Preparation and Properties of Some Amine Complexes of Uranium Tetrachloride and Uranyl Chloride

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Summary: Some complex compounds of uranium tetrachloride and uranyl chloride of the types UCl_4, $2NR_3$; UO_2Cl_2, $2NR_3$, $(NR_3H)_2UCl_6$ and $(NR_3H)_2UO_2Cl_4$ have been prepared where NR_3=$PrNH_2$, Et_2NH, Et_3N and C_5H_5N. The pyridine complexes have been reported previously [1-3], and have been prepared for compartive purposes. Molecular weights and conductivity measurements of solutions of these complexes were carried out and the results are reported.

Introduction

Divalent radical $[O=U=O]^{2+}$ forms stable salts with Lewis Bases [4]. Both anionic and cationic complexes of uranyl ion are known with halide ions the complex species, UO_2X^+, $UO_2X^-{}_3$ and $UO_2X_4^{2-}$ are reported [5]. Literature includes references for the preparations and properties of both uranium (IV) [6-11] and uranium (VI) with a variety of Lewis bases [12-15].

Results and Discussion

Molecular weights

The compounds UCl_4, $2NR_3$ and UO_2Cl_2, $2NR_3$ are soluble in ethanol, but cannot be recovered from solution because of decomposition, so no measurements were made on these compounds. The salts (py $H)_2UCl_6$ and $(pyH)_2UO_2Cl_4$ are slightly soluble in ethanol, and their molecular weights were determined at one concentration only.

The plot of lowering of varpour pressure, ΔR (measured in arbitrary units), against concentration C (mole/L.) for benzil in ethanol gives a straight line which passes through the origin. The plot of ΔR against C for the other compounds is also linear, but in some cases there is an intercept on the ΔR axis, attributed to hydrolysis caused by traces of water in the solvent Table 1 gives the slops of these lines together with the factor F which compares the slope with that for benzil, and which is equal to the number of particles produced by each molecule of solute.

Uranyl chloride has a factor F which is equal to unity within the limits of experimental error, suggesting that the compound behaves as a monomeric species in solution. This would be consistent with a monomeric species or with ionization producing no net increase in the number of particles according to:

Table 1: Molecular weights

Compounds	ΔR/C	F
Benzil	320	1
UCl_4	657	2.05
UO_2Cl_2	318	1
$(EtNH_3)_2UCl_6$	929	2.9
$(Et_2NH_2)_2UCl_6$	904	2.8
$(Et_3NH)_2UCl_6$	945	2.9
$(Et_3NH)_2UCl_4$	873	2.7
$(Et_2NH_2)_2UO_2Cl_4$	818	2.6
$(Et_3NH)_2UO_2Cl_4$	945	
$(PyH)_2UCl_6$	930	2.95
$(PyH)_2UO_2Cl_4$	850	2.7

$$2UO_2Cl_2 \rightleftharpoons UO_2^{2+} + UO_2Cl_4^{2-}$$

For uranium tetrachloride the factor is 2, which could be simply explained as

$$2UCl_4 \rightleftharpoons UCl_3^+ + Cl^-$$

But as it is reported that uranyl tetrachloride is easily solvolysed in ethanol [18] so dissociation and solvolysis of the following type would account for the observed factor.

$$2UCl_4+2EtOH \rightleftharpoons UCl_2(OEt)_2+2H^+ + UCl_6^{2-}$$

The formation of $UO_2Cl_4^{2-}$ and UlC_6^{2-} anions in case of the UO_2Cl_2 and UCl_4 solutions in ethanol are consistent with the reported complexes.

$(LH)_2UO_2Cl_4$ and $(LH)_2UCl_6$ obtained by the action of organic ligands on uranyl chloride and uranium tetrachloride respectively [14].

The factors for the hexachlorouranates (IV) and tetrachlorodioxouranates (F = 2.7 - 2.95) are consistent with the simple dissociation into ions.

$$(R_3NH)_2\,UCl_6 \rightleftharpoons 2R_3NH^+ + UCl_6^{2-}$$

$$(R_3NH)_2\,UO_2Cl_4 \rightleftharpoons 2\,R_3NH^+ + UO_2Cl_4^{2-}$$

Conductivities

(Table 2) gives the molar conductivities at infinite dilution Ω_o, these values can give an indication of the number and types of ions in solution [19].

