Structure and Exchange of Ionic Adducts of Uranyl Bis(hexafluoroacetylacetonate)[1]

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The chloride, bromide, azide, fluoborate, and perchlorate adducts of uranyl bis(hexafluoroacetylacetonate) were synthesized. Exchange parameters for the magnetically nonequivalent trifluoromethyl groups of the chloride and azide were determined. Rates of intermolecular exchange between the chloride and tetrahydrofuran adducts were measured. The rates and mechanisms of exchange were correlated with the structures of the adducts as determined by single-crystal X-ray diffraction.

Introduction

The tetrahydrofuran adduct of uranyl bis(hexafluoroacetylacetonate) was found to be easily synthesized and volatile.[2a] On solution in methylene chloride it contains two magnetically nonequivalent trifluoromethyl groups, which are fluxional on the NMR time scale.[2b] From fluorine resonance studies of the tetrahydrofuran, trimethyl phosphate, and dimethyl sulfoxide adducts it was concluded that the averaging of the CF_3 resonances occurred by an intramolecular base migration.[2b,3] The structures of the solid tetrahydrofuran and two polymorphic trimethyl phosphate adducts have been determined.[2b,4-6] In each, the five coordinating oxygen atoms girdling the uranyl group were nearly coplanar with it. There are variations in the planarity and tilt angles of the five-membered rings formed by the chelated hexafluoroacetylacetonate species. It was decided to investigate species with other adducts to try to elucidate in more detail the mechanism of the exchange reaction.

Experimental Section

Fluorine resonance spectra were obtained in the Fourier transform mode on a Varian Associates XL-100 spectrometer equipped with a Nicolet computer, its pulsing and power amplifier components operating at 94.18 MHz. The variable-temperature apparatus was calibrated via a methanol sample. Fluorine chemical shifts are reported relative to $CFCl_3$ as zero. Details of the X-ray structural determinations will be presented separately. Exchange rates were determined by comparing experimental spectra with ones calculated by using a stochastic approach.[7]

Uranyl nitrate, hexafluoroacetylacetone, and benzene, all reagent grade, were used as supplied. Tetramethylammonium salts, methylene chloride, and sulfur dioxide were used as previously reported.[8] Uranyl bis(hexafluoroacetylacetonate)–tetrahydrofuran was prepared as reported[2a] but purified either by solution in carbon tetrachloride, filtration to remove a white insoluble impurity, and evaporation of the solvent under vacuum at room temperature or by vacuum sublimation. The product purified by the solution procedure had no impurities observable by fluorine resonance spectroscopy, while that purified by vacuum sublimation had one extra weak signal.

The chloride, bromide, azide, perchlorate, and fluoroborate adducts were prepared by dissolving a slight excess of the tetramethylammonium salt and the tetrahydrofuran adduct in liquid sulfur dioxide. After a few minutes all volatile materials were removed under vacuum and the reaction product was dissolved in methylene chloride. Filtration removed the excess of unreacted tetramethylammonium salt.

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Table I. Rates of Exchange for the Trifluoromethyl Groups of Uranyl Bis(hexafluoroacetylacetonate)–Tetrahydrofuran

concn, M	temp, °C						E_a, kcal/mol
	−109	−100	−90	−80	−70	−60	
0.01[a]		23.6		72		255	4.2 ± 2.0
0.037		1.37	5.26	11.0	30.3	71.4	6.0 ± 0.4
0.04[a]		8.2		17.6	53.0		4.4 ± 1.5
0.064[b]		2.44	5.00	35.7	80	333	
0.064[c]	1.96	8.33	16.1	52.6			

[a] These unpublished data were kindly supplied by Dr. G. Kramer. [b] Purified by vacuum sublimation. [c] After 3 months at room temperature.

The solvent was removed under vacuum to give the pure adduct. A typical preparation follows.

Uranyl Bis(hexafluoroacetylacetonate)–Tetramethylammonium Azide. Sulfur dioxide (10.6 mmol) was condensed onto 0.0461 g of uranyl bis(hexafluoroacetylacetonate)–tetrahydrofuran (0.0613 mmol) and 0.0075 g of tetramethylammonium azide (0.0647 mmol). After the mixture was warmed to room temperature and briefly mixed, all volatile materials were pumped away to leave a residue weighing 0.0491 g (theoretical 0.0492 g). The residue was dissolved in methylene chloride, filtered, and very slowly evaporated to give crystals of adequate quality for an X-ray structure determination.

