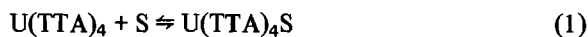


Nine-coordinate Adducts of Tetrakis(thenoyltrifluoroacetate)uranium(IV). Equilibrium Constants from ^1H NMR Spectroscopy

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Received September 5, 1981

The isomorphous, eight-coordinate [1, 2] thenoyltrifluoroacetates of uranium(IV) and thorium(IV), $\text{M}(\text{TТА})_4$, form nine-coordinate adducts in the solid state [3] and in solution [4] with monodentate substrates S, $\text{M}(\text{TТА})_4\text{S}$. The investigation of these is relevant to synergism [4] in solvent extraction systems and equilibrium constants, K, for the reactions



have been determined in benzene solution [4] from the changes in the UV/visible spectra obtained on varying the concentration of S. Because ^1H NMR spectra of uranium(IV) complexes in solution are often little broadened [5, 6] as compared with the free ligands it occurred to us that the equilibrium constants for (1) might also be determined from such spectra. This has been done for S=N,N-diethylacetamide (DEA) and triethylphosphate (TEP) in d_6 -acetone solution.

$\text{U}(\text{TТА})_4$, prepared from HTTA and Cs_2UCl_6 in ethanol (96%), was added at a fixed concentration (L_0) to d_6 -acetone solutions containing S at various concentrations (S_0). The ^1H NMR spectrum of each was recorded using a Bruker WH-90 Fourier transform spectrometer at 90.02 MHz and the induced, time-averaged, chemical shifts ($\delta\Delta$) in the resonances of S obtained by comparison with the spectra of the free substrates. The expression [7]

$$S_0 \left(1 - \frac{\delta\Delta}{\Delta_B} \right) = \frac{L_0\Delta_B}{\delta\Delta} - \left(\frac{1}{K} + L_0 \right) \quad (2)$$

(where Δ_B is the bound chemical shift of any proton on S) was then applied using an assumed value of Δ_B to calculate the left-hand side of (2) which was then plotted against $1/\delta\Delta$ to give a first estimate of the slope, $L_0\Delta_B$, from a linear least-squares analysis with solutions of relatively high S_0 . The new value of Δ_B was then used to recalculate the left-hand side of

(2) and the process repeated until the difference in successive values of Δ_B was insignificant (less than 1 part in 1000 for both slope and intercept); this usually required 6 or 7 cycles of least-squares. The final value of the intercept was used to calculate K. The results are shown in Table I.

TABLE I. Equilibrium Constants from ^1H NMR Spectra^a.

DEA ^b	$L_0 = 0.178$; $S_0 = 0.356 - 0.214$; $\delta\Delta = 6.461 - 10.315$; 4^c ; $K = 358 \pm 1^d \text{ dm}^3 \text{ mol}^{-1}$; $\Delta_B = 13.088$.
TEP ^e	$L_0 = 0.0891$; $S_0 = 0.446 - 0.071$; $\delta\Delta = 1.722 - 7.326$; 8^c ; $K = 1040 \pm 100^d \text{ dm}^3 \text{ mol}^{-1}$; $\Delta_B = 8.845$.

^aAll concentrations mol dm^{-3} , all shifts upfield of TMS (ppm). ^bFor methyl group adjacent to amide C atom. ^cNo. of solutions. ^dCalculated standard deviation, see text. ^eFor methylene group.

The standard deviation in K for TEP was much larger than for DEA because the lower value of L_0 and, more particularly, the higher value of K both serve to reduce the numerical value of the intercept and in addition the DEA resonance was generally much sharper and better defined.

Both K values were also obtained in acetone solution from the UV/visible spectra [4] with the following results:

DEA: $592 \text{ dm}^3 \text{ mol}^{-1}$ (DEA $1.740 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{U}(\text{TТА})_4$ $1.450 \times 10^{-3} \text{ mol dm}^{-3}$; spectral range 510–640 nm).

TEP: $2220 \text{ dm}^3 \text{ mol}^{-1}$ (TEP $2.900 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{U}(\text{TТА})_4$ $7.250 \times 10^{-4} \text{ mol dm}^{-3}$; spectral range 510–660 nm).

Whilst the differences found from the two methods are not understood at least the results agree to well within an order of magnitude. As expected, the equilibrium constants in acetone are lower than those likely to be found [4] in benzene.

The ^1H NMR spectrum of DEA was as expected with non-equivalence of the ethyl groups induced by the partial sp^2 character of the nitrogen atom but much of the resolution was lost on adding $\text{U}(\text{TТА})_4$. The resonance of the methyl group adjacent to carbonyl was observed as a singlet in all the spectra and was shifted much more than any other in DEA and was readily followed. The spectrum of free TEP had a group of eight signals derived from methylene protons near 4 ppm which consisted of two superimposed 1:3:3:1 sets ($J = 7.026 \text{ Hz}$ for each) with chemical shifts of 4.0939 and 4.0029 ppm. Similarly

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for the methyl groups there were two superimposed 1:2:1 sets ($J = 7.026$ Hz for each) with chemical shifts of 1.2876 and 1.2779 ppm. Water was present (near 3 ppm) and may have been the cause of the unexpected spectrum. On complexing with $U(TTA)_4$, the resolution of the methylene groups was lost giving way to a broad absorption with two ill-defined shoulders. To calculate $\delta\Delta$ for the methylene group 4.053 ppm was used as the chemical shift for free TEP. The methyl group appeared as a single triplet in the presence of $U(TTA)_4$ and as expected the induced shifts were less than for methylene. Whilst K could, in theory, be calculated from $\delta\Delta$ for the methyl group, in practice the shifted resonance was often very close to that of TMS.

As far as we know this is the first report of the calculation of equilibrium constants from the NMR spectra of an actinide ion containing 5f-electrons. Since uranium(IV) chemistry closely resembles that

of plutonium(IV) except with respect to redox properties it is possible that uranium(IV) may be a useful NMR probe for plutonium in biological systems as the intense radioactivity of plutonium would be avoided.

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