 2100 instrument with a heating rate of 5 °C/min under 70 cm^3/min flowing helium. *WARNING: There is a potential for the PFTB ligand to generate perfluoroisobutylene (a potent carcinogen) during thermolysis. The other fluorocarbon ligands will have lower, yet still significant, hazards upon thermolysis. Care must be exercised!*

$Na(OR_f)$ (1a−d). Sodium hydride (0.96 g, 40 mmol) was suspended in 60 mL of Et_2O. To this was added, dropwise, fluorinated alcohol (38 mmol). After gas evolution had ceased, the reaction mixture was stirred for an additional 30 min, filtered, and the solvent was removed from the filtrate in vacuo. The resulting oily colorless solid was sublimed giving colorless crystals (Table 1); typical yield 90%.

$Zr(OR_f)_4$ (2a−d). $Zr(neopentyl)_4$ (0.50 g, 1.33 mmol was dissolved in 30 mL of toluene at 0 °C. To this was added dropwise 5.55 mmol of fluorinated alcohol via syringe. The reaction mixture was allowed to come to room temperature and stir for 30 min, during which time colorless solid precipitated (a colorless solution resulted for **2b**). The solution was warmed to dissolve the solid and then allowed to return to room temperature to precipitate colorless solid. The solvent was removed in vacuo, and the resulting white solid was sublimed producing colorless crystals for solid products or distilled under nitrogen for liquids (Table 1); typical yield 80%.

X-ray Structure Determination of $[NaOCMe_2(CF_3)]_4$ (1b). A suitable single crystal grown via sublimation in a sealed ampule, was selected using inert-atmosphere handling techniques. The crystal was transferred to the goniostat where it was cooled to -168 °C for characterization and data collection ($6° < 2\theta < 45°$).[5] A systematic search of selected regions of reciprocal space yielded a set of reflections which exhibited cubic $m3$ diffraction symmetry. The systematic extinction of $0kl$ for $k = 2n + 1$, ($h0l$ for $l = 2n+1$ and of $hk0$ for $h = 2n + 1$) uniquely identified the space group as $Pa\overline{3}$ (No. 205). The choice of this space group was confirmed by the solution and refinement of the structure. Plots of the four standard reflections showed no signficant trends. No absorption correction was carried out. The structure was solved using SHELXS-86. Following initial refinement, the hydrogen atoms on the ordered methyl groups (see below) were located. The full matrix, least-squares refinement was completed using anisotropic thermal parameters on the non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The Na_4 cube is situated on a 3-fold axis (position c in the International Tables), Na(1) is in a general position and Na(2) and O(4) as well as C(12) are on the symmetry axis. As a consequence of the molecular symmetry, the $C(CF_3)(CH_3)_2$ on O(4) is disordered. The disordered atoms are F(14), F(15), and F(16). It was not possible to locate the partial hydrogen atoms. The final difference map was essentially featureless, the largest peak being 0.209 and the deepest hole being -0.195 e/Å^3. Results of the structure determination are shown in Tables 2−4 and Figures 1 and 2.

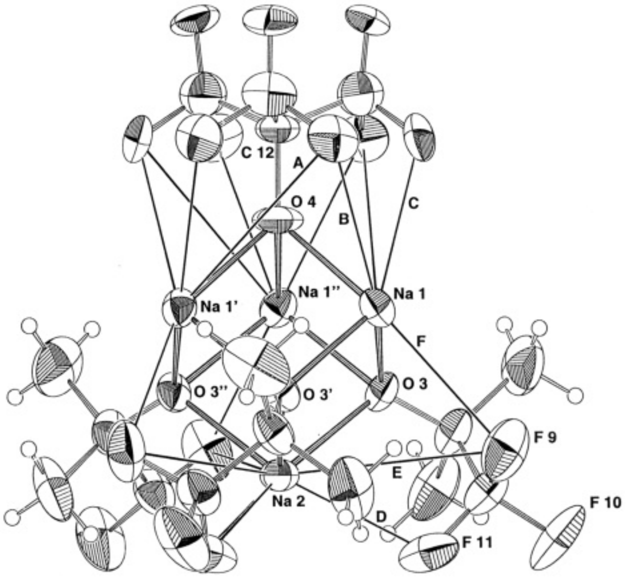

Figure 1. ORTEP drawing of $[Na(TFTB)]_4$ (**1b**), showing selected atom labeling. The three possible positions of the disordered $O(4)C(CH_3)_2(CF_3)$ group are shown. Distances A−F correspond to those in Table 4.

X-ray Structure Determination of $[NaOC(CF_3)_3]_4$ (1d). This was wholly analogous to the structure determination of

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[4] Davidson, P. J.; Lappert, M. F.; Pearce, R. *J. Organomet. Chem.* **1973**, *57*, 269.

