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NMR Spectra of Uranyl Complexes having Substituted Beta-diketonate Ligands

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Recently we have reported on the synthesis and characterization of a number of four-coordinate palladium and beryllium, six-coordinate aluminum, gallium, indium and scandium and eight-coordinate zirconium chelates having unsymmetrical substituted beta-diketonate ligands [1–6]. The four-coordinate palladium chelates are square planar and they exist as *cis* and *trans* isomers. The beryllium complexes are tetrahedral and dissymmetric. The zirconium complexes are of a square antiprism geometry.

We now report on the synthesis and characterization of twelve bis(β-diketonate)uranyl chelates, UO_2L_2·solvent, where L is RCOCHCOR′ and the solvent is ethanol or water.

Experimental

The uranyl complexes were prepared by our previously published method [7]. Analytical data for the four uranyl complexes not previously reported are presented in Table I (Galbraith Laboratories, Inc.).

The NMR spectra were recorded in $CDCl_3$ and CD_3CN with ^1H, ^{13}C and ^{19}F spectra taken on a JEOL-FX60Q NMR Spectrometer. The ^1H and ^{13}C chemical shifts are referenced to TMS and ^{19}F chemical shifts used $CFCl_3$ as the internal standard. The carbon resonances of the C_2F_5 and C_3F_7 group were determined using the fluorine noise decoupling technique, $^{13}C\{^{19}F\}$, described elsewhere [3].

Results and Discussion

Table II presents ^{13}C NMR chemical shift and coupling constant data for the carbonyl and methine carbons of the beta-diketonate ring. Several observations are apparent from these data. The methine carbon is more shielded for fluorine containing R′ groups and as the fluorine content of this substituent increases some deshielding of this carbon resonance occurs (electronic effect). The effect of the electron releasing CH_3 groups *versus* the electron withdrawing CF_3 group is shown by the methine carbon resonance of $UO_2(CH_3COCHCOCH_3)_2$, 104.3 ppm *versus* $UO_2(CH_3COCHCF_3)_2$, 101.0 ppm. When R′ contains fluorine, the CHF_2 groups gives a more R′–C–O deshielded carbon resonance than the R′-group CF_3, C_2F_5 or C_3F_7. A more distinguishable trend is seen in the shielding of the R–C–O carbon resonance when R′ contains fluorine: 2′-furyl > 2′-thienyl > aryl > methyl.

The carbon resonances of the C_2F_5 and C_3F_7 as given in the experimental were obtained by the $^{13}C\{^{19}F\}$ technique [3]. By this technique the C–H resonances for $UO_2(C_4H_3SCOCHCOC_2F_5)_2 \cdot C_2H_5OH$ and $UO_2(C_4H_3SCOCHCOC_3F_7)_2 \cdot C_2H_5OH$ were recorded at 97.6 ppm ($^1J_{C-H}$ 164.1 Hz) and 97.7 ppm ($^1J_{C-H}$ 165.0 Hz), respectively.

It is interesting to note that those seven-coordinate uranium complexes can be added to the geometry relationship established for our ^{13}C NMR chemical shift data in perfluorinated β-diketonate complexes. A comparison of the identical ligand for

TABLE I. Analytical Data for some $UO_2(RCOCHCOR')_2$·Solvent Chelates.

R	R′	Solvent	M.P. (°C)	Calc. (%)			Found (%)		
				C	H	U	C	H	U
C_6H_5	CHF_2	H_2O	176–8[a]	35.20	2.36	34.90	35.22	2.42	35.06
C_6H_5	CH_3	C_2H_5OH	251–2[a]	41.39	3.79	37.30	41.47	3.90	37.49
C_6H_5	C_6H_5	C_2H_5OH	264–6	50.39	3.70	31.23	50.32	3.77	31.36
2′-C_4H_3S	CHF_2	C_2H_5OH	164–166[a]	29.92	2.23	32.96	29.63	2.23	33.16

[a] Decomposed.

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TABLE II. ^{13}C NMR Chemical Shift Data for some $UO_2(RCOCHCOR')_2\cdot$Solvent Chelates.

R	R′	Solvent	$R-\underline{C}-O$	$\underline{C}-H$	$R'-\underline{C}-O$
CH_3[a]	CH_3[e]	–	193.4	104.3	193.4
C_6H_5[b]	CHF_2[f]	H_2O	192.8	97.5(2.9)[k]	182.8(22.9)[l]
C_6H_5	CH_3[g]	C_2H_5OH	195.7	101.2	186.4
C_6H_5	C_6H_5	C_2H_5OH	188.0	98.0	188.0
CH_3[b]	CF_3[h]	H_2O	205.4	101.0(2.0)	172.5(33.2)
C_6H_5	CF_3	C_2H_5OH	193.4	96.0(2.0)	174.0(33.2)
C_4H_3S[c]	CF_3	C_2H_5OH	186.1	96.1(2.0)	173.1(34.2)
C_4H_3O[b,d]	CF_3	C_2H_5OH	182.3	96.6(2.0)	174.0(34.2)
C_6H_5	C_2F_5[i]	C_2H_5OH	193.2	97.9(2.9)	175.4(24.2)
C_6H_5	C_3F_7[j]	C_2H_5OH	192.9	97.7(2.0)	175.0(24.4)
C_4H_3S	C_2F_5	C_2H_5OH	185.9	97.7(2.3)	174.2(25.2)
C_4H_3S	C_3F_7	C_2H_5OH	185.8	97.9(2.9)	172.2(23.4)
C_4H_3S	CHF_2	C_2H_5OH	184.4	96.5(2.9)	178.3(24.4)

