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Spectroscopic Studies of some Uranyl Chelates

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Recently we have reported on the synthesis and characterization of some bis(β-diketonate)uranyl chelates, UO_2L_2•solvent, where L is RCOCHCOR′ and the solvent is ethanol or water [1, 2]. We now report on the further characterization of some of these compounds by their infrared and Raman spectra and their ^{13}C and ^{19}F NMR spectra.

Experimental

The uranyl complexes were prepared by our previously reported method [1]. The Raman spectra were taken on a Spex Model 1403 with a photon counting detector. The solid samples were attached to the cold tip of the Raman spectrometer then cooled to 20 K with CTI Model 21 closed cycle helium refrigerator. The spectra were collected by a Spex DM1B (average 30 scans). Standard smoothing operation was used to eliminate noise. The exciting source was a Kr-ion laser with a 647.1 nm line (Specta-Physics Model 164-01). To avoid thermal decomposition of the sample, the laser power was maintained at 1.5 mW. Frequency reading accuracy was ±1 cm^{-1}. The IR spectra were obtained in CsI pellets (1% by weight) and they were taken on a Beckman Model 4260. Polystyrene film bands were used for frequency reading calibration with an accuracy of ±1.0 cm^{-1}. NMR spectra were taken in $CDCl_3$ and CD_2Cl_2 on a Bruker WH-400 FT NMR Spectrometer at a spectrum frequency of 100.6 MHz for ^{13}C NMR spectra and 375.6 MHz for ^{19}F NMR spectra. Sealed tubes were employed for the variable temperature studies with spectra recorded between 25 and −57 °C. Chemical shifts are reported relative to external $CFCl_3$ (^{19}F NMR) and TMS (^{13}C NMR).

Results and Discussion

Of the twelve UO_2L_2•solvent complexes previously reported, four were chosen for further study as they would be representative of this group. The ligands (L) on these chelates are unsymmetric, RCOCHCOR′, with R and R′ being C_6H_5, CH_3; C_6H_5, CF_3; C_4H_3S (2′-thienyl), CF_3; and C_6H_5, C_2F_5; respectively and the solvent is ethanol. Complexes containing R′ as CHF_2 were too insoluble at low temperature to give reasonable NMR spectra. The complexes are seven-coordinate having pentagonal bipyramid geometry with two bidentate ligands and the ethanol in the pentagon plane and the uranyl oxygens are perpendicular to the pentagonal plane [3, 4].

The IR and Raman bands of the uranyl chelates for UO_2(sym), UO_2(asym) and $UO_2(\delta)$ are displayed in Table I. The 930 cm^{-1} Raman band of compound **I** is in very good agreement with its IR at 932 cm^{-1}. This band is due to ν_{as}(O=U=O). The ν_s(O=U=O) is found at 846 cm^{-1} (Raman) and at 849 cm^{-1} (IR). For compound **II** one observes in the ν_{as}(O=U=O) region a very complex band; however, one of the strongest bands is found at 945 cm^{-1} which agrees with the Raman data. The $\nu_s(UO_2)$ is not found in the IR spectrum but is found at 846 cm^{-1} (Raman). Compound **III**'s spectra is somewhat puzzling. The IR shows a strong band at 916 cm^{-1}, ν_{as}(O=U=O), which shows as a weak band at 912 cm^{-1} in the Raman. From the 912 cm^{-1} Raman

TABLE I. IR and Raman Assignments (cm^{-1}) for $UO_2(RCOCHCOR')_2 \cdot C_2H_5OH$ Chelates

Compound No.	R	R′	UO_2(sym)	UO_2(asym)	$UO_2(\delta)$
I	C_6H_5	C_2F_5	846	930	265
II	C_6H_5	CF_3	846	945	263
III	C_6H_5	CH_3	849	916	264
IV	2′-$C_4H_3S^a$	CF_3	849	934	260

[a] 2′-thienyl.

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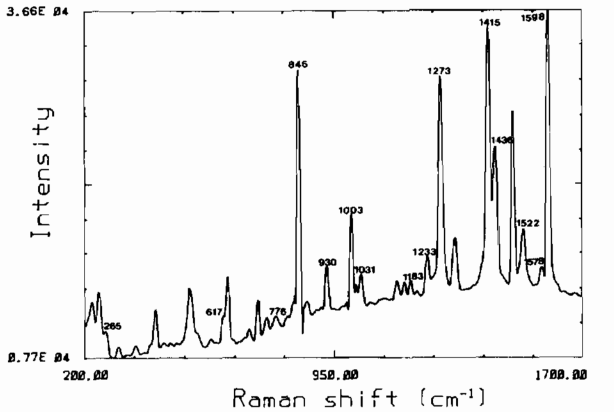