[5] For a general description of diffractometer and programs, see: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table 2[a,b]

chemical formula	$C_{16}H_{24}F_{12}Na_4O_4$	space group	$Pa\bar{3}$ (No. 205)
a, Å	17.897(3) Å	T, °C	−168 °C
V, Å^3	5732.48	λ, Å	0.710 69
Z	8	ϱ_{calcd}, g cm^{-3}	1.391
formula weight	600.30	μ(Mo Kα), cm^{-1}	1.89
		R	0.0360
		R_w	0.0378
chemical formula	$C_{16}F_{36}O_4Na_4$	space group	$Pa\bar{3}$ (No. 205)
a, Å	18.418(3)Å	T, °C	−172 °C
V, Å^3	6244.78	λ, Å	0.71069
Z	8	ϱ_{calcd}, g cm^{-3}	1.097
formula weight	1032.08	μ(Mo Kα), cm^{-1}	1.626
		R	0.0266
		R_w	0.0259

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

1b, and, at −173 °C, was isomorphous ($Pa\bar{3}$). The final difference Fourier map was essentially featureless, the largest peak being 0.84 e/Å^3. The results are shown in Tables 2, 5, and 6 and Figure 3.

Results

Na(OR$_f$) (1a–d). *(a) Synthesis and Characterization.* The synthesis of the homometallic sodium fluoroalkoxides Na(OR$_f$) (OR$_f$ = HFIP (hexafluoroisopropoxide) (**1a**),[6a] TFTB (trifluorotertbutoxide) (**1b**), HFTB (hexafluoro-*tert*-butoxide) (**1c**), PFTB (perfluoro-*tert*-butoxide) (**1d**)[6b]) used the technique of H–OR$_f$ deprotonation with sodium hydride in diethyl ether (eq 1).[7] Removal of solvent and subsequent sublimation produced **1a–d** as colorless crystals.

$$NaH + H{-}OR_f \xrightarrow{Et_2O} Na(OR_f) + H_2 \quad (1)$$

1a: NaHFIP, $OCH(CF_3)_2$
1b: NaTFTB, $OCMe_2CF_3$
1c: NaHFTB, $OCMe(CF_3)_2$
1d: NaPFTB, $OC(CF_3)_3$

The compounds are soluble in ethers and hexafluorobenzene but have low solubility in aromatic solvents. The volatility of the NaOR$_f$ compounds is greater than their hydrocarbon analogues for both the isopropoxy and *tert*-butoxy derivatives. Sublimation temperatures (10^{-2} mmHg) range from 120 °C for Na(TFTB) to 30 °C for Na(PFTB). $NaOCH(CH_3)_2$ and $NaOC(CH_3)_3$ sublime, with some decomposition, at 190 and 140 °C, respectively, at 10^{-2} mmHg.[8]

The ^{19}F and ^1H NMR spectral data for **1a-d** in either C_6F_6 or benzene-d_6 are shown in Table 1. In each case, a single chemical shift is observed in the ^{19}F and in the ^1H NMR spectrum. This spectroscopic information indicates that the fluoroalkoxides are equivalent on the NMR time scale but fails to establish their degree of aggregation. It was shown previously[7] that Na(HFIP) is tetrameric (cubane) in the solid state. To determine the degree of oligomerization of the fluorinated *tert*-butoxy species, single-crystal X-ray diffraction studies were performed on Na(TFTB) and Na(PFTB). [Na(O^t-Bu)]$_n$ has been shown to be a mixture of hexamers and nonamers in the solid state.[9]

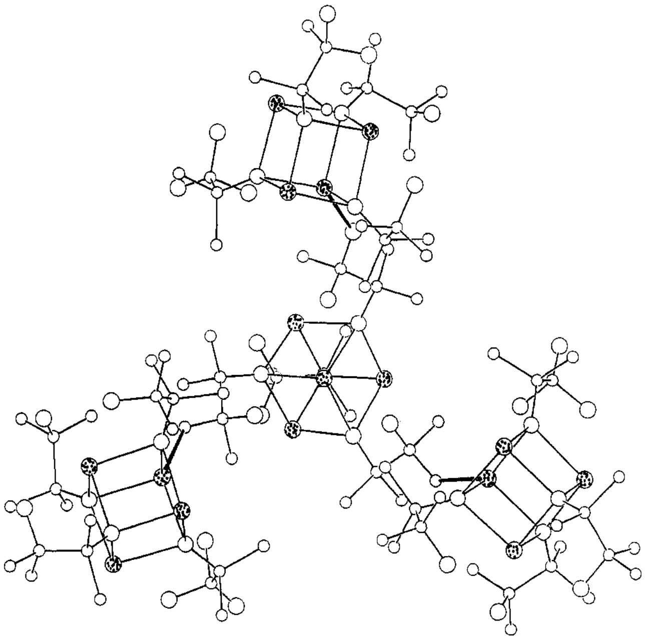

Figure 2. Ball-and-stick drawing of $[Na(TFTB)]_4$ (**1b**) showing polymeric nature of the system. View is of four tetrameric units and is down the crystallographic C_3 axis. Broad solid lines are intermolecular contacts between Na(1) and F(10). Stippled atoms are sodium.