It was not possible to isolate solid samples of the fluoborate and perchlorate adducts. When a sulfur dioxide solution was concentrated, the original components separated. All manipulations were carried out either in a good-quality drybox or on a vacuum line under rigorously anhydrous conditions. Samples used for fluorine resonance spectra were stored in the dark at −85 °C except during spectral measurements.

Results and Discussion

The rates for exchange between the nonequivalent trifluoromethyl groups of uranyl bis(hexafluoroacetylacetonate)–tetrahydrofuran for several samples in methylene chloride solutions are listed in Table I. We propose that exchange can occur by two mechanisms in the same sample. One of these is intramolecular as proposed by Kramer et al.[2b] The second is displacement of the tetrahydrofuran by a Lewis base present as an impurity in the solution. The observed rate is, of course, a weighted average of the contributions from both mechanisms. It is safe to say that the slowest rate that one observes for an exchange process is most likely to be that for intramolecular exchange. If intermolecular exchange via an impurity is slower than for the intramolecular route, it will make a negligible contribution to the overall observed rate. For roughly equal amounts of impurities that exchange by a lower energy pathway, the contribution from the impurities to the observed exchange rate will be greatest for the most dilute solution.

The adduct for the 0.064 M solution was purified by vacuum sublimation in this laboratory. An additional very weak signal, which did not exchange with the trifluoromethyl signals, was seen in the fluorine resonance spectrum. The exchange rates for this sample and the 0.04 M sample of Dr. Kramer are

Table II. Exchange Rates (Given as log k) of Nonequivalent Trifluoromethyl Groups in Some Adducts

	adduct			
$10^3/T$, °C^{-1}	tetrahydro-furan (THF)	Cl$^-$	Cl$^-$ + THF	N$_3^-$
5.75	0.137			
5.46	0.721			
5.16	1.04			
4.90	1.48			
4.65			0.979	
4.45	1.85		1.04	
4.24		0.658	1.20	0.505
4.03		1.46	1.36	0.949
3.86		1.75	1.80	1.19
3.70		2.03		
3.56			2.41	
E_a, kcal/mol	6.0 ± 0.4	7.8 ± 0.2	3, 10	8.3 ± 0.5
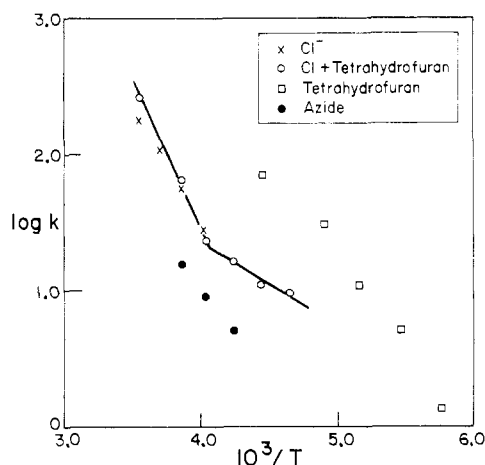
Figure 1. Exchange rates as a function of temperature and adduct.

about the same and slower than for the 0.01 M solution. After 3 months on the laboratory bench additional impurity signals were observed in the fluorine resonance spectrum of the 0.064 M sample and the exchange rates had increased. The slowest rates were observed for the 0.037 M solution where the solute had never been exposed to elevated temperatures. These are listed in Table II and plotted in Figure 1. The increase in impurity concentrations with time for the 0.064 M sample is consistent with the reported photochemical sensitivity of the tetrahydrofuran adduct.[9] The increase in exchange between the nonequivalent trifluoromethyl groups must be caused by species produced in the slow decomposition over a 3-month interval. These results suggest that the activation energy of 4.4 ± 1.5 kcal/mol reported[2b] for a sample purified by vacuum sublimation is probably too low since all impurities are not removed by such a procedure. A more accurate value for the activation energy for intramolecular exchange of the tetrahydrofuran adduct in methylene chloride solution is 6.0 ± 0.4 kcal/mol. It follows that the upper limit to the barrier for exchange by displacement with some impurity in the solution is 4.2 ± 2.0 kcal/mol. In sulfur dioxide solution exchange of the trifluoromethyl groups of the tetrahydrofuran adduct is immeasurably fast. This is presumably due to displacement of the tetrahydrofuran ligand by a solvent molecule and contrasts with the methylene chloride results.