Fig. 1. Raman spectrum of $UO_2(C_6H_5COCHCOC_2F_5)_2 \cdot C_2H_5OH$.

band, it is reasonable to assume that the 849 cm^{-1} Raman band of low intensity is assigned to ν_s(O=U=O). This latter band is absent in the IR. Both compounds **II** and **III** show a strong unassigned band in the Raman at 827 cm^{-1}. Compound **IV** shows a very strong ν_s(O=U=O) Raman band at 849 cm^{-1} with a very weak IR band at 846 cm^{-1}. The ν_{as}(O=U=O) is very strong in the IR (934 cm^{-1}) and is of medium intensity in the Raman (934 cm^{-1}). All four compounds show δ(O=U=O) in the region, 260–265 cm^{-1}. This band is, of course, not a pure vibration. One observes corresponding bands in the Raman spectra except for compound **II** where a very strong band at 252 cm^{-1} (probably CF_3 rock) masks the bending UO_2 band. The assignments are in agreement with those reported for δ(O=U=O), but the ν_{as}(O=U=O) and ν_s(O=U=O) assignments are lower than those reported for $UO_2(hfac)_2 \cdot S$ taken in the gas phase, where S is THF, DMSO, TMP and HMPA [5, 6].

The Raman spectrum for $UO_2(C_6H_5COCHCOC_2F_5) \cdot C_2H_5OH$ is shown in Fig. 1. The bands at 265, 846, 930 cm^{-1} have been assigned above. The phenyl ring bands are assigned to 617, 776, 1003, 1031, 1183 and 1598 cm^{-1} (coupled to CO and/or C=C ring). These same five bands are also found in compounds **II** and **III**. The CO frequencies occur at 1415 and 1436 cm^{-1}, ν_s(CF) at 1273 cm^{-1}, CF coupled to C=C ring at 1233 cm^{-1} and C=C coupled to C=O at 1522 and 1578 cm^{-1}.

The thienyl vibrations are easily assigned from the Raman spectrum of compound **IV**. They occur at 1407, 1355, 1085 and 1067 cm^{-1}. These are assigned modes No. 3, A, sym; No. 4, A, sym; No. 5, A, sym; and No. 6, A, sym, respectively [7]. The CH_3 deformation bands are observed in the Raman spectra of compound **III** at 1367 and 1436 cm^{-1}. These bands disappear upon fluorination (R′-group).

These seven-coordinate uranyl acetylacetonate complexes containing unsymmetrically substituted ligands exist as both *cis* and *trans* isomers with respect to the solvent (ethyl alcohol). There are two *cis* isomers corresponding to the C_2H_5OH being near or remote from the R′ groups. If the complexes are cooled to a low temperature where they are rigid, one would expect to observe two equal ^{19}F NMR resonances for the *trans* complex; such as the nonequivalent CF_3 groups of compounds **II** and **IV**. Kramer has shown that the two *cis* complexes are in equilibrium with a ΔG between them of only ±2 kcal/mol and thus only a single *cis* component will be observed [8]. The *cis* and *trans* isomers for $UO_2(RCOCHCOR')_2 \cdot C_2H_5OH$ are shown in Fig. 2.

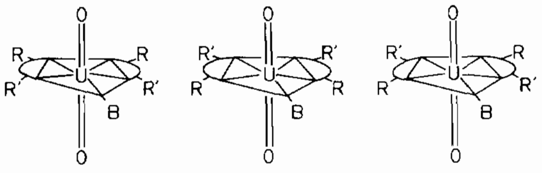

Fig. 2. Geometrical isomers of $UO_2(RCOCHCOR')_2 \cdot B$.

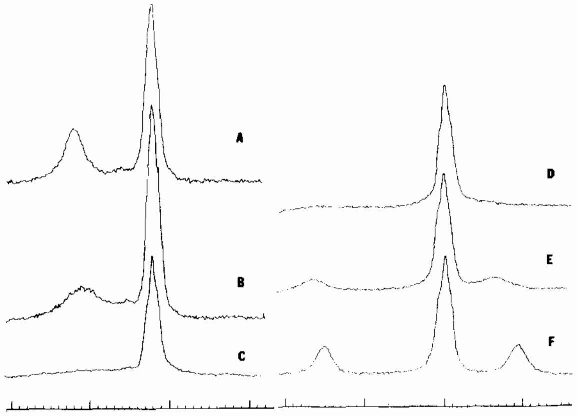

Fig. 3. Temperature dependence of the CF_3 regions of the ^{19}F NMR spectra of $UO_2(C_6H_5COCHCOC_2F_5)_2 \cdot C_2H_5OH$. (A) 293 K, (B) 284 K, (C) 273 K, (D) 266 K, (E) 254 K, (F) 243 K.