Table 3. Fractional Coordinates[a,b] **and Isotropic Thermal Parameters**[c] **for $[NaOC(CF_3)(CH_3)_2]_4$**

atom	x	y	z	$10B_{iso}$
Na(1)	1047(1)	6895(1)	7532(1)	28
Na(2)	2625(1)	7625*	7375*	28
O(3)	2138(1)	6511(1)	6993(1)	27
O(4)	1372(1)	6372*	8628*	41
C(5)	2217(2)	61289(2)	6259(2)	34
C(6)	1974(2)	6944(2)	5791(2)	39
C(7)	1713(3)	5631(3)	6071(2)	64
C(8)	3028(3)	6112(3)	6062(2)	56
F(9)	1268(1)	7163(1)	5915(1)	53
F(10)	2022(1)	6828(1)	5042(1)	66
F(11)	2391(1)	7558(1)	5923(1)	51
C(12)	925(1)	5925*	9075*	32
C(13)	626(2)	5266(2)	8619(2)	46
F(14)	261(3)	4848(3)	8927(3)	40
F(15)	312(3)	5623(3)	8026(3)	43
F(16)	1266(3)	4984(2)	8327(3)	43
H(1)	117(2)	573(2)	618(2)	52(9)
H(2)	175(2)	551(2)	553(2)	63(8)
H(3)	183(3)	520(3)	637(3)	95(10)
H(4)	314(2)	571(2)	637(2)	61(8)
H(5)	309(2)	598(2)	558(2)	50(7)
H(6)	335(3)	657(3)	619(3)	100(10)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] Parameters marked by an asterisk were not varied. [c] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

(b) Solid-State Structures. Single-crystal, X-ray diffraction studies were performed on Na(TFTB) (**1b**) and Na(PFTB) (**1d**) in order to determine the degree of oligomerization and the effect of differences in fluorination on the molecular structure. Both samples were grown via slow sublimation in a temperature gradient

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(6) (a) Koetzsch, H. *Chem. Ber.* **1966**, *99*, 1143. (b) Dear, R. E. A.; Fox, W. B.; Fredericks, R. J.; Gilbert, E. E.; Huggins, D. K. *Inorg. Chem.* **1970**, *9*, 2590.

(7) Samuels, J. A.; Lobkovsky, E. B.; Streib, W. E.; Folting, K.; Huffman, J. C.; Zwanziger, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5093.

(8) Naiini, A. A., private communication. See also: Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 337.

(9) Weiss, E.; Greisler, T. *Chem. Ber.* **1977**, *110*, 3388.

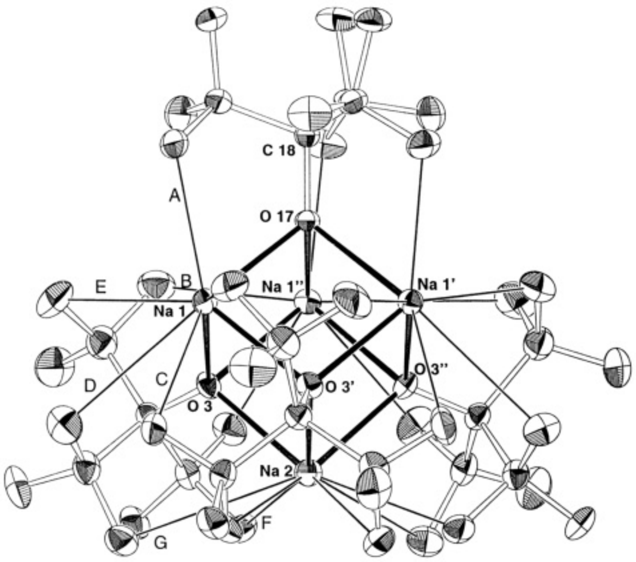

Figure 3. ORTEP drawing of [Na(PFTB)]$_4$ (**1d**), showing selected atom labeling. Distances A–G correspond to those in Table 6.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [NaOC(CF$_3$)(CH$_3$)$_2$]$_4$