Uranyl bis(hexafluoroacetylacetonate)–tetramethyl-ammonium chloride solutions in sulfur dioxide also show two trifluoromethyl signals at low temperature, merging to a single

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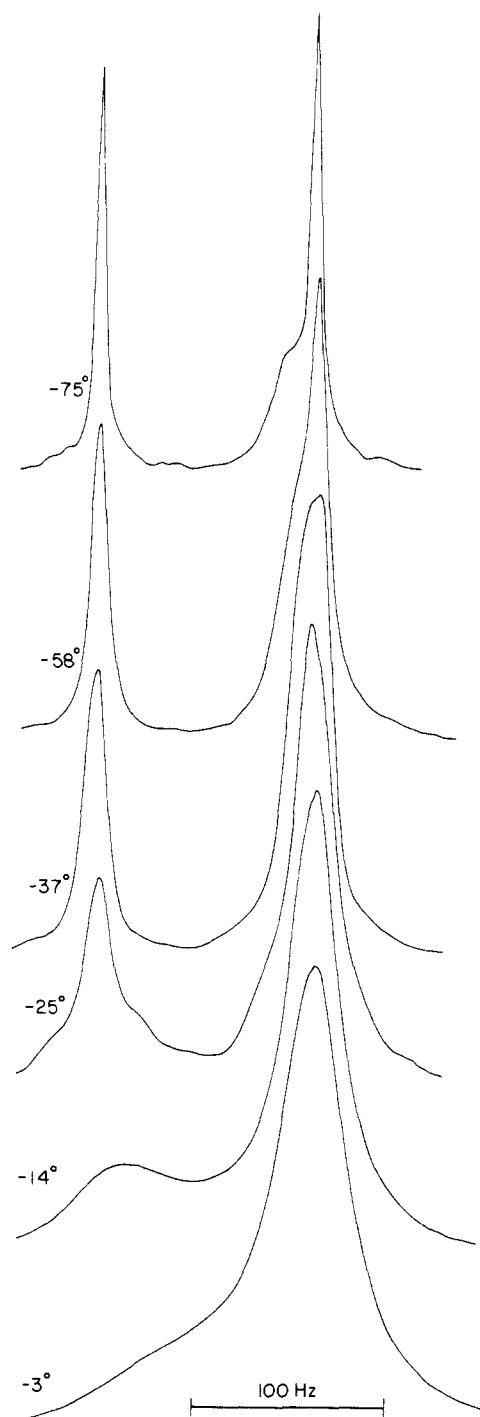
Figure 2. Fluorine resonance spectra of a mixture of the chloride and tetrahydrofuran adducts.

line at higher temperature. Rates and thermodynamic parameters are listed in Table II. A mixture of the chloride and tetrahydrofuran adducts gives the spectra shown in Figure 2. At higher temperatures the exchange rate, which is given in Table II, is about the same as for the chloride itself. At lower temperatures the exchange in the mixture is faster than in the chloride alone. This is shown in Figure 1 and Table II. Theoretical spectra were calculated for a three-site exchange for the chloride–tetrahydrofuran mixture because of the very rapid exchange of the trifluoromethyl groups of the tetrahydrofuran adduct in sulfur dioxide solution.

From the data of Figure 1 one can conclude that there is one exchange mechanism with a low energy barrier but a slight probability of an encounter and a second mechanism with a higher energy barrier and a higher probability. It is proposed
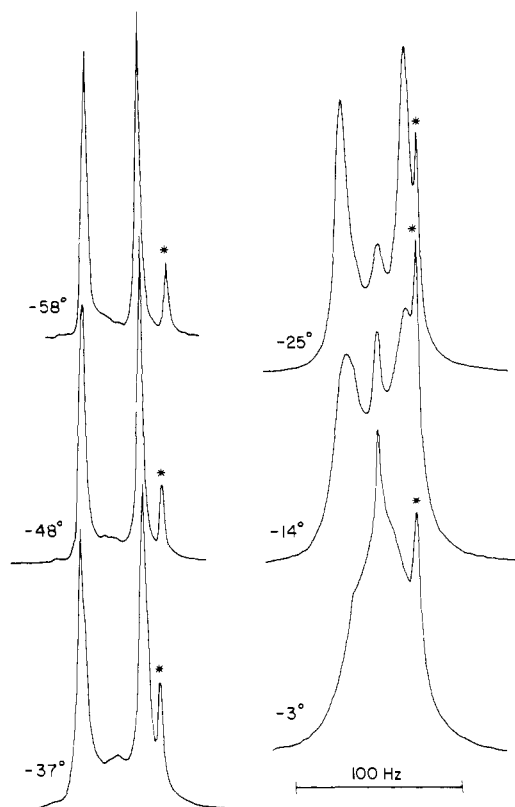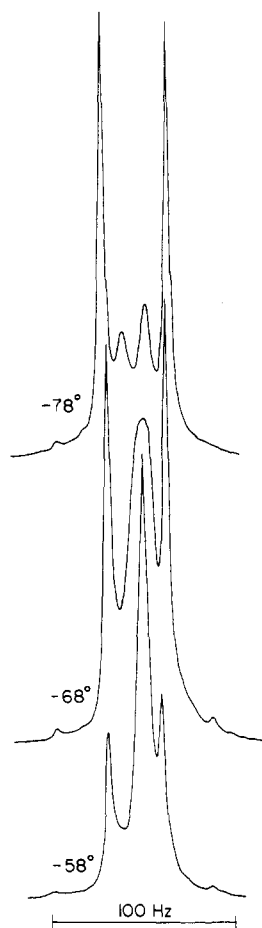
Figure 3. Fluorine resonance spectra of the azide adduct.

