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Publication Date

1978-10-01

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October 1978

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FLUOROALKOXIDES OF URANIUM (IV).

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Insoluble and relatively nonvolatile uranium(IV) alkoxides derived from primary or secondary alcohols have been known for some time(1). In contrast, no t-butoxides have been described. Tetra(t-butoxo)uranium has been claimed,(2,3) but this material has been shown to be a mixture of $U(O-t-Bu)_5$ and $U(O-t-Bu)_6$ (1). In this note we describe some alkoxide coordination complexes derived from $(CF_3)_3COH$ and $(CF_3)_2CHOH$.

Addition of $NaOC(CF_3)_3$ to a tetrahydrofuran solution of uranium tetrachloride yields lavender $[(CF_3)_3CO]_4U(thf)_2$, m.p. 210-213°C (decomp.)(4). The complex sublimes at 80-90°C in vacuum. The magnetic susceptibility follows Curie-Weiss behavior from 40-80K, μ_{eff} being 2.91 B.M. The complex is insoluble in hydrocarbon solvents but is soluble in diethyl ether (from which it may be crystallized), chlorinated hydrocarbons, and acetone.

The blue-green hexafluoroisopropoxide, $[(CF_3)_2CHO]_4U(thf)_2$, can be prepared in an analogous manner, m.p. 238-241°C (decomp.) (4). The magnetic susceptibility follows Curie-Weiss behavior over the temperature range 30-80K, μ_{eff} being 3.01 B.M. This complex is also insoluble in hydrocarbon solvents but is readily soluble in diethyl ether or chloroform. The coordinated tetrahydrofuran in the latter complex can be displaced by N,N,N',N'-tetramethylethylenediamine, yielding blue-green $[(CF_3)_2CHO]_4U(tmed)$, m.p. 265-267° (decomp.) (4).

We have been unable to observe ^{19}F n.m.r. spectra of these paramagnetic fluoro-alkoxides. This might be due to excessive line-broadening or large chemical shifts caused by the paramagnetic U(IV) ions. This observation is in contrast to the easy observation of the ^{19}F n.m.r. spectrum of diamagnetic $O_2U[OC(CF_3)_3]_2(thf)_2$ which occurs at δ - 80.0 (5).

Acknowledgment: This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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