Na(1)	O(3)′	2.2357(20)
Na(1)	O(3)	2.2836(21)
Na(1)	O(4)	2.2506(21)
Na(2)	O(3)	2.2798(20)
F(9)	C(6)	1.341(4)
F(10)	C(6)	1.361(3)
F(11)	C(6)	1.349(4)
F(14)	C(13)	1.137(5)
F(15)	C(13)	1.360(6)
F(16)	C(13)	1.356(6)
O(3)	C(5)	1.379(3)
O(4)	C(12)	1.384(5)
Na(1)′	F(16)	3.726(5)A
Na(1)	F(16)	2.899(5)B
Na(1)	F(15)	2.774(5)C
Na(2)	F(11)	2.635(5)D
Na(2)	F(9)	3.662(5)E
Na(1)	F(9)	2.960(5)F
Na(1)	F(11)	3.637(5)[a]
Na(1)	F(10)	2.332(5)[a]
Na(1)	F(9)	3.746(5)[a]

O(3)A	Na(1)	O(3)	93.55(10)
O(3)	Na(1)	O(4)	91.30(7)
O(3)A	Na(1)	O(4)	92.56(7)
O(3)A	Na(2)	O(3)	92.48(7)
Na(1)	O(3)′	Na(1)′	87.78(8)
Na(1)	O(3)	Na(2)	86.37(7)
Na(1)	O(3)′	Na(2)	87.51(7)
Na(1)	O(3)	C(5)	125.28(17)
Na(1)	O(3)′	C(5)′	135.42(16)
Na(2)	O(3)	C(5)	119.94(17)
Na(1)	O(4)	Na(1)′	88.23(10)
Na(1)	O(4)	C(12)	126.50(7)

[a] Intermolecular contacts.

in sealed ampoules, producing colorless prismatic plates. The two compounds are crystallographically isomorphous.

1b is tetrameric (Figure 1 and Table 4) with a distorted cubane configuration. A crystallographic C_3 axis contains C(12), O(4), and Na(2). As a result, three sodiums (Na(1), Na(1)′, Na(1)″) and three fluoroalkoxides (O(3), O(3)′, O(3)″) are equivalent by symmetry.

Table 5. Fractional Coordinates[a,b] and Isotropic Thermal Parameters[c] for [NaOC(CF$_3$)$_3$]$_4$

atom	x	y	z	$10B_{\mathrm{iso}}$
Na(1)	987(1)	6869(1)	7534(1)	14
Na(2)	2618(1)	7618*	7382*	16
O(3)	1520(1)	7936(1)	7891(1)	14
C(4)	1278(2)	8624(2)	7881(2)	15
C(5)	1603(2)	5617(2)	6288(2)	22
F(6)	965(1)	5755(1)	6622(1)	26
F(7)	1875(1)	5029(1)	6605(1)	32
F(8)	1447(1)	5452(1)	5601(1)	33
C(9)	1047(2)	8846(2)	7101(2)	20
F(10)	1632(1)	8911(1)	6676(1)	23
F(11)	628(1)	8335(1)	6804(1)	26
F(12)	684(1)	9470(1)	7072(1)	28
C(13)	1861(2)	6894(2)	5871(2)	16
F(14)	−158(1)	6972(1)	6785(1)	21
F(15)	1154(1)	7020(1)	5959(1)	23
F(16)	2200(1)	7519(1)	6036(1)	20
O(17)	1382(1)	6382*	8618*	12
C(18)	961(2)	5961*	9039*	13
C(19)	151(2)	6162(2)	8940(2)	18
F(20)	−317(1)	5678(1)	9198(1)	25
F(21)	5(1)	6240(1)	8226(1)	26
F(22)	1(1)	6800(1)	9243(1)	28

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] Parameters marked by an asteristk were not varied. [c] Isotropic values for those atoms refine anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

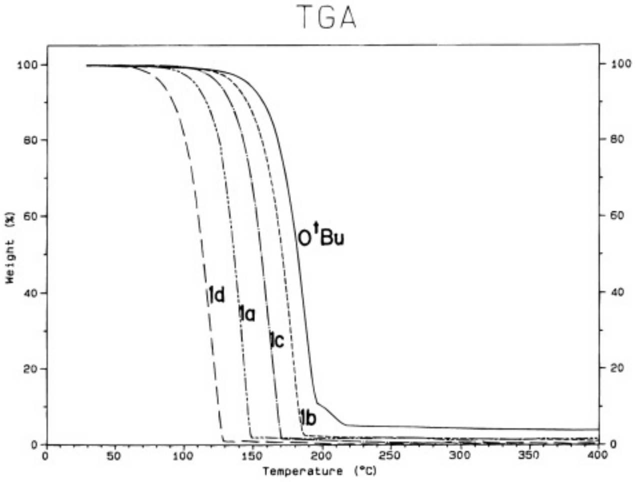

Figure 4. Thermogravimetry of [NaO^{t}Bu]$_6$; [NaTFTB]$_4$, **1b**; [NaHFTB]$_4$, **1c**; [NaHFIP]$_4$, **1a**; [NaPFTB]$_4$, **1d**.

Metal–oxygen distances within the cube range from 2.236(2)–2.284(2) Å. This is comparable to those previously observed in [Na(HFIP)]$_4$ (2.298 Å average)[7] and [Na(O^{t}Bu)]$_6$ (2.239 Å average).[9] Each sodium coordination sphere consists of three oxygens in a trigonal pyramidal geometry. The coordination number of the metal center is augmented by metal–fluorine contacts less than the sum of the Na and F van der Waals radii. To Na(1), four intramolecular Na–F contacts are observed, ranging from 2.774(5) to 3.726(5) Å. For Na(2), two intramolecular contacts occur from each adjacent fluoroalkoxide, giving six contacts in all (3 × 2.635(5) Å and 3 × 3.662(5) Å). There are also three intermolecular Na–F contacts to each Na(1) from F(9), F(11) and F(10) of a neighboring molecule. The former two are at distances of 3.746(5) and 3.637(5) Å, while the latter, 2.332(5) Å, is well within the combined ionic radii for Na$^+$ (eight-coordinate) and F$^-$ (two-coordinate) (1.15 and 1.32 Å, respectively).[10] This would indicate significant interactions between adjacent molecules producing

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(10) Huheey, J. E. *Inorganic Chemistry*, 3rd ed., Harper and Row: New York, 1983, Chapter 5, p 15.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[NaOC(CF_3)_3]_4$

Na(1)	O(3)		2.2918(23)
Na(1)	O(3)′		2.3315(24)
Na(1)	O(17)		2.3064(22)
Na(2)	O(3)		2.3058(24)
F(6)	C(5)		1.350(4)
F(7)	C(5)		1.327(4)
F(8)	C(5)		1.333(4)
F(10)	C(9)		1.338(4)
F(11)	C(9)		1.334(4)
F(12)	C(9)		1.331(4)
F(14)	C(13)		1.343(3)
F(15)	C(13)		1.332(3)
F(16)	C(13)		1.345(3)
F(20)	C(19)		1.328(4)
F(21)	C(19)		1.350(4)
F(22)	C(19)		1.329(4)
O(3)	C(4)		1.344(3)
O(17)	C(18)		1.341(6)
Na(1)	F(21)		2.497(4)A
Na(1)	F(6)		2.653(4)B
Na(1)	F(15)		2.930(4)C
Na(1)	F(11)		3.088(4)D
Na(1)	F(7)		3.492(4)E
Na(1)	F(22)		3.635(4)
Na(1)′	F(22)		3.677(4)
Na(1)	F(16)		3.747(4)
Na(2)	F(16)		2.601(4)F
Na(2)	F(10)		3.265(4)G
O(3)′	Na(1)	O(3)	87.90(11)
O(3)	Na(1)	O(17)	86.23(8)
O(3)′	Na(1)	O(17)	87.16(8)
O(3)′	Na(2)	O(3)	88.19(9)

a three-dimensional polymer (Figure 2). Such Na-F contacts have been observed previously in $[Na(HFIP)]_4$[7] and $Na_2Cu(HFIP)_4$[11] but not at such short distances. It is interesting to note that there is no lengthening of the C(6)−F(10) bond, consistent with the idea that the metal−fluorine interactions are primarily electrostatic in nature. Further evidence of this conclusion is that the sodium center with the most and the shortest Na−F contacts (Na(1)) does *not* have lengthened Na−O distances (2.257 Å average) compared to the other sodium site (2.280 Å).

The structure of **1d** (Figure 3 and Table 6) is very similar to that of **1b**, with the molecule being tetrameric in a distorted cubane geometry. The C_3 axis is defined by C(18), O(17), and Na(2). There is a systematic difference between **1b** and **1d** in that all angles O−Na−O in **1b** are larger than 90° (by 1.3−3.6°), while in **1d** they are less than 90° (by 1.8−3.8°). Thus, the $OC(CF_3)_3$ ligand causes a greater flattening of the NaO_3 coordination geometry. The sodium−oxygen distances average 2.309(2) Å, slightly longer than that observed (2.262 Å) in **1b** and other sodium alkoxide species (see above). This lengthening can be due to the greater steric bulk of the perfluoro-*tert*-butoxy groups as well as to diminished oxygen nucleophilicity.

As in **1b**, short metal−fluorine contacts are observed. For Na(1), eight Na−F intramolecular interactions (2.497(4)−3.747(4) Å) are found to be within the combined metal−fluorine van der Waals radii (3.8 Å). There are six intramolecular contacts to Na(2) (3 × 2.601(4), 3 × 3.265). Similar to **1b**, these Na−F contacts do not result in significant lengthening of the C−F or Na−O bonds. Since these Na/F distances are generally shorter than those in $[NaTFTB]_4$, the lower nucleophilicity of the PFTB oxygen seems to leave sodium more electrophilic and thus able to bind fluorine more tightly.

Unlike **1b** and other structurally-characterized sodium fluoroalkoxides,[7,11] **1d** does *not* have intermolecular metal−fluorine contacts. This is the result of the large steric bulk of the perfluoroalkoxide groups and the large number of intramolecular Na−F contacts, thus shielding the sodium center.

$Zr(OR_f)_4$ (2a−d). The reaction of tetraneopentylzirconium with alcohols of varying degree of fluorination (eq 2) gave the desired products[7] as colorless crystals

$$\begin{aligned} Zr(CH_2CMe_3)_4 + \text{excess } R_fOH \xrightarrow{C_6H_6} \\ Zr(OR_f)_4 \quad + 4CMe_4 \quad (2) \\ \mathbf{2a}\text{: } Zr(HFIP)_4 \\ \mathbf{2b}\text{: } Zr(TFTB)_4 \\ \mathbf{2c}\text{: } Zr(HFTB)_4 \\ \mathbf{2d}\text{: } Zr(PFTB)_4 \end{aligned}$$

which could be purified by sublimation (or distillation) under very mild conditions (Table 1). This synthetic procedure was found to be very effective in the synthesis of all the $Zr(OR_f)_4$ species (OR_f = HFIP (hexafluoro-*tert*-isopropoxide) (**2a**),[12] TFTB (trifluoro-*tert*-butoxide) (**2b**), HFTB (hexafluoro-*tert*-butoxide) (**2c**),[7] PFTB (perfluoro-*tert*-butoxide) (**2d**)). **2a,c,d** are found to be solids at room temperature while **2b** is a liquid similar to zirconium *tert*-butoxide. All were found to be extremely reactive with moist air, with the solid species quickly liquefying to oils and eventually producing insoluble white solids. **2b** was found to smoke in air and produce a white solid (similar to the behavior of zirconium *tert*-butoxide). The zirconium compounds have increasing solubility in aromatic and aliphatic solvents with decreasing degree of fluorination, but all are very soluble in hexafluorobenzene.

The ^1H NMR spectrum of **2a** in hexafluorobenzene shows a broad septet at 4.79 ppm (J = 5.4 Hz) and the ^{19}F NMR spectrum shows a very broad singlet at −77.3 ppm ($\Delta\nu_{1/2}$ = 260 Hz). A variety of dynamic processes could account for the broadness of the signal. Association of zirconium fluoroalkoxide units bridged by oxygen (i.e., $[Zr(OR)_4]_x$) or fluorine is possible. Alternatively, intramolecular interaction of γ-fluorines with the metal center also would produce broadening of the NMR signal by restricting the rotation of the $-CF_3$ groups about the carbon−carbon single bond. Species **2b−d** all show sharp signals in both proton and fluorine NMR spectra (Table 1). This spectroscopic simplicity of **2b−d** must be the result of the increased ligand bulk which prevents association via bridging alkoxides.[13]

Volatility Studies. To obtain information on the relative volatility of the homometallic fluoroalkoxide species, studies were performed on freshly sublimed samples using a thermogravimetric analyzer. This allows for controlled heating rates (5 °C/min) and helium flow (70 cm^3/min) with temperatures measured at the sample. For the $Na(OR_f)$ systems (Figure 4), all the fluoroalkoxides vaporized without significant resi-

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(11) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.* **1991**, *30*, 2812.

(12) Mazdiyasni, K. S.; Schafer, B. J.; Brown, Z. M. *Inorg. Chem.* **1971**, *10*, 889.

(13) $Zr(HFTB)_4$ has been shown to be a monomer by X-ray diffraction.[7]

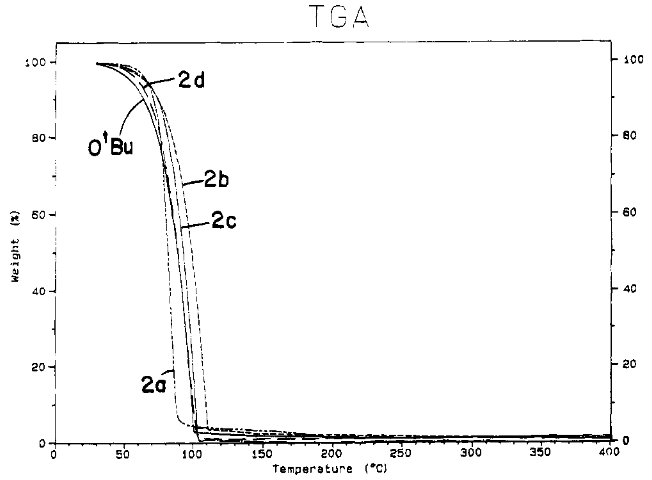

Figure 5. Thermogravimetry of $\mathrm{Zr(O^tBu)_4}$; $\mathrm{Zr(TFTB)_4}$, **2b**; $\mathrm{Zr(HFTB)_4}$, **2c**; $\mathrm{Zr(HFIP)_4}$, **2a**; $\mathrm{Zr(PFTB)_4}$, **2d**.