Figure 4. Fluorine resonance spectra of the fluoborate adduct.

Table III. Fluorine Chemical Shifts, in Sulfur Dioxide Solution, of Some Uranyl Bis(hexafluoroacetylacetonate) Adducts

adduct	chem shift, ppm
tetrahydrofuran	−74.98
chloride	−74.50, −75.10
azide	−74.75, −75.15
	−74.97[a]
fluoborate	−74.35, −74.73
	−74.47,[a] −74.60[a]
perchlorate	−74.53, −74.65
bromide	−74.19, −74.75

[a] The less abundant isomer at low temperature.

Table IV. Activation Energies and Deformation of Some Uranyl Bis(hexafluoroacetylacetonate) Adducts

		dev, A	
adduct	E_a, kcal/mol	uranium	β-diketone ring
trimethyl phosphate (α)	4.4 ± 1.5	0.024	0.02, 0.04
trimethyl phosphate (β)	4.4 ± 1.5	0.004	0.03, 0.03
tetrahydrofuran	6.0 ± 0.4	0.001	0.08, 0.12
bromide		0.052	0.10, 0.22
chloride	7.8 ± 0.2	0.26	0.16, 1.35
azide	8.3 ± 0.5	0.012	0.02, 0.03

with the results and interpretation for the tetrahydrofuran and chloride adducts alone. It is not possible to draw detailed conclusions about the mechanism of intermolecular exchange because of the very rapid exchange of trifluoromethyl groups of the tetrahydrofuran adduct. However, this result makes it quite unlikely that any significant concentration of a bimolecular complex could be involved as was proposed for a methylene chloride solution of tetrahydrofuran and trimethyl phosphate adducts.[2b]

The changes in the fluorine resonance spectra for the azide and fluoborate in sulfur dioxide as a function of temperature are rather different from those of the preceding cases. Spectra of the azide are shown in Figure 3, and those of the fluoborate in Figure 4. All of the temperature effects illustrated are completely reversible. With both the azide and the fluoborate it is seen that a second isomeric adduct increases in relative concentration with increasing temperature. In the case of the azide possibly nonequivalent trifluoromethyl groups of the second isomer are averaged at all the temperatures studied. There is a sufficient difference in chemical shift for the two species that approximate exchange rates can be calculated for the first isomer. These are listed in Table II and plotted in Figure 1. The second isomer of the fluoborate shows signals from nonequivalent trifluoromethyl groups at low temperature, but these merge over too brief a temperature interval to allow meaningful calculations of the activation energy for exchange. It is not possible from the data to specify whether trifluoromethyl exchange for the more slowly exchanging isomer occurs by a mechanism unique to it or by slow interconversion to the rapidly exchanging isomer. Discussion of the mechanism for rapid intramolecular exchange follows shortly.

The perchlorate adduct shows nonequivalent trifluoromethyl groups at −78 °C, but these are almost completely merged by −58 °C. Therefore, no attempt has been made to calculate exchange rates. The bromide had an asymmetric three-line fluorine resonance spectrum at −78 °C, which broadened and averaged to a single line with increasing temperature. This pattern may arise from overlap of two possible isomers as found for the azide and fluoborate, but it cannot be definitively assigned. All of the adducts discussed have characteristic chemical shifts and separations of the nonequivalent trifluoromethyl groups. These are listed in Table III.