The variable temperature ^{19}F NMR was recorded for compounds **I**, **II**, **IV** and the ^{13}C NMR was taken on compound **III**. Each compound showed two resonances at room temperature due to the *cis* and *trans* species. As the temperature is lowered the low field *trans* resonance moves into the base line and at about 250 K two *trans* resonances of equal intensity are formed. The *cis* resonance for all compounds is only slightly shifted over the entire range of temperatures studied. Figure 3 shows the variable temperature spectra taken on $UO_2(C_6H_5COCHCOC_2F_5)_2 \cdot C_2H_5OH$ and Table II shows the corresponding exchange parameters on compounds **I** to **IV**.

Kramer has argued that the fluxional process is not a ‘D’ mechanism but rather an intramolecular rearrangement. His data is based on a kinetic study

TABLE II. Exchange Parameters for $UO_2(RCOCHCOR')_2 \cdot C_2H_5OH$ Chelates

Compound[a]	T_c (K)	k_c (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
I	262 (CF_3)	146	12.7 ± 0.5
	267 (CF_2)	96	13.1 ± 0.2
II	262 (CF_3)	210	12.5 ± 0.2
III	254 (ligand CH_3)	148	12.3 ± 0.2
	254 (phenyl carbons)	169	12.2 ± 0.2
IV	254 (CF_3)	136	12.3 ± 0.1

[a] ^{19}F NMR (I, II, IV); ^{13}C NMR (III).

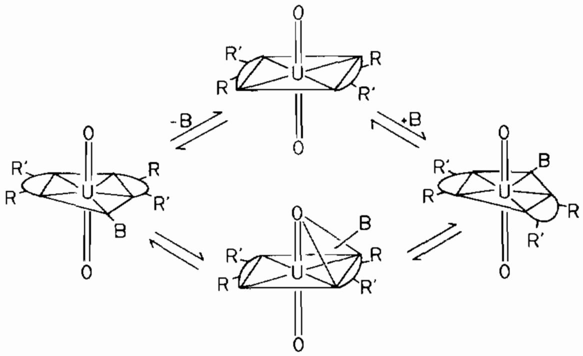

Fig. 4. Intermolecular and intramolecular rearrangements of *trans*-$UO_2(RCOCHCOR')_2 \cdot B$.

of $UO_2(hfac)_2 \cdot THF$ which shows a large negative value of ΔS, the NMR studies of the equimolar mixture of the THF and TMP adducts of UO_2(hfac) at low temperature, heat of solution data for $UO_2(tfac)_2 \cdot THF$ in various bases and a study of the fluxional process as the Lewis base changes in size and basicity [8–11]. Brownstein has proposed both an intermolecular displacement of the solvent and an anion rotation of the ligand [12]. Fukutoni and coworkers support an intermolecular displacement [13].

The ^{19}F NMR of the unsymmetrically substituted uranyl acetylacetonate, $UO_2(tfac)_2 \cdot DMSO$, showed no coalescence of the *cis* and *trans* isomers. This rules out an anion rotation mechanism as the *trans* and *cis* resonance should yield a singlet as the temperature is increased. This was not the NMR spectrum obtained on $UO(tfac)_2 \cdot DMSO$ [8] nor was it the NMR spectra obtained on our compounds, Fig. 3. Dissociation of the ligand from the complex followed by rapid displacement reactions can be discounted as one would expect to see an inverse relation between the strength of the uranyl–base bond and the rate of the process, Fig. 4. This relationship was not found for $UO_2(hfac)_2 \cdot$base complexes [9]. The purity of the complexes can be questioned, since a small amount of free base would initiate the intermolecular process [14]. We believe that our complexes as well as Kramer's complex to be of adequate purity [1, 2, 8].

Examination of Table II shows a free energy of activation at the coalescence temperature (T_c) for the compounds studied all to be of the same value. These values indicate that ligand dissociation is not the fluxional process as the unsymmetrically substituted ligands used in this study would have a different electronic effect on the strength of the UO_2–base bond. Also the vapor phase $UO_2(hfac)_2 \cdot THF$ equilibrium measured by Woolin show the free base, THF, to be detectable by mass spectrometry only at temperatures greater than 400 K [15]. We support Kramer's intramolecular rearrangement, Fig. 4, in which the base migrates about uranyl moiety [8, 9]. Finally, it is also interesting to note that all of the compounds studied contained the same ratio of *cis* to *trans* (2:1) which is also that observed for the $UO_2(tfac)_2 \cdot DMSO$ complex [8].

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