Table 2: Molar conductivities Ωo ($ohm^{-1}cm^2$)

Compounds	nitrobenzene	in ethanol
$(EtNH_3)_2UCl_6$	66	254
$(Et_2NH_2)_2UCl_6$	64	250
$(Et_3NH)_2UCl_6$	68	256
$(PyH)_2UCl_6$	62	248
$(EtNH_3)_2UO_2Cl_4$		117
$(Et_2NH_2)_2UO_2Cl_4$		151
$(Et_3NH)_2UO_2Cl_4$		133
$(PyH)_2UO_2Cl_4$		144
UO_2Cl_2		35
UCl_4		170
Et_3NHCl		49

The molar conductivities of the hexachlorouranates (IV) in nitrobenzene (Ω_o 62-68) are consistent with the expected mode of ionization.

$$(R_3NH)_2UCl_6 \rightleftharpoons 2R_3NH^+ + UCl_6^{2-}$$

The molar conductivity of triethyl-ammonium chloride in ethanol has the value expected for a 1:1 electrolyte. The hexachlorouranates (Ω_o 250-256) are high, suggesting that the molar con ductivity of $[UCl_6]^{2-}$ is about 205. Similar high value for the ionic conductivity of $[ThCl_6]^{2-}$, is reported [20].

The value for the molar conductivity of uranium tetrachloride is consistent with its solvolysis in ethanol. The value for the tetrachlorodioxouranates (IV) (Ω_o 117-151) suggests that the molar conductivity of $[UO_2Cl_4]^{2-}$ is about 185. This value is in consistent with simple dissociation into UO_2Cl^+, Cl^- ions.

The values of the specific conductivities for some amine complexes are given (Table 3) and show that all are non-electrolytes in nitrobenzene.

Table 3: Specific conductivities x, for some amine complexes in nitrobenzene

UO_2Cl_2, $2PrnNH_2$	sat.	0.03
UO_2Cl_2. $2Et_2NH$	sat.	0.02
UO_2Cl_2,$2Et_3N$	sat	0.04
UO_2Cl_2. 2Py	sat.	0.03

Experimental

Materials

All solvents were dried carefully by conventional methods [16], and were stored in bottles or columns containing molecular sieves. Amines were distilled from barium oxide and phosphorus pentaoxide. Reactions carried out in solvents containing traces of moisture give unsatisfactory results. Anhydrous unranium tetrachloride was prepared from uranium trioxide and hexachloropropene [17]. Hydrated uranyl chloride was purchased from B.D.H; this material has a water content of up to 10% by weight and is difficult to dehydrate [18]. Heating in vacuum causes the loss of hydrogen chloride. Distillation of a suspension in benzene did not appear to remove the water. Distillation of an ethanol-benzene solution gave a product whose composition approximated to that of chloroethoxy-dioxyuranium (VI), UO_2ClOEt.

The method adopted for dehydration was to heat the hydrated material in a stream of hydrogen chloride, the temperature being raised to 350 °C over a period of 4 hours and maintained at this level for 2 hours. The yellow product obtained thus was anhydrous uranyl chloride (Found: Cl, 21.2; H, 69.4 Calc. for UO_2Cl_2, Cl, 20.8; U, 69.8%).

Molecular weights

A merchrolab vapour pressure osmometer model 301 A fitted with a 65 °C probe was used with ethanol as solvent. The instrument was calibrated with benzil, for which the relation between the measured variable ΔR and the concentration was found to be linear over the range 0-0.1 mole/L. Absolute ethanol, dried by distillation from magnesium ethoxide, was used for all measurements. Its water

content, was less than 20 p.p.m. or 10^{-3} mole/L., which is low compared with the concentration of uranium compounds.

Conductivities

Conductivities were measured using Backman Electronic Switchgear bridge model RA-2A with balance indicator. The cell constant, measured by using KCl solutions, was 0.105 cm^{-1}. Experiments were carried out in an atmosphere of nitrogen.

Saturated solutions of the addition compounds in nitrobenzene were prepared by adding the solute (Ca 0.1 g), to the solvent (40 ml.) in the conductivity cell, and shaking until the conductance rose no further. The weight of solute in solution was about 1 mg. and could not easily be measured. The addition compounds are slightly soluble and this is confirmed by using arsenazo III as indicator.