[a] $NH_4[UO_2(CH_3COCHCOCH_3)_3$. [b] Run in CD_3CN solvent. [c] 2′-thienyl. [d] 2′-furyl. [e] $\underline{C}H_3$, 27.9 ppm. [f] $\underline{C}HF_2$, 113.5 ppm (244.6 Hz). [g] $\underline{C}H_3$, 29.0 ppm. [h] $\underline{C}F_3$, 117.8 ppm (284.2 Hz). [i] C_2H_5; $-\underline{C}F_2$, 110.7 ppm; $-\underline{C}F_3$, 118.7 ppm. [j] $\underline{C}_3F_7$; $-\underline{C}F_2$, 111.9 ppm; $-\underline{C}F_2$, 108.8 ppm; $-\underline{C}F_3$, 117.7 ppm. [k] $^3J_{C-F}$. [l] $^2J_{C-F}$.

TABLE III. ^1H and ^{19}F NMR Chemical Shift Data for $UO_2(RCOCHCOR')_2\cdot$Solvent Chelates.

R	R′	$C\underline{H}$	$CHF_{\underline{2}}$	$C\underline{F}_2$	$CF_{\underline{2}}$	$CF_{\underline{3}}$
CH_3[a]	CH_3[a]	7.2	–	–	–	–
C_6H_5	CHF_2	6.5	–126.8	–	–	–
C_6H_5	CH_3	6.6	–	–	–	–
C_6H_5	C_6H_5	6.9	–	–	–	–
CH_3	CF_3	6.4	–	–	–	–75.8
C_6H_5	CF_3	6.8	–	–	–	–75.1
C_4H_3S	CF_3	6.9	–	–	–	–75.2
C_4H_3O	CF_3	6.9	–	–	–	–75.7
C_6H_5	C_2F_5	6.8	–	–	–122.0	–82.7
C_6H_5	C_3F_7	7.0	–	–126.8	–119.8(7.6)[b]	–80.9(7.4)[c]
C_4H_3S	C_2F_5	6.9	–	–	–121.9	–82.5
C_4H_3S	C_3F_7	6.9	–	–126.8	–119.8(7.6)	–80.9(7.4)
C_4H_3S	CHF_2	6.6	–127.9	–	–	–

[a] $NH_4[UO_2(CH_3COCHCOCH_3)_3]$. [b] q, $^3J_{F-F}$. [c] t, $^3J_{F-F}$.

the ^{13}C NMR chemical shift of the R–C–O carbon resonance when R is methyl or aryl gives a deshielding order of seven-coordinate U > six-coordinate Sc, Al, Ga, In > eight-coordinate Zr > four-coordinate Pd (square planar) chelates. For four-coordinate tetrahedral beryllium chelates, the chemical shift data suggest a placement between the six-coordinate and eight-coordinate chelates [6].

^{19}F and ^1H NMR spectral data are presented in Table III for the R′-group fluorines and the methine protons, respectively. The CF_2 fluorines adjacent to the carbonyl carbon do not show spin–spin coupling for the C_2F_5 and C_3F_7 substituents. For uranyl compounds having a R′ substitutent containing fluorine, a more deshielded CH proton resonance is shown when R is phenyl or aryl as compared to a methyl substituent. These data are in agreement with that previously reported [6].

These $UO_2L_2\cdot H_2O$ and $UO_2L_2\cdot C_2H_5OH$ complexes most likely exist as seven-coordinate uranium. The two β-diketonate ligands and the solvent molecule are in a pentagonal plane with the uranyl oxygens forming a pentagonal-bipyramid uranium polyhedron. The CH_2 group of C_2H_5OH was deshielded by up to 5.5 ppm from its respective position in neat C_2H_5OH. This shift is indicative of strong complexing of the ethyl alcohol to the uranyl ion which results in a net transfer of electron density towards uranium. X-ray studies on similar molecules have confirmed this geometry [8–10]. For any unsystematically substituted beta diketone ligand both *cis* and *trans* isomers of $UO_2(RCOCHCOR')_2$ solvent should exist. The *trans* isomer would have the solvent molecule near to both one R group of one ligand and one R′ of the other ligand. Two *cis* isomers are possible with the solvent molecule being near and remote to both R (and also both R′) groups. Thus a total of four resonances, two for the chemical nonequivalent groups of the *trans* isomer and one each for the two *cis* isomers, should be observed. The ambient temperature NMR spectral data presented herein show only one resonance; however, a previous NMR study has shown three resonances for the *cis* and *trans* isomers for the $UO_2(CF_3COCHCOCH_3)_2 \cdot DMSO$ complex. This complex is reported to be fluxional on the NMR time scale [11]. Conflicting reports now appear in the literature as to the nature of this exchange process [10, 12–13]. The investigation of this process via a high field NMR using variable temperature will be the subject of a future publication.

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