All of the adducts have the uranium atom surrounded by, and approximately in the plane of, the four oxygen atoms of

that the first mechanism is an intermolecular exchange with the tetrahydrofuran or possibly the sulfur dioxide adduct while the second mechanism is intramolecular. This is consistent

the diketone groups and the chelating atom of the adduct. A postulated intramolecular exchange mechanism has the adduct rise above this plane and rotate about the uranyl axis to the other side.[2b] If this mechanism is correct, one would expect a greater activation energy for intramolecular exchange the greater the distance of the uranium above the plane of the ligands. These distances and the activation energies are listed in Table IV. There is not good agreement between the two sets of parameters.

Another possible intramolecular exchange mechanism is the rotation of the β-diketone ring about an axis perpendicular to that of the uranyl group. This would have the effect of changing the positions of two, rather than all four, of the trifluoromethyl groups. It is reasonable to suppose that the more nearly planar the β-diketone ring the more easily it might rotate. In Table IV are listed the maximum deviations from planarity for a carbon in each of the β-diketone rings of the adduct. There is a good correlation between these deformations and the activation energy for trifluoromethyl exchange, except for the azide adduct. In this case it is not possible to determine which of the two isomers observed in solution is isolated in the solid. If it is the more rapidly averaging isomer, which would have a lower activation energy than that reported, then the correlation is good for all the compounds. It is therefore suggested that in these adducts the exchange occurs

by rotation of the β-diketone ring.

Conclusions

Two different structural forms of the azide and fluoborate adducts coexist in sulfur dioxide solution. The higher energy form has a faster averaging for the trifluoromethyl groups in both adducts. There are two concurrent exchange mechanisms for the tetrahydrofuran and chloride adducts. The lower energy pathway is by an intermolecular displacement mechanism, and the higher energy one by an intramolecular exchange. In all the adducts the intramolecular exchange probably occurs by rotation of the β-diketone ring.

Hydrogen-Bonding-Induced Solvatochromism in the Charge-Transfer Transitions of Ruthenium(II) and Ruthenium(III) Ammine Complexes

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The ligand to metal and metal to ligand charge-transfer transitions in a variety of Ru(II) and Ru(III) polypyridyl–ammine complexes have been shown to be exceedingly solvent dependent. The solvatochromic behavior cannot be explained in terms of simple bulk dielectric properties of the solvents. Evidence is presented that specific solvent interactions between coordinated NH_3 and donor solvents change the redox asymmetry within the molecule (estimated as $\Delta E_{1/2} = E_{1/2}(\text{Ru donor}) - E_{1/2}(\text{polypyridine acceptor})$) and that this is the principal contributor to the change in the CT band energies. It is also demonstrated that preferential outer-sphere solvation can be observed in binary solvent mixtures, the result being that the stronger donor solvent of the mixture is found in close proximity to the ion. Evidence is also presented for specific donor–acceptor effects in an ion pair involving the iodide ion.

Introduction

Many transition-metal complexes display solvatochromatic behavior resulting from the solvent dependence of the energies of visible charge-transfer absorption bands.[1–4] Solvatochromic behavior is not solely a property of charge-transfer transitions, and in fact subtle solvent effects on the d–d transitions of various Co(III) and Cr(III) complexes were investigated as early as 1956 by Bjerrum et al.[5] However, the majority of known cases involve transitions which are largely charge transfer in character. For example, Miller and Dance[6] have noted the strong solvent effects on the interligand charge-transfer transition in some mixed-ligand dithiolene complexes and have found that the observed solvatochromic shifts correlate with the gas-phase dipole moments of the various solvents employed. Burgess has demonstrated that the charge-transfer band maximum for the metal to 2,2′-bipyridine ligand transition, $\pi^*(\text{bpy}) \leftarrow d\pi$, in such complexes as $[\text{Fe}^{II}(\text{bpy})_2(\text{CN})_2]$ and $[\text{M(bpy)(CO)}_4]$ (M = W, Mo), is influenced strongly by the solvent and correlates with the E_T solvent scale of Reichardt–Dimroth and the Z scale due to Kosower.[1,7,8] Similarly, Gidney et al. have correlated the solvatochromatism observed in the series of square-planar d^8 complexes $M^{II}(\text{bpy})X_2$ (M = Pt, Pd; X = Cl, Br, I, py) with the E_T scale.[2,7]

Briefly, the E_T scale of Reichardt and Dimroth is an ordering of solvent polarity based on the position of the energy maximum for the intramolecular charge-transfer band in a pyridinium *N*-phenolbetaine molecule (see eq 1). The charge-transfer transition in the betaine is exceedingly solvent dependent, changing from 453 nm in water to 810 nm in diphenyl ether.

The Z scale of Kosower correlates roughly linearly with that of Reichardt and is also based on an organic charge-transfer transition involving a pyridinium site. In this case it is the

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