Preparation of the compounds UO_2Cl_2, $2NR_3$

Reactions between *i*-propylamine and anhydrous uranyl chloride in ethyl acetate solution in the mole ratio of 2:1, gave a yellow precipitate which was separated by decantation, washed with ethyl acetate and benzene, and dried under reduced pressure at room temperature. The compound was identified as uranyl chloride-bis-(*i*-pro-pylamine). (Found: Cl 15.2, U; 51.6, $C_6H_{18}Cl_2N_2O_2U$ requires Cl, 15.5; U; 51.9%).

Similar reactions between uranyl chloride and other amines gave the corresponding complex compounds. Analytical data and yields are given in (Table 4).

Preparation of the compounds $(NR_3H)_2$ UCl_6

The preparation of bis(diethylammonium) hexachlorouranate (IV) and bis(pyridinium) hexachlorouranate (IV) was performed by the addition of a solution of amine hydrochloride in chloroform to a suspension of uranium tetrachloride in the same medium. The hexachlorouranates of ethylamine, *i*-propylamine, and triethylamine could not be prepared from chloroform solution, presumably because of the lower solubilities of these amine hydrochlorides.

A solution of uranium tetrachloride in methanol was added to *i*-propylamine hydrochloride in methanol. The solution was evaporated to dryness under reduced pressure at room temperature, and the residue dissolved in ethyl acetate. This solution was evaporated to dryness, and the residue was extracted with benzene. The pale green residue obtained was dried under reduced pressure at room temperature. The product was recrystallized from ethanol and identified as bis-(*i*-propylammonium) hexachlorouranate-(IV), decomp. 193 °C. (Found: C, 12.1; H, 3.6; Cl, 37.0; N, 4.7; U, 41.3, $C_6H_{20}C_{16}N_2U$ requires: C, 12.6; H, 3.5; Cl, 37.2; N, 4.9; U, 41.6%).

Table 4: Analytical Results

Compound	Yield (%)		C	H	Cl %	N	U	Formula
1. $UO_2Cl_2.2Et_2NH$	83	Found	19.2	4.9	14.8	5.4	48.3	
		Required	19.7	4.6	14.6	5.7	48.9	$C_8H_{22}Cl_2N_2O_2U$
2. $UO_2Cl_2.2Et_3NH$	77	Found	26.1	5.8	13.3	5.2	43.2	
		Required	26.5	5.6	13.0	5.1	43.8	$C_{12}H_{32}Cl_2N_2O_2U$
3. $UO_2Cl_2.2C_5H_5N$	75	Found	24.1	2.3	14.0	5.2	47.8	
		Required	24.0	2.0	14.2	5.6	47.6	$C_{10}H_{10}Cl_2N_2O_2U$
4. $[EtNH_3)_2UCl_6$	86	Found	9.1	3.3	39.0	5.0	43.6	$C_4H_{16}Cl_6N_2U$
		Required	8.9	3.0	39.2	5.2	43.9	$C_4H_{16}Cl_6N_2U$
5. $[Et_3NH)_2UCl_6$	88	Found	22.4	5.1	32.3	4.6	36.5	
		Required	22.0	4.9	32.5	4.3	36.3	$C_{12}H_{32}Cl_6N_2U$
6. $[Et_3NH)_2UO_2Cl_4$	92	Found	23.3	5.0	22.8	4.3	39.3	
		Required	23.0	5.2	23.0	4.5	38.7	$C_{12}H_{32}Cl_4N_2O_2U$
7. $[Et_2NH_2)_2UO_2Cl_4$	85	Found	17.4	4.0	25.0	5.1	42.8	
		Required	17.1	4.3	25.4	5.0	42.5	$C_8H_{24}Cl_4N_2O_2U$
8. $(Et\ NH_3)_2UO_2Cl_4$	88	Found	9.3	3.3	28.0	5.4	47.6	
		Required	9.5	3.2	28.1	5.6	47.3	$C_4H_{16}Cl_4N_2O_2U$

Similar reactions between uranyl chloride and other amine hydrochlorides in methanol gave a pale yellow precipitate which after drying and recrystallization gave the corresponding tetrachlorodioxouranate (VI). Analytical data and yields are given in Table 4.

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