due. $\mathrm{[Na(O^tBu)]_6}$[14] was also studied for comparison purposes and did leave a small residue (~5%). The most notable result of this study is that with increasing fluorination of the alkoxide ligand, there is a corresponding decrease of volatilization temperature.[15] This produces the relative order of volatility as $\mathrm{[Na(O^tBu)]_6}$ < $\mathrm{[Na(TFTB)]_4}$ < $\mathrm{[Na(HFTB)]_4}$[16] < $\mathrm{[Na(HFIP)]_4}$ < $\mathrm{[Na(PFTB)]_4}$. Since there is a change of molecular complexity in the series between $\mathrm{[Na(O^tBu)]_6}$ and $\mathrm{[Na(TFTB)]_4}$, a direct comparison of the whole series cannot be made, but the general trend of volatility as a function of fluorination does hold for the tetrameric species. It should be noted that the observed volatility of the $\mathrm{Na(OR_f)}$ species does not appear to be a function of molecular weight since the two most massive molecular species $\mathrm{[Na(HFTB)]_4}$ and $\mathrm{[Na(PFTB)]_4}$ (816 and 1032, respectively) are not the least volatile. This would seem to imply other effects are involved (see Discussion).

In contrast to the sodium fluoroalkoxides, the $\mathrm{Zr(OR_f)_4}$ systems do not show the same relationship between the degree of fluorination and volatility (Figure 5). The results indicate that the relative order of volatility is $\mathrm{Zr(TFTB)_4} < \mathrm{Zr(HFTB)_4} < \mathrm{Zr(PFTB)_4} \cong \mathrm{Zr(O^tBu)_4} < \mathrm{Zr(HFIP)_4}$. Note, however, that the volatility of the *fluorinated tert*-butoxides alone does indeed increase with increasing fluorine content. It should also be noted that the range of volatilization temperatures for the $\mathrm{Zr(OR_f)_4}$ species is ~20 °C, as compared to ~70 °C for the sodium fluoroalkoxides. This indicates that the degree of fluorination of the ligands does not have the same relative effect on the zirconium species as on the sodium system (see Discussion). As with the sodium systems, molecular weight alone does not control volatilization temperatures since the most massive species ($\mathrm{Zr(PFTB)_4}$, MW = 1031) and the least massive species ($\mathrm{Zr(O^tBu)_4}$, MW = 383) have nearly identical temperatures of volatilization.

Discussion

In actuality, molecular weight has only a minor contribution to the volatility of a material. This is best demonstrated by the comparison of the boiling points of $\mathrm{Zr(O^tBu)_4}$ and $\mathrm{Hf(O^tBu)_4}$. While the molecular weights of these two compounds differ by 18.5% (383.7 vs 471.0, respectively), their boiling points are within 2 °C of each other (91 °C vs 89 °C at 5 Torr).[17,18] The nearly identical volatility in this case is due to the outward appearance of the molecules being nearly identical because of the same ligand set and similar metal radii and geometry.

If molecular weight does not have a significant effect on volatility, then the similarities of boiling points between isostructural hydrocarbons and fluorocarbons could be simply due to the structural similarities of the molecules. Yet the fluorination of many metal–organic complexes does significantly increase volatility,[2] even when there is no change in molecular complexity. In the above study, we observe a significant increase in the volatility of the $\mathrm{Na(OR_f)}$ series with each increase of the degree of fluorination. This occurs without a dramatic change in the molecular structure (tetrameric cubanes). In the case of $\mathrm{Zr(OR_f)_4}$, such a trend is not observed or is only weakly present. One explanation is that the numerous weak fluorine interactions can help stabilize the positive charge of the metal. This stabilization does not require direct lone pair donation but can be coulombic in nature, where the close intramolecular approach of the negatively-charged fluorines helps neutralize the charge of the metal ion. This effect is likely to be much more pronounced in the asymmetric geometry of the sodium in the $\mathrm{[Na(OR_f)]_4}$ system than the symmetrical tetrahedral geometry of the zirconium in the $\mathrm{Zr(OR_f)_4}$ species. With the fluorines shielding the positive charge of the sodium ions, intermolecular *Coulombic* forces between adjacent molecules are reduced, thus increasing the volatility of the bulk material. Increasing the fluorination of the alkoxide ligands shields the metal center more, resulting in enhanced volatility. Shielding by fluorines cannot occur in hydrocarbon analogues resulting in the lower volatility of $\mathrm{[Na(O^tBu)]_6}$. For $\mathrm{Zr(OR)_4}$ systems, the metal is in a spherically symmetrical coordination environment for both the *tert*-butoxy and fluoroalkoxy systems. In this geometry, the charge of the metal is effectively shielded by the four tetrahedrally arranged alkoxide oxygens,

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(14) The assignment of the degree of oligomerization of $\mathrm{[Na(O^tBu)]_n}$ as hexameric is problematic. Single-crystal X-ray diffraction studies of samples recrystallized from benzene show a cocrystallization of hexamers and nonamers in a 1:1 ratio. Our mass spectral analysis of sublimed material does give evidence for the presence of oligomers higher than six. Thus, the system has a greater complexity than simply consisting of hexamers. By the same token, TGA plots of either sublimed or recrystallized material are identical, neither showing indications of the presence of *variable* amounts of two species with different volatilities. This would imply that either the volatility is independent of the overall sample composition (neither component can leave until a temperature is reached at which both are volatile) or more likely the difference of volatilization temperatures between the two oligomers is indistinguishable by the TGA technique. The discussion of volatility in this paper will use the hexameric formula since this is expected to be the predominant form in which it vaporizes.

(15) Temperature determined at the inflection point of TGA curve. (a) $\mathrm{[Na(O^tBu)]_6}$ = 186 °C, $\mathrm{[Na(TFTB)]_6}$ = 177 °C, $\mathrm{[Na(HFTB)]_6}$ = 162 °C, $\mathrm{[Na(HFIP)]_4}$ = 140 °C, $\mathrm{[Na(PFTB)]_4}$ = 119 °C. (b) $\mathrm{Zr(O^tBu)_4}$ = 96 °C, $\mathrm{Zr(TFTB)_4}$ = 106 °C, $\mathrm{Zr(HFTB)_4}$ = 98 °C, $\mathrm{Zr(HFIP)_4}$ = 82 °C, $\mathrm{Zr(PFTB)_4}$ = 96 °C.

(16) The assignment of the degree of oligomerization for Na(HFTB) is based on structural precedent (i.e., the TFTB and PFTB analogs) and mass spectral data. See: Samuels, J. A.; Chiang, W.-C.; Yu, C.; Apen, E.; Smith, D. C.; Baxter, D. V.; Caulton, K. G. *Chem. Mater.* **1994**, *6*, 1684.

(17) The volatilities of Ti, Zr and $\mathrm{Hf(OCMe_3)_4}$ differ only slightly and in the unconventional order Ti < Zr < Hf. This has been attributed to greater mass giving greater translational *entropy* in the vapor phase. See: Bradley, D. C.; Swanwick, J. D. *J. Chem. Soc.* **1959**, 3773.

(18) (a) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. (b) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978; p 68.

thus minimizing any intermolecular Coulombic interactions. Any additional shielding achieved by the fluorination of the ligands would have minimal effect. This conclusion is supported by the minimal effect of fluorination on the volatility of the $Zr(OR_f)_4$ species.

The *inter*molecular metal–fluorine interactions observed in $[Na(HFIP)]_4$ here might be expected to decrease volatility. However, they may be readily replaced by intramolecular contacts. This replacement process would be more efficient for the more fully fluorinated $Na(OR_f)$ systems since there would be more intramolecular fluorines to replace the departing intermolecular contacts. The effect of this phenomenon on the overall volatility of the system opens a second possibility that the intermolecular contacts are the primary reason for the range of sublimation temperatures for the $[Na(OR_f)]$ series. The hypothesis is that if all the $[Na(OR_f)]_4$ species did not have intermolecular contacts, then the sublimation temperatures would have a similar range to that of the $Zr(OR_f)_4$ series. Thus, for $[Na(TFTB)]_4$, the lower number of intramolecular fluorines available for binding to the sodium would make the molecule less able to adapt to the loss of the intermolecular contacts and thus reduce the volatility. This does not explain why $[Na(HFTB)]_4$ and $[Na(HFIP)]_4$ have different sublimation temperatures with the same number of fluorines per molecule. The difference in volatility of $[Na(PFTB)]_4$ and $[Na(O^tBu)]_6$, where there are no intermolecular contacts, would be the difference in gross molecular geometry (cubic vs hexagonal prismatic). This difference in geometry would result in different molecular interactions and thus different sublimation temperatures. At this point, we cannot prove one hypothesis over the other.

Conclusions

Studies of the volatility of fluoroalkoxide species indicate that for $[Na(OR_f)]_4$, there is a dramatic decrease in the sublimation temperature with an increase of the degree of fluorination of the alkoxide ligand. In contrast, the $Zr(OR_f)_4$ series shows no significant influence of fluorination on the volatilities of the species. One explanation for the effects of fluorination on the $[Na(OR_f)]_4$ species is that the intramolecular Na–F contacts observed in the solid state shield the sodium center, with greater shielding with increase fluorination. An alternative is that observed intermolecular contacts decrease the volatility of certain $[Na(OR_f)]_4$ systems.

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Supplementary Material Available: Full crystallographic details and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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