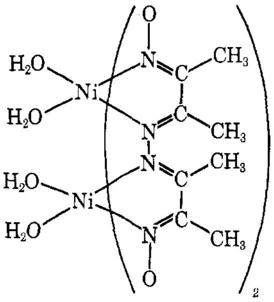
hydrogen bonds at each end, analogous to Ni(DMG)$_2$. This may be attributed to interaction of the two central methyl groups which force twisting of the ligand in order to permit chelation with two metals.



VI

A second ligand, biacetyl methoxime azine (III), has been investigated for its complexing ability toward nickel. No evidence for any reaction with nickel was observed in neutral or basic solution. Examination of models reveals that the terminal methyl groups would create considerable steric strain if the ligands were coordinated to nickel in a manner similar to that in VI. This strain is apparently sufficient to prevent formation of stable complexes.

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Volatile Fluorinated Alkoxides of the Alkali Metals

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The fully fluorinated methoxides $CF_3O^-M^+$ have been reported, where M = K, Rb, or Cs.[1] These were found to be nonvolatile and to decompose at 80–100°; the fully fluorinated ethoxides, *n*-propoxides, isopropoxides, and *n*-butoxides were even less stable.[2] Among alkoxides of partially fluorinated alcohols, sodium hexafluoroisopropoxide, $(CF_3)_2CHONa$, has been reported to melt at 68°, with decomposition beginning at 110° and becoming violent about 170°.[3] Contrary to this report, we find that sodium hexafluoroisopropoxide, prepared by the action of sodium on the free alcohol, has a melting point of 114–116° and is, moreover, surprisingly volatile. Although the hexafluoroisopropoxide cannot be distilled at atmospheric pressure, the fact that it can be sublimed at 70° under vacuum is noteworthy for a compound of sodium; the corresponding lithium compound sublimes at 50° under vacuum. Trifluoroethanol and hexafluoro-2-propanol also form transition metal alkoxides which can be distilled or sublimed under reduced pressure.[4,5]

We have now found that perfluoro-*tert*-butyl alcohol forms lithium and sodium alkoxides which can be melted and distilled at atmospheric pressure, with no apparent change in composition. The perfluoro-*tert*-butoxides may be prepared either by reaction of the parent alcohol with the appropriate metal[6] or, more conveniently, by reaction of the alcohol with metal hydride in anhydrous ether: $(F_3C)_3COH + MH \rightarrow (F_3C)_3COM + H_2$ (M = Li, Na, K). That the lithium compound should show some volatility is not surprising since organolithiums are known to have considerable covalent chaacter.[7] The covalent character of sodium zirconium ethoxide also has been reported.[8] However, to our knowledge, this is the first example to be reported of a stable organosodium which survives distillation and is thus probably covalent rather than ionic.

The infrared spectra of lithium and sodium perfluoro-*tert*-butoxide (Nujol mulls) show the O–H region to be devoid of any absorbance, but sharp bands at about 1610–1616 cm^{-1} may be due to the C–O stretching frequency in $R_3C{-}OM$.[2] In contrast, the liquid phase spectrum of neat perfluoro-*tert*-butyl alcohol shows strong O–H stretching vibrations at 3704 and 3610 cm^{-1} and nothing further until the C–F region begins around 1400 cm^{-1}. The mass spectrum of sodium perfluoro-*tert*-butoxide (other salts were not examined) was complex and somewhat variable from one experiment to another, but the data clearly indicated the presence of polymeric species in the vapor. Samples examined with an AEI No. 902 mass spectrometer (source block 65°, ionizing potential 70 V) produced intense fragments containing from one to four sodium atoms associated with a varying number of C_4F_9O groupings, along with a plethora of lower breakdown fragments. A thorough investigation of the mass spectrometry of perfluoroalkoxide salts is in progress and will be reported at a later date.

Other alkoxides were examined briefly to see if they possessed similar properties. Potassium perfluoro-*tert*-butoxide and the sodium salt of $Cl_3CC(CF_3)_2OH$ were prepared and it was observed that although both compounds could be sublimed under reduced pressure in an ordinary vacuum sublimator, neither melted below 300° and both began to decompose at about 220°. Sodium chlorooctafluoro-*tert*-butoxide exhibited properties midway between those of the fully fluorinated sodium and potassium compounds, since distillation proved to be possible only on a microscale at atmospheric pressure and was accompanied even then by gas

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TABLE I

PROPERTIES OF $RC(CF_3)_2OM$

R	M	Mp, °C	Bp, °C	Deg of molecular assocn[a]		Elemental anal, %	
						Calcd	Found
CF_3	Li	142	218	1.4	C	19.85	19.64
					F	70.66	70.00
					Li	2.86	2.87
CF_3	Na	143	232	1.4	C	18.62	18.56
					F	66.28	66.13
CF_3	K	>300	Decomposes above 220, subl 140 (0.2 mm)	1	C	17.51	17.10
					F	62.38	61.20
					K	14.26	14.21
CF_2Cl	Na	122–124	250–260 dec, subl 80 (1 mm)	1	C	17.50	18.01
					F	55.37	54.19
					Cl	12.92	12.42
CCl_3	Na		Decomposes 210–230, subl 170 (0.1 mm)	. . .[b]	C	15.63	15.24
					Cl	34.60	34.30
H	Na	114–116	Decomposes at 170, subl 70 (0.05 mm)	. . .	Na	12.03	12.08
H	Li	194.5–196.5	Subl 50 (0.05 mm)	. . .	C	20.71	19.74
					F	65.52	62.51
					Li	3.99	3.97

[a] Vapor pressure osmometry, CH_3CN solution. [b] Insoluble in CH_3CN.

evolution and other signs of decomposition. More detailed properties of the alkoxides studied are listed in Table I.

All of the compounds described are very soluble in diethyl ether, acetone, and, with the exception of $Cl_3CC(CF_3)_2ONa$, in acetonitrile. Most were considerably less soluble in benzene, and this proved to be a good recrystallization solvent.

The properties described for the lithium and sodium butoxides suggest that these materials have markedly covalent character. The remaining compounds, while less volatile than these, are nevertheless considerably more so than is normally anticipated for alkali metal derivatives.[7] The inference is that these compounds, too, are more covalent than ionic in nature.

It may be noted that the fully fluorinated primary and secondary alkoxides have been described as completely ionic species whose stability, with regard to dissociation to MF and starting carbonyl compounds, increases.[1,2] The tertiary alkoxides described here do not have the possibility of α elimination of fluorine so that their mode of decomposition is necessarily different. The lithium and sodium compounds are more stable than the potassium derivative; *i.e.*, the stability of the alkoxides decreases as the atomic weight of the metal atom increases.

In an effort to obtain information regarding the structure of solid sodium perfluoro-*tert*-butoxide, crystals of the material were grown. These proved to be transparent cubes which were not birefringent between crossed polars in the optical microscope. Weissenberg and sodium chloride calibrated precession X-ray diffraction patterns showed that the compound crystallized in the cubic crystal system with a unit cell dimension of $a = 18.82 \pm 0.02$ Å. The systematic extinctions in the diffraction patterns were as follows: reflections of the type $h0l$ with l odd, $hk0$ with h odd, and $0kl$ with k odd.

The indicated space group is thus $Pa3$ [T_h^6, no. 205].[9] The calculated density for 32 molecules in the unit cell is 2.06 g/cm^3 and the measured density at 23° is 2.07 g/cm^3. A complete set of single-crystal data has been collected and measured and a three-dimensional molecular structure determination is in progress.

Experimental Section

The alcohols used in this work may be made by procedures described in the literature.[10] Potassium perfluoro-*tert*-butoxide was purified by Dr. D. E. Young. This compound and sodium hexafluoroisopropoxide were analyzed by Mrs. R. Hogan. All other microanalyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All alkoxides were made by the action of the metal hydride on the alcohol in anhydrous diethyl ether, except for the hexafluoroisopropoxides, which were made from the metal and the alcohol in ether. In the absence of ether, sodium and lithium react with hexafluoro-2-propanol very sluggishly. Sublimations were conducted in a conventional vacuum apparatus. A typical preparation is described below.

Sodium Perfluoro-*tert*-butoxide.—A 100-ml three-necked flask was fitted with a magnetic stirring bar, a reflux condenser protected with a calcium sulfate drying tube, and a dropping funnel. Sodium hydride (4 g of 59% dispersion; 2.36 g of NaH; 0.1 mol) was added to 50 ml of anhydrous diethyl ether in the flask and slurried to remove the mineral oil. The ether was decanted and replaced with more dry ether. Perfluoro-*tert*-butyl alcohol (23.6 g; 0.1 mol) was added through the dropping funnel at 0–5°. Gas evolution began immediately and continued throughout the addition and until all the alcohol had reacted. The crude product formed a clear solution in ether. The solution was allowed to reach ambient temperature and then the ether was removed by evaporation under reduced pressure, and the crude solid was pumped dry at 0.1 mm. The crude product weighed 24 g (93% of theoretical). The dry solid (2 g) was placed in a small flask fitted with a short-path distillation head and an uncooled air condenser. Upon the application of heat the solid melted, boiled smoothly with steady reflux from the small column, and distilled at 232°. It solidified immediately in the condenser. The infrared spectrum of the distilled material was identical with that of the crude product. Pure sodium perfluoro-*tert*-butoxide melts at 143° and its ^{19}F nmr spectrum (in acetone-d_6) is a singlet at 77.5 ppm relative to $CFCl_